Inaugural-Dissertation

towards the academic degree

Doctor rerum naturalium (Dr. rer. nat.)

New Insights into the Reactivity and Structural Diversity of Organotellurium Compounds

Submitted to the Institute of Biology, Chemistry and Pharmacy

Freie Universität Berlin

Jens Roland Bolsinger

aus Kirchheim/Teck

Oktober 2011

The present work was carried out under the supervision of Prof. Dr. Jens Beckmann from May 2006 to October 2011 at the Institute of Biology, Chemistry and Pharmacy at the Freie Universität Berlin.

1st Referee:	Prof. Dr. Jens Beckmann
2nd Referee:	Prof. Dr. Konrad Seppelt

Disputation:	09.12.2011

This work is dedicated to

my grandparents Kaspar und Maria Zech,
who unfortunately could not see its conclusion,
my parents Roland und Helene Bolsinger, my brother Boris and
the most important woman in my life Ann-Mirja Böhm.

CONTENTS

Manuscript 1:

The Reactivity of Diorganotellurium Oxides Towards Phenol and *o*-Nitrophenol. Hypervalent and Secondary Bonding of Four Different Product Classes.

Jens Beckmann, Jens Bolsinger and Andrew Duthie

Aust. J. Chem. **2008**, *61*, 172–182; http://dx.doi.org/10.1071/CH07329
Published by CSIRO Publishing

Manuscript 2:

The structural diversity of Te-I interactions within tetraorganotelluroxane diiodides and related compounds

Jens Beckmann, Jens Bolsinger and Johann Spandl

J. Organomet. Chem., **2008**, *638*, 957-964; http://dx.doi.org/10.1016/j.jorganchem.2007.12.006
Reprinted with permission from Elsevier

Manuscript 3:

A New Series of Intramolecularly Coordinated Diaryltellurium Compounds. Rational Synthesis of the Diarylhydroxytelluronium Triflate $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$

Jens Beckmann, Jens Bolsinger, Pamela Finke and Andrew Duthie

Organometallics, received; http://dx.doi.org/10.1021/om2008259
Reprinted with permission from ACS. Copyright (2011) American Chemical Society

Manuscript 4:

Diarylhalotelluronium(IV) Cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl, Br, I) Stabilized by Intramolecularly Coordinating N-Donor Substituents

Jens Beckmann, Jens Bolsinger, Pamela Finke and Andrew Duthie
Organometallics, to be published

Manuscript 5:

Reactivity of $(p\text{-}MeOC_6H_4)_2TeO$ toward $t\text{-}Bu_2Si(OH)_2$. Synthesis of a 12-Membered Tellurasiloxane Ring, *cyclo*-$[(p\text{-}MeOC_6H_4)_2TeOSi\,t\text{-}Bu_2O]_3$

Jens Beckmann and Jens Bolsinger

Organometallics **2007**, *26*, 3601–3603; http://dx.doi.org/10.1021/om070084l
Reprinted with permission from ACS. Copyright (2007) American Chemical Society

Manuscript 6:

Molecular Stannoxane

Jens Beckmann, Jens Bolsinger and Malte Hesse

Organometallics, **2009**, 28, 4225-4228; http://dx.doi.org/10.1021/om900189s
Reprinted with permission from ACS. Copyright (2009) American Chemical Society

Manuscript 7:

Carbon Dioxide Fixation with Dialkyltellurium(IV) Dihydroxides

Jens Beckmann, Jens Bolsinger and Andrew Duthie

Z. Anorg. Allg. Chem., **2010**, *636*, 765-769; http://dx.doi.org/10.1002/zaac.200900432
Reprinted with permission from John Wiley and Sons

Manuscript 8:

New Insights into the Formation and Structure of Diaryl Tritellurides

Jens Beckmann, Jens Bolsinger and Andrew Duthie

Organometallics, **2009**, 28, 4610-4612; http://dx.doi.org/10.1021/om900494d
Reprinted with permission from ACS. Copyright (2009) American Chemical Society

Manuscript 9:

Intramolecularly Coordinated Telluroxane Clusters and Polymers

Jens Beckmann, Jens Bolsinger and Andrew Duthie

Chem. Eur. J., **2011**, *17*, 930-940; http://dx.doi.org/10.1002/chem.201002371
Reprinted with permission from John Wiley and Sons

Manuscript 10:

The Photooxidation of Bis(8-dimethylaminonaphthyl) Ditelluride

Jens Beckmann, Jens Bolsinger, Pamela Finke and Andrew Duthie

Z. Anorg. Allg. Chem. **2011**, *637*, 29–30; http://dx.doi.org/10.1002/zaac.201000343
Reprinted with permission from John Wiley and Sons

Manuscript 11:

A Well-Defined Dinuclear Telluronic Acid $[RTe(\mu\text{-}O)(OH)_3]_2$

Jens Beckmann, Jens Bolsinger, Pamela Finke and Andrew Duthie

Angew. Chem. Int. Ed. **2010**, *49*, 8030 – 8032; http://dx.doi.org/10.1002/anie.201002545
Reprinted with permission from John Wiley and Sons

Manuscript 12:

Synthesis, Structure and Reactivity of an Intramolecularly Coordinated Diarylditelluronic Acid $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$

Jens Beckmann, Jens Bolsinger, Pamela Finke and Andrew Duthie

Organometallics, to be published; http://dx.doi.org/10.1021/om2008953
Reprinted with permission from ACS. Copyright (2009) American Chemical Society

1 INTRODUCTION

Despite the increasing attention directed to the structure and reactivity of organotellurium compounds in the last decades their chemistry has still to be considered as only moderately examined compared to the related lighter group 16 elements sulfur and selenium.

Sulfur was - due to its elemental occurrence – already known and used in ancient times. One of its well-known use was in the historic production of gunpowder. Nowadays, sulfur compounds count among the most extensively examined compounds in chemistry.

This can be attributed to the diversity of sulfur chemistry – to nearly every known carbon-oxygen compound exists a sulfur analogue – and their multiple different possible applications as well as their extensive use in the industry. The production of sulfuric acid amounts to 165 Mio. tons (dates from 2001 -2007)[1], which is one of the most essential resource in the industrial production process. The main amount is used in the production of fertilizer (e.g. for the chemical extraction of phosphates or used as sulfates additives in fertilizer). Other applications of sulfur compounds are in the paper industry (aluminum sulfate), the production of synthetic colorants (e.g. thioindigo[2]), tensides (like alkylbenzene sulfonate) or as insecticides (e.g. like the diemethoate PESTANAL® from Sigma-Aldrich) to name just a few.

Beside a use in large-scale production organosulfur compounds are also important reagents in the organo chemistry, which are extensively described in the literature. For example is the *Julia-Lythogoe-Olifination* a vital reaction pathway for the syntheses of C=C *trans*-olefines using an alkylphenylsulfone. Another application is the *Corey-Seebach-Reaction* – for the synthesis of aldehydes and ketones from formaldehyde – featuring the propan-1,3-dithiol[3].

Selenium was discovered 1782 by *J. J. Berzelius* as the last non-radioactive element of the group 16 elements. Organoselenium compounds show a similar behavior as their corresponding sulfur compounds and are today the object of extensive research.

Although the first organoselenium compound was synthesized 1836 by *Löwig*[4], selenium was of little importance concerning preparations in the organic chemistry. Besides elemental selenium only selenium dioxide – for the oxidation of olefines and carbonyl-compounds – was used in organic synthesis.

However, in 1976 due to the new reaction pathway of a *syn*-elimination via PhSeOH, which was independently developed by *Sharpless*[5-7], *Clive*[8] and *Reich*[9], the application of selenium compounds in the organic synthesis took an important leap forward. These findings of the *syn*-elimination via PhSeOH and applications of other selenium compounds (like vinylic selenides) – which could be used for the functionalization of alkenes – lead to an extensive research concerning organoselenium compounds. However, in comparison with the above mentioned sulfur compounds there are still several unsolved issues concerning some selenium compound classes.

In comparison to the lighter related elements of tellurium the examination of organotellurium compounds could be described as moderately at best. Despite the facts that the first organotellurium compound was already described by *Wöhler*[10] 1840 and the pioneering work of *Lederer* concerning diorganotellurium oxides, R_2TeO (R=alkyl, aryl), nearly a century ago[11], the development in the organotellurium chemistry stagnated more or less thereafter.

The reasons for this lack of interest are divers. The limited progress was due to the difficult handling and low stability of some organotellurium compounds and the poor availability of tellurium, which has only increased in modern times due to the progress in electrolytic refining of copper, whereby the tellurium could be isolated in the anode sludge.

Another explanation could be the common misconception that tellurium chemistry closely resembles selenium chemistry, which probably dates back to the discovery of selenium. Nearly twenty years after the discovery of tellurium by *F. J. Müller von Reichenstein* (1782), whereby the name was given by *Klaproth* in reference to the earth (lat.: *tellus* = earth), selenium was named after the Greek moon goddess

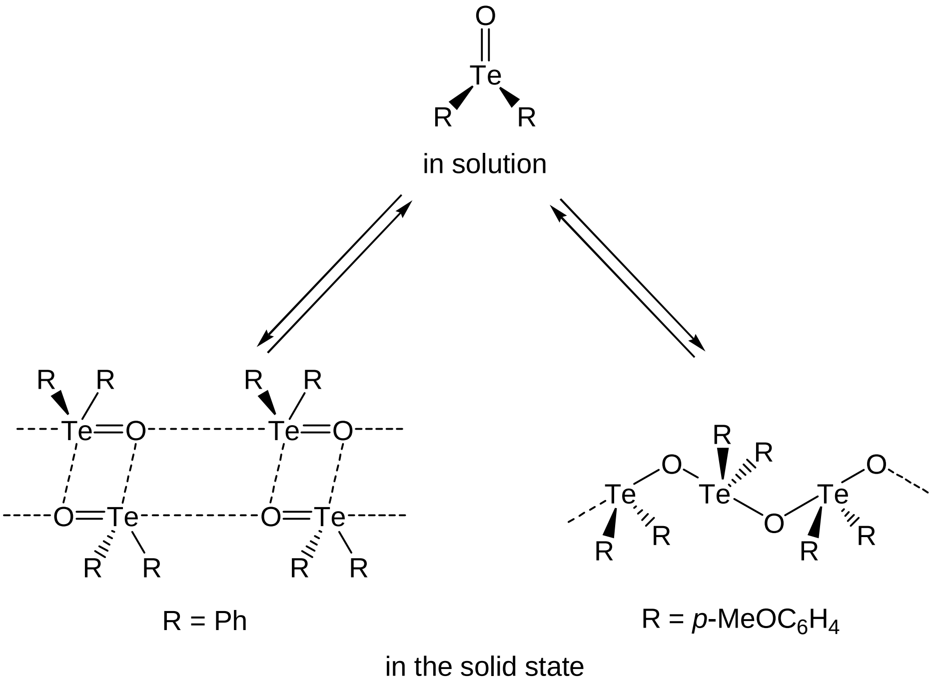
Selene. This name was chosen to point to the close relation with the element tellur, named after the earth, and the newly found element selenium[12].

However, the interest in organotellurium compounds has increased in recent years. New results point to a different reactivity of organotellurium compounds compared to the reactivity of organoselenium compounds. Due to their different behavior a growing amount of work is directed to the examination of organotellurium compounds and their possible applications. An increasing number of organotellurium compounds are used, like the diaryltellurium(IV) oxides, R_2TeO (e.g. R = Ph, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, Mes), which comprise reactive, polar (formal) Te-O double bonds, in organic[13] and organometallic[14] syntheses, for example as oxygen transfer reagents, and for their antioxidant activity[15].

Another reason for the increased attention could be attributed to the fascinating wealth of molecular and supramolecular structures of organotellurium compounds in the solid state[16], which differs significantly from that of organoselenium compounds. The structural diversity can be attributed to the different equally stable valence states and coordination modes tellurium can adopt. These are often closely associated with hypervalent and/or secondary bonding.

For example, diorganotelluriumoxides R_2TeO aggregate in the solid state and show surprisingly diverse structures, as opposed to their lighter group 16 congeners. The diorganotelluroxides Ph_2TeO[17] and $(C_6F_5)_2TeO$[18] comprise in the solid state an asymmetric, dimeric structure interconnected by secondary interactions, whereas the analogue compound bis(*p*-methoxyphenyl)telluroxide, (p-$MeOC_6H_4)_2TeO$, comprises a polymeric structure[19] with an alternating sequence of Te-O single bonds (Scheme 1).

The secondary interactions seem to play - depending on the organic ligand - an integral part in the solid state structure of diorganotelluriumoxides.



Scheme 1: Structures of diorganotelluriumoxides in the solid state and in solution.

Despite the recent development in field of diorganotellurium compounds the knowledge concerning the reactivity and structural characterization of some diorganotellurium compounds is still comprising gaps, which remain to be filled.

It has to be noted that the behavior of organotellurium compounds is in many cases comparable to the behavior of carbon compounds. For example, monomeric *p*-($MeOC_6H_4$)TeO crystallizes from solution as a polymer (see Scheme 1). This is reminiscent of aqueous formaldehyde solutions, which deposit polymeric paraformaldehyde upon standing. With proton acids, such as carboxylic acids[20], HNO_3[21], HO_3SCF_3 and HO_2-PPh_2[22] diorganotellurium oxides react as Lewis bases and undergo condensation reactions to give tetraorganoditelluroxanes.

In moist solvents, diaryltellurium(IV) oxides are slightly basic and appear to exist ‘hydrated’ as diaryltellurium(IV) dihydroxides, $R_2Te(OH)_2$, which partly undergo dissociation into diarylhydroxytelluronium(IV) ions $[R_2Te(OH)]^+$ and hydroxide ions[23].

Although it was possible to produce in solution the diarylhydroxytelluronium(IV) cation $[(4\text{-}MeOC_6H_4)_2TeOH]^+$ via a protonation of the diaryltellurium(IV) oxide

$(4\text{-MeOC}_6H_4)_2TeO$ with triflic acid, no isolation of the ionic compound was achieved. All attempts lead to condensation and formation of the related tetraarylditelluroxane ditriflate $[(4\text{-MeOC}_6H_4)_2Te]_2O(SO_3CF_3)_2$[22], which is stabilized by structural directing secondary Te···O interactions. The above described mononuclear diarylhydroxytelluronium(IV) cations are very rare. Only one such compound, namely $[(2\text{-MeNCH}_2C_6H_4)_2TeOH]_2(SiF_6)$, comprising an intramolecularly coordinating ligand, was reported very recently, which was obtained by the accidental hydrolysis of the diaryltellurium(IV) difluoride $(2\text{-MeNCH}_2C_6H_4)_2TeF_2$ in a glass vial[24].

The examination of organotellurium compounds comprising intramolecularly coordinating ligands is now receiving an increasing attention, however, the examination of such compounds has still to be considered incomplete. For example, despite the fact that diorganotelluriumoxides count among the first known organotellurium compounds[11] intramolecularly coordinated diaryltellurium(IV) oxides are still very rare. The first fully characterized example, namely $(2\text{-Me}_2NCH_2C_6H_4)_2TeO$, is a monomer that lacks any secondary Te···O bonds, which was attributed to the intramolecular coordination of both N-donor ligands[25]. By contrast, the very recently reported $(2\text{-PhNNC}_6H_4)_2TeO$ contains an asymmetric dimer in the solid-state, which is presumably due to the fact that only one of the two N-donor substitutions is involved in intramolecular coordination[26].

Concerning the diaryltellurium (VI) dioxides only one fully characterized compound is known, namely $(2,4,6\text{-}i\text{-Pr}_3C_6H_2)_2TeO_2$, which was obtained during the course of this work using the kinetic stabilization of a bulky organic substituent[27]. Most of the previously known compounds, R_2TeO_2 (e.g. R = 4-MeC_6H_4, 4-MeOC_6H_4), are ill-defined compounds with a presumably random polymeric structures[28].

Apart from organotellurium oxides the secondary interactions between organotellurium halides are of particular interest concerning the structural diversity of organo tellurium compounds.

Since the intermolecular associative forces within organotellurium halides give rise to supramolecular self-assembly in the solid state structures[29], these compounds have attracted an increasing interest. The presence of electron-rich centers beside heavier chalcogens like tellurium causes secondary X···X and Te···X (X=Cl, Br, I) bonds, whereby the latter are comparable to the well-recognized Te···O intermolecular interactions. It appears that in many of the supramolecular motifs structurally directing secondary Te···X interactions play an important role.

The involvement of intermolecular secondary Te···X interactions, which are common for diorganotellurium(IV) dihalides R_2TeX_2, have been analyzed in detail, however, it has to be noted that some are associated by intermolecular X···X interactions, like the bis(*p*-dimethylaminophenyl)tellurium(IV) dihalides[30].

The interactions of tellurium and iodine are of particular interest since the size difference and the electronegativity of these elements are only marginal. The pseudohalide character of organotellurenyl groups is substantial and these groups are even interchangeable with iodine in many structures (e.g. I_2 vs. RTeI, ICl vs. RTeCl or I_3^- vs. $RTeI_2^-$)[33]. Organotellurium(IV) iodides were extensively investigated by variation of the number and size of the organic ligand[34] and supramolecular motifs were observed[35].

Concerning the previously discussed existence of diarylhydroxytelluronium(IV) ions $[R_2Te(OH)]^+$ in solution a similar observation was made in respect to the related diarylhalotelluronium(IV) ions $[R_2TeX]^+$ (X = F, Cl, Br, I; R = alkyl, aryl).

Usually the halogenation of diorganylchalkogenides R_2E affords two principles products.[36]. A molecular (charge transfer) complex R_2E···X-X is initially formed (E = S, Se, Te; X = F, Cl, Br, I; R = alkyl, aryl), which rearranges into the trigonal bipyramidal product R_2EX_2 – when taking into account the active lone pair of the chalcogen –, if the electronegativity of the halogen is larger than that of the chalcogen[36], otherwise the molecular complex is persistent.

With reference to the diorganotellurium(IV) dihalides R_2TeX_2 (X = F, Cl, Br, I; R = alkyl, aryl) usually trigonal bipyramidal products are provided upon halogenation of diorganyltellurides. A notable exception is the iodination of bulky diaryltellurides

R_2Te (R = 2,4,6-trimethylphenyl, 2,3,5,6-tetramethylphenyl), which comprise a molecular complex $R_2Te\cdots X\text{-}X$[31].

If the energy difference is small enough, it is possible that the molecular complexes and the trigonal bipyramidal products may be in equilibrium in solution. A possible reaction pathway for the interconversion of molecular complexes and trigonal bipyramidal products via diarylhalotelluronium halides has been suggested on the basis of stop-flow kinetic measurements in solution[37] featuring cationic intermediates $[R_2TeX]^+Y^-$. In order to isolate such a cationic intermediate $[R_2TeX]^+$ (X = Cl, Br, I) an intramolecularly coordinating ligand could be used, which compensates the charge on the tellurium atom, whereby the stabilization of the ionic compound prevents further aggregation.

However, isolated products of such diarylhalotelluronium(IV) ions $[R_2TeX]^+$ (X = Cl, Br, I) are rare. At the beginning of this work, only two members, namely $[(2\text{-}Me_2NCH_2C_6H_4)PhTeX]^+ X^-$ (X = Br, I), were isolated and characterized by X-ray crystallography. It has to be noted that their ^{1}H-NMR analysis was complicated. This could be attributed to the dynamic behavior of the intramolecularly coordinating, albeit flexible 2-dimethylaminomethyphenyl groups in solution[38]. Another diarylhalotelluronium cation, namely $[(2\text{-}PhNNC_6H_4)_2TeI]^+I_3^-$, which contains two intramolecularly coordinating rather flexible 2-phenylazophenyl groups was reported during the course of this work[26].

Therefore, there are only very few fully characterized examples of isolated diaryltelluronium(IV) cations $[R_2TeX]^+$ (X= OH, Cl, Br, I) and diaryltellurium(IV) oxides R_2TeO featuring intramolecularly coordinating ligands. Regarding the related diaryltellurium(VI)dioxides R_2TeO_2 there exists no example comprising such a ligand.

Another field of research concerning the organotellurium chemistry has also attracted more and more attention in the recent years, namely the examination of novel organometalla telluroxanes, in order to develop more advanced catalysts with multiple active centers by incooperating a heavy element into the structure of another organometal compound.

However, in some fields of this research concerning binary metal oxides the use of tellurium is still more or less neglected.

For example, the metallasiloxanes, compounds containing M-O-Si linkages, have attracted considerable attention in recent years, due to their many possible applications in material science and catalysis[39]. However, there are very few reports on tellurasiloxanes[40], although extensive studies on metallasiloxanes have been executed for most elements of the periodic table.

Aside from the metallasiloxanes, organostannoxane clusters and polymers have also been the focus of extensive research due to their fascinating structural diversity and applications[41]. Especially compounds that can bind and activate CO_2 are getting increasingly important. The increasing CO_2 levels in the atmosphere are a constant strain on the environment. The rapidly growing amount of CO_2 is a constant strain on the environment. This growth is especially due to the rising demand of electricity, which is still causing – despite the developments in green energy – a major contribution to the CO_2 pollution of the environment. Other contributors are, for example, the increasing amount of transportation or the energy consuming industries like the steel industry. Aside from an environmental problem there is also an economical problem to be considered, since the production of CO_2 gets more and more expensive for the industry.

Thus, extensive research was conducted in the area of binding and recycling CO_2 in order to prepare for example commodities, such as poly(propylenecarbonate) (PPC), poly(cyclohexene carbonate) (PCHC), dimethyl carbonate (DMC) and diphenyl carbonate (DPC)[42].

In contrast to the *s*-, *d*- and *f*-block metals, for which a number of compounds are known to bind and activate CO_2[43], similar examples for the *p*-block elements are rarer. Notable exceptions are for example the organotin carbonates $[(Me_3Sn)_2CO_3]_n$, $[(i\text{-}Bu_3Sn)_2CO_3]_n$[44], $O[(2\text{-}Me_2NCH_2C_6H_4)_2Sn]_2CO_3$[45], $[(t\text{-}Bu_2Sn)_3O(OH)_2CO_3 \cdot 3\ MeOH]$[46] and $[(Bz_2Sn)_5O_3(OH)_2CO_3]_2$[47]. It was further demonstrated by our work group that diorganotellurium oxides, such as

(p-$MeOC_6H_4$)TeO showed potential for applications in the fixation of carbon dioxide[48].

Recently, our work group discovered a cooperative effect when using the two organometallic oxides (t-$Bu_2SnO)_3$ and (p-$MeOC_6H_4)_2TeO$ for the CO_2 fixation, yielding a unique tetranuclear tellurastannoxane carbonate cluster [(p-$MeOC_6H_4)_2TeOSn$-t-$Bu_2CO_3]_2$[48]. The structural characterization of (p-$MeOC_6H_4)_2TeOSn$-t-$Bu_2CO_3]_2$ and the related tellurastannoxane [(p-$MeOC_6H_4)_2Te(OSn$-t-$Bu_2OH)_2$] showed the important influence of hypervalent and secondary bonding for the fixation of carbon dioxide, the degree of aggregation and the supramolecular association[48,49].

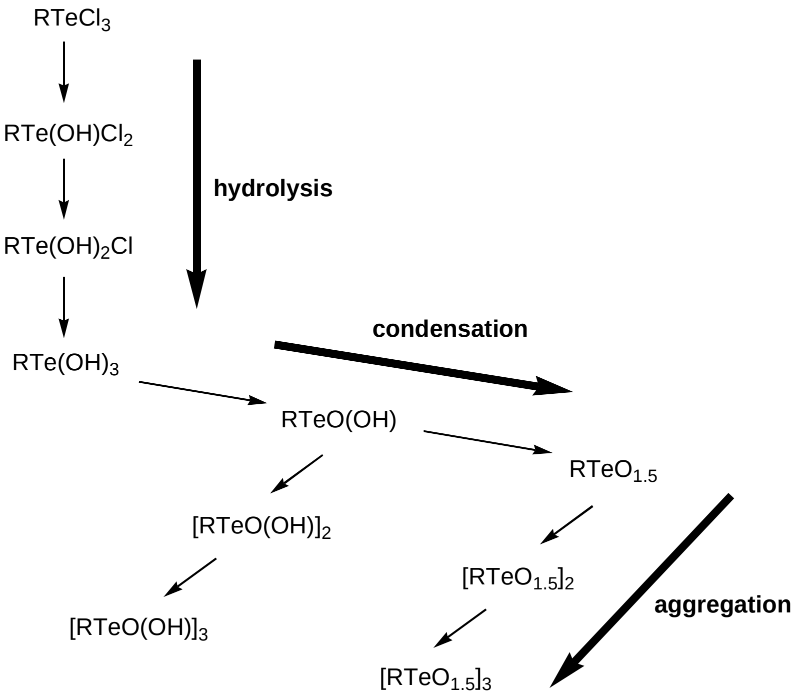
Thus, compounds containing substituents which are suited for hypervalent and secondary bonding could be of interest in the synthesis of new tellurastannoxane for the fixation of carbon dioxide.

It has to be further noted that despite the growing attention towards organotellurium compounds the complete characterization and examination of the reactivity of two essential organotellurium compound classes is more or less neglected in comparison to the related organoselenium or the well-established organosulfur chemistry.

For example, little is still known about the structure and reactivity of one elementary compound class, namely the monoorganyltellurinic acids RTe(O)OH, regardless of the pioneering work of Lederer concerning aryltellurinic(IV) acids nearly a century ago[50].

In contrast to the corresponding organosulfinic and organoseleninic acids RE(O)OH (E=S, Se; R=alkyl, aryl), which are well-defined molecular compounds, most of the previously known organotellurinic acids, $[RTe(O)(OH)]_n$ or their corresponding anhydrides $[RTeO_{1.5}]_n$, are ill-defined, amorphous substances with random polymeric structures.

The preparation of organotellurinic acids involves usually base hydrolysis of organotellurium trichlorides $RTeCl_3$, which generally proceeds with condensation and aggregation in case of small organic substituents (Scheme 4)[32].



Scheme 2: Base hydrolysis route for the preparation of organotellurinic acids and related compounds[51]

It has to be noted that our work group achieved the preparation of the first well-defined molecular organotellurinic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$ (Mes=mesityl) and partial hydrolyzed products $[m\text{-}2,6\text{-}Mes_2C_6H_3Te(O)X]_2$ (X=Cl, Br, I). In order to limit the condensation and aggregation process the kinetic stabilization of a bulky *m*-terphenyl substituent was used[51], however, other partial hydrolyzed products and aggregation products remained elusive.

Beside the limited knowledge concerning organotellurinic acids RTe(=O)(OH) (R = alkyl, aryl) even less is known about the related organotelluronic acids $RTe(=O)_2(OH)$ (R = alkyl, aryl). This stands in contrast to organosulfonic acids $RS(=O)_2(OH)$ (R = alkyl, aryl), which are a well-established compound class that finds extensive utility in organic synthesis[52]. In general, concerning the heavier congeners, little is known, which is probably due to their difficult preparation and handling[53-57].

For example, in comparison with their analogues, organosulfonic acids $RS(=O)_2(OH)$ (R = alkyl, aryl), only little information is available concerning the organoselenonic acids $RSe(=O)_2(OH)$ (R = alkyl, aryl). Their main characteristics are a very high acidity[53] comparable to their analogue sulfur compounds. However, unlike their sulfur analogues, selenonic acids are also strong oxidizing reagents[54] and comprise a low thermal stability[55]. For instance concentrated solutions of trifluoromethaneselenonic acid, F_3CSeO_3H decompose violently at ambient temperature. A general route for the preparation of organoselenonic acids, $RSe(=O)_2(OH)$, involves the oxidation of organoseleninic acids, $RSe(=O)(OH)$, by $KMnO_4$ to give the potassium selenates $K[RSeO_3]$, which upon treatment with $HClO_4$ liberate the free acids[57].

As already described at least some information is available on the organoselenonic acids $RSe(=O)_2(OH)$ (R = alkyl, aryl) but concerning the related organotelluronic acids $RTe(=O)_2(OH)$ (R = alkyl, aryl) the examination is even less advanced.

Despite the recent increase of attention directed to the reactivity and structural diversity of organotellurium compounds several areas in the organotellurium chemistry remain incompletely investigated. Especially the influence of intramolecularly coordinating ligands on the isolation of diorganotellurium ions and on diorganotellurium oxides respectively monoorganyltellurinic acids is currently insufficiently explored.

2 AIM OF THE PROJECT

The aim of this project was to examine the reactivity and structural diversity of organotellurium compounds

The examination of the reactivity towards alcohols such as phenol or *o*-nitrophenol in order to determine the influence of secondary and hypervalent bonding on the structures of these compounds is one aspect of this project. Since the interactions between tellurium and iodine are of particular interest concerning the structure of organotellurium compounds tetraorganoditelluroxane diiodides and related compounds should be also examined.

The reactivity of diorganotellurium oxides towards other organometal compounds is another aspect of this project, whereby especially the ability of possible new metallatelluroxanes to absorb carbon dioxide is of interest. Since some organotellurium oxides have shown such an ability the same studies will be carried out with organotellurium oxides.

The main focus of the project is the examination of the influence on the reactivity of mono- and diorganotellurium compounds comprising an intramolecular coordination by a N donor ligand system, namely the (8-dimethylaminonaphthyl) ligand. Especially the possibility of stabilizing an organotellurium compound in the cationic state $R2TeX^{+}$ Y^{-} by intermolecular coordination and the possible access to novel telluroxane cluster or polymers by such an intermolecular coordination will be in the center of this project.

MANUSCRIPT I

3 The Reactivity of Diorganotellurium Oxides Towards Phenol and *o*-Nitrophenol. Hypervalent and Secondary Bonding of Four Different Product Classes.

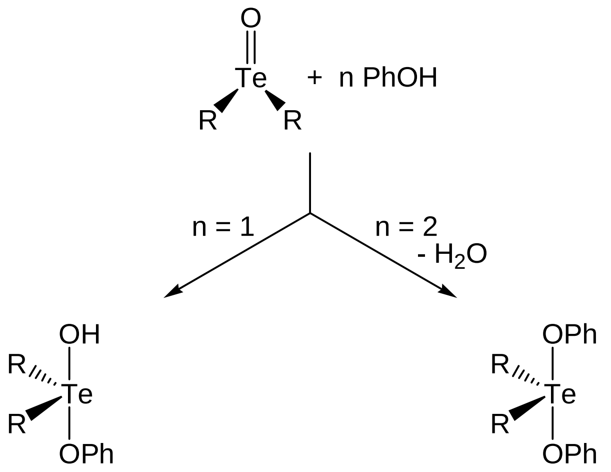
Jens Beckmann, Jens Bolsinger and Andrew Duthie; *Aust. J. Chem.* **2008**, *61*, 172–182; http://dx.doi.org/10.1071/CH07329

3.1 SYNOPSIS

The aim of this project was to examine the reactivity of diorganotellurium compounds towards alcohols such as phenol or *o*-nitrophenol and to determine the influence of secondary and hypervalent bonding on the structures of these compounds.

The reactions of the diorganotellurium oxides, R_2TeO (R=Ph, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$), with phenol or *o*-nitrophenol lead to four different product classes, namely diorganotellurium hydroxy phenolates, diorganotellurium bis(phenolates), and tetraorganoditelluroxane and hexaorganotritelluroxane bis(*o*-nitrophenolates).

It was possible to obtain the diorganotellurium hydroxy phenolates and diorganotellurium bis(phenolates) by the reaction of the diorganotellurium oxides, R_2TeO (R=Ph, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$), with one and two equivalents of phenol, PhOH (Scheme 3).



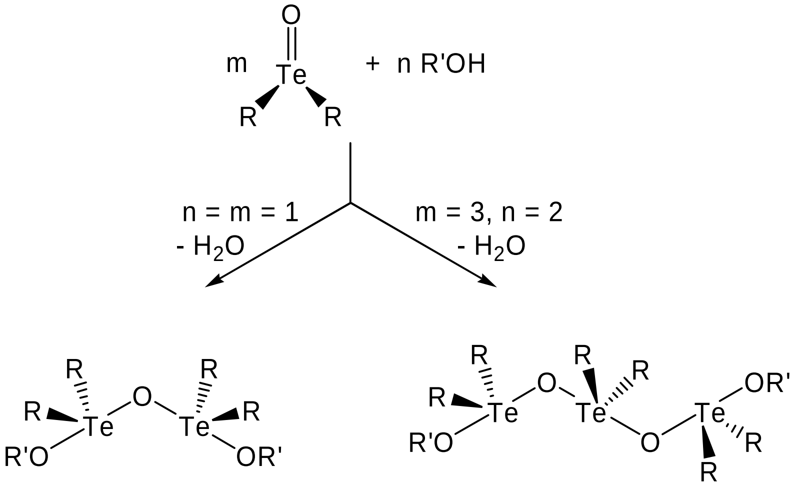
1, R = Ph
2, R = *p*-$MeOC_6H_4$
3, R = *p*-$Me_2NC_6H_4$

4, R = Ph
5, R = *p*-$MeOC_6H_4$
6, R = *p*-$Me_2NC_6H_4$

Scheme 3: Reaction of the diorganotellurium oxides R_2TeO with phenol

The molecular structures of (*p*-$MeOC_6H_4$)$_2$Te(OH)OPh, $Ph_2Te(OPh)_2$, and (*p*-$Me_2NC_6H_4$)$_2$Te(OPh)$_2$ show – comparable to the polymer (*p*-$MeOC_6H_4$)$_2$TeO[19] – no secondary Te···O interactions. There is only an indication for weak hydrogen bonding in the compound (*p*-$MeOC_6H_4)_2Te(OH)OPh$, whereby the phenolate group of an adjacent molecule acts as a hydrogen acceptor.

However, the reaction of the diorganotellurium oxides, R_2TeO with *o*-nitrophenol (R' =*o*-$NO_2C_6H_4$) proceeds with condensation and produces, depending on the organic ligand, tetraorganoditelluroxane bis(*o*-nitrophenolates) (R'O)$R_2TeOTeR_2$(OR'), respectively hexaphenyltritelluroxane bis(*o*-nitrophenolate) (R'O)$Ph_2TeOTePh_2OTePh_2$(OR') (Scheme 4).



7, R = *p*-$MeOC_6H_4$
8, R = *p*-$Me_2NC_6H_4$

9, R = Ph

R' = *o*-$O_2NC_6H_4$

Scheme 4: Reaction of the diorganotellurium oxides R_2TeO with *o*-nitrophenol

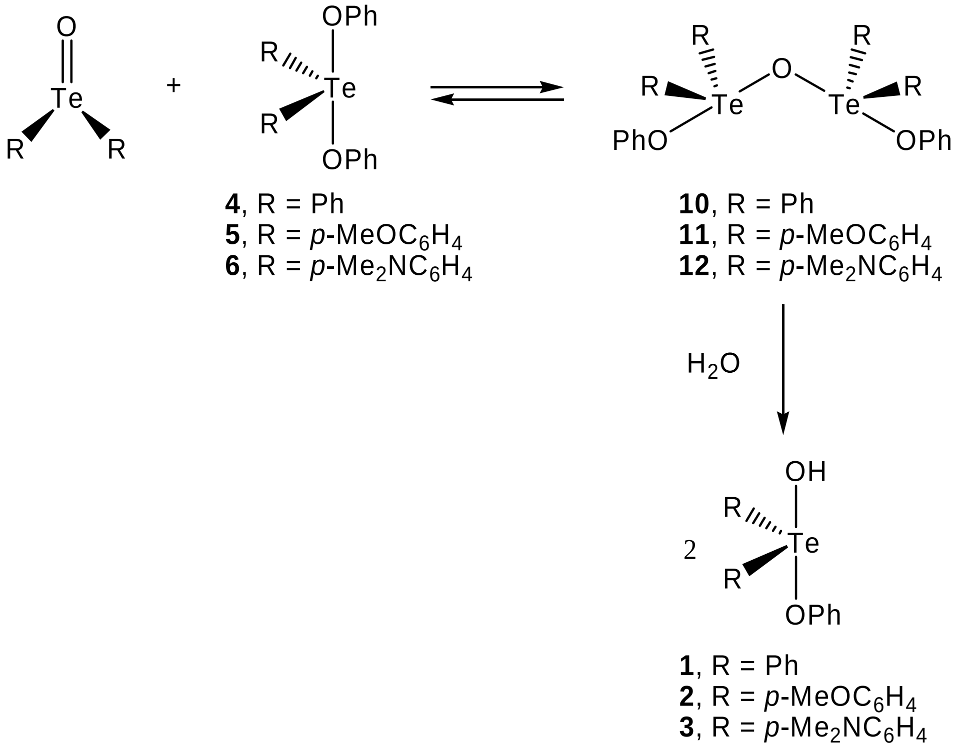
It is to note that it was not possible to obtain the mononuclear diorganotellurium bis(*o*-nitrophenolates) by an equimolare reaction. Furthermore, regardless of the stoichiometric ratio the reaction of diphenyltellurium oxide, Ph_2TeO, with *o*-nitrophenol gives rise to the formation of the hexaphenyltritelluroxane bis(*o*-nitrophenolate).

The structures of (R'O)$R_2TeOTeR_2$(OR') and (R'O)$Ph_2TeOTePh_2OTePh_2$(OR') (R=*p*-$MeOC_6H_4$; R' =*o*-$NO_2C_6H_4$) reveal several secondary Te···O interactions, whereby the mean Te-O distance of the *o*-nitrophenolate anions is shorter than those of related tetraorganotelluroxanes[21,22,58,59].

The ^{125}Te NMR spectra of the tetraorganoditelluroxanes and the hexaorganotritelluroxane, respectively give rise to single broad signals, which is indicative of a dynamic process that compromises the configurational stability of the Te atoms in solution.

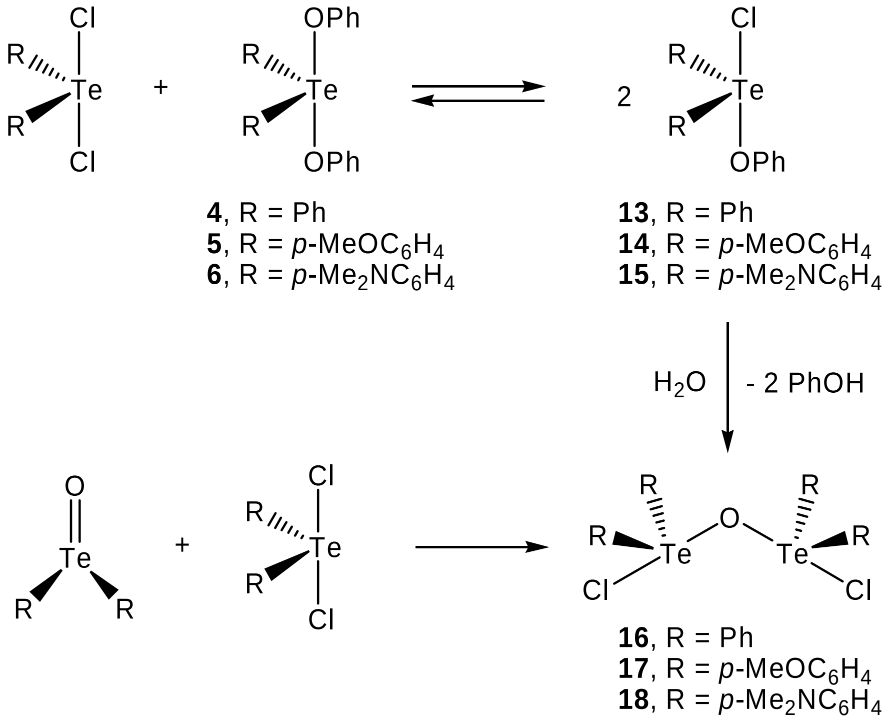
The elusive analogous tetraorganoditelluroxanes (PhO)R_2TeOTeR_2(OPh) were attempted to be isolated by the equimolar reaction of the diorganotellurium oxides R_2TeO with the respective diorganotellurium bis(phenolates) under rigorous exclusion of moisture. However, no solid compound could be isolated. The solutions show ^{125}Te NMR signals, which were assigned to the respective tetraorganoditelluroxane.

The removal of the solvent provided moisture sensitive oils, whose reaction with water from the air upon standing furnished the respective solid diorganotellurium hydroxy phenolates R_2Te(OH)OPh (Scheme 5).



Scheme 5: Reaction of the diorganotellurium oxides R_2TeO with the respective diorganotellurium bis(phenolates)

However, concerning a similar reaction of diorganotellurium dichlorides R_2TeCl_2 and the respective diorganotellurium bis(phenolates) $R_2Te(OPh)_2$ an equilibrium of the starting compounds and the diorganotellurium chloro phenolates $R_2Te(Cl)OPh$ was observed in solution. The removal of the solvent leaves colorless sensitive oil, whose reaction with moist air gives rise to the formation of solid tetraorganotelluroxane dichlorides $ClR_2TeOTeR_2Cl$ and phenol (Scheme 6).



4, R = Ph
5, R = p-MeOC$_6$H$_4$
6, R = p-Me$_2$NC$_6$H$_4$

13, R = Ph
14, R = p-MeOC$_6$H$_4$
15, R = p-Me$_2$NC$_6$H$_4$

16, R = Ph
17, R = p-MeOC$_6$H$_4$
18, R = p-Me$_2$NC$_6$H$_4$

Scheme 6: Reaction of the diorganotellurium dichlorides R_2TeCl_2 with the respective diorganotellurium bis(phenolates)

The crystal structures of $ClR_2TeOTeR_2Cl$ reveal secondary Te···Cl interactions that link individual molecules and gives rise to an infinite coordination polymer in the crystal lattice. Several not completely characterized tetraorganotellurium dichlorides have been obtained previously[60].

The reactivity of diorganotellurium oxides towards phenol and *o*-nitrophenol is surprisingly diverse and affords diorganotellurium hydroxy phenolates, diorganotellurium bis(phenolates), tetraorganoditelluroxane bis(*o*-nitrophenolates), and hexaorganotritelluroxane bis(*o*-nitrophenolates) depending on the stoichiometry and the reaction conditions applied, which stands in contrast to the other main group element oxides.

Thus, the reactivity of the Te=O double bond sharply contrasts that of most light p-block element oxides that have polar E–O double bonds (e.g., Ph_3PO, Ph_3AsO, Ph_2SO, Ph_2SeO), which form hydrogen-bonded complexes with phenol and related compounds[61].

The reactivity of diorganotellurium oxides towards phenol and *o*-nitrophenol is another example for a comparable behavior of tellurium compounds and carbon compounds. As already discussed, monomeric *p*-$(MeOC_6H_4)_2TeO$ crystallize from solution as a polymer, which is comparable to aqueous formaldehyde solutions, which deposit polymeric paraformaldehyde upon standing. Similarly, the condensation reactions of diorganotellurium oxides with phenol resemble the acetalization of ketones with alcohols.

Furthermore, the stabilizing effect of secondary interactions with the tellurium atom seems to play an important role in the structural diversity and stability of the organotellurium compounds. The possibility of secondary interactions (e.g. through *o*-nitrophenol or chlorine atoms) leads to stabile tetraorganotellurium or hexaorganotellurium compounds, whereas the absence of such interactions leads to monoroganotellurium compounds (e.g. phenol). This could also be seen in the highly moister sensitive tetraorganoditelluroxane $(PhO)R_2TeOTeR_2(OPh)$ compared with the stabile $ClR_2TeOTeR_2Cl$ comprising secondary Te···Cl bonds.

3.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann.

X-Ray Crystallography: Prof. Dr. Jens Beckmann
^{125}Te MAS-NMR spectra and analysis thereof: Dr. Andrew Duthie

MANUSCRIPT II

4 The structural Diversity of Te-I interactions within tetraorganotelluroxane diiodides and related compounds

Jens Beckmann, Jens Bolsinger and Johan Spandl; *J. Organomet. Chem.*, ***2008***, *693*, 957–964

4.1 SYNOPSIS

In preceding work our work group was interested in the structures[19] and reactivity of telluroxanes[62]. In this context we have now structurally investigated two tetraorganoditelluroxane diiodides and three related compounds showing a number of structural directing secondary Te···I interactions.

The redistribution reaction of equimolar amounts of (p-$MeOC_6H_4)_2TeI_2$ and (p-$MeOC_6H_4)_2TeO$ produced the tetraorganoditelluroxane diiodide [(p-$MeOC_6H_4)_2Te]_2OI_2$, which comprises secondary Te···I interactions. The structure can be described as two centrosymmetric $R_2TeOTeOR_2$ units, linked by four iodine atoms. This structure closely resembles the structure of the tetraorganoditelluroxane ditriflate [(p-$MeOC_6H_4)_2Te]_2O(O_3SCF_3)_2$[22] or the hexaphanyldistiboxane diiodide $(Ph_3Sb)_2OI_2$[63]. The dimeric structure of [(p-$MeOC_6H_4)_2Te]_2OI_2$ differs – probably due to the steric effect of the iodide – from the structure of the previously described tetraorganoditelluroxane dichlorides $ClR_2TeOTeR_2Cl$[64], which comprise an infinite coordination polymer.

Attempts to form a complex of [(p-$MeOC_6H_4)_2$-$Te]_2OI_2$ and iodine – analogous to $(Ph_3Sb)_2OI_2 \cdot \frac{1}{4} I_2$[65] – failed and co-crystals of (p-$MeOC_6H_4)_2TeI_2 \cdot \frac{1}{2} I_2$ were surprisingly obtained. The crystal structure consists of a centrosymmetric tetramer made of (p-$MeOC_6H_4)_2TeI_2$ molecules, which are associated via secondary Te···I interactions, whereas the iodine molecule links adjacent tetramers in the crystal lattice via I···I contacts. It seems that there are only three known similar adducts ($Me_2TeI_2 \cdot I_2$[66]; $C_5H_{10}TeI_2 \cdot I_2$ and $C_4H_8TeI_2 \cdot \frac{1}{2} I_2$)[67].

Furthermore, full structural details of the tetraorganoditelluroxane, namely $(Me_2Te)_2OI_2$, already prepared by *Vernon*[68], were obtained. The structure contains two crystallographically independent molecules of $(Me_2Te)_2OI_2$, which are associated via secondary Te···I interactions and give rise to the formation of a coordination polymer, comparable to the tetraorganoditelluroxane dichlorides $ClR_2TeOTeR_2Cl$[64].

According to Vernon the redistribution reaction of Me_2TeI_2 and freshly prepared $Me_2Te(OH)_2$[68] produced the hexaorganotritelluroxane $(Me_2Te)_3O_2I_2$. An attempt to reproduce this product lead to a crystalline product of the composition 2 $(Me_2Te)_2O(I)OH \cdot H_2O$ in good yield, which has a melting point similar to the reported hexaorganotritelluroxane $(Me_2Te)_3O_2I_2$. The structure is complex and essentially contains two 1D polymers with a Te–O backbone, whereas the first polymer string can be regarded as $(Me_2TeO)_n$ polymer similar to the polymeric structure of $[(p\text{-}MeOC_6H_4)_2TeI]_n$[19]. The compound 2 $(Me_2Te)_2O(I)OH \cdot H_2O$ is a near completely hydrolyzed condensation product of $Me_2Te(OH)_2$ with structural directing secondary interactions. Notably, the structures of $Me_2Te(OH)_2$ and potential condensation products, such as $(Me2TeO)_n$, are still unknown. The second polymer string comprises $R_2Te(OH)TeR_2(OH)$ units that are associated by short secondary Te···O(H) interactions. The two crystallographically independent iodide ions are not involved in a primary bonding to the Te atoms. However, they appear to play an integral role for the supramolecular association as they form secondary bonds to all Te atoms.

Since no single crystals could be obtained for the compound $Me_2Te(OH)_2$ another alkydiiodide, namely the $C_4H_8TeI_2$[69], was hydrolyzed in order to synthesize a comparable alkyltellurium diole. Treatment with an excess of aqueous NaOH solution yielded the tritelluroxane diiodide $(C_4H_8Te)_3O_2I_2$, which comprises a number of secondary Te···I interactions

It appears that even small alterations of the tellurium ligands or the reaction conditions will yield to a diversity of structures like di- or tritelluroxanes or structures with supramolecular associations.

4.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann.

X-Ray Crystallography: Prof. Dr. Jens Beckmann and Dr. Johann Spandl

Available online at www.sciencedirect.com
ScienceDirect
Journal of Organometallic Chemistry 693 (2008) 957–964
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

The structural diversity of Te–I interactions within tetraorganoditelluroxane diiodides and related compounds

Jens Beckmann [*], Jens Bolsinger, Johann Spandl

Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34-36, 14195 Berlin, Germany

Received 22 October 2007; received in revised form 3 December 2007; accepted 6 December 2007
Available online 15 December 2007

Abstract

Two tetraorganoditelluroxane diiodides $(R_2Te)_2OI_2$ (**3**, R = *p*-$MeOC_6H_4$; **5**, R = Me) were prepared by the reaction of (*p*-$MeOC_6H_4)_2TeI_2$ (**1**) and (*p*-$MeOC_6H_4)_2TeO$ (**2**) and the base hydrolysis of Me_2TeI_2 (**4**), respectively. The base hydrolysis of $C_4H_8TeI_2$ (**8**) afforded the tritelluroxane diiodide $(C_4H_8Te)_3O_2I_2$ (**9**). The reaction of Me_2TeI_2 (**4**) and $Me_2Te(OH)_2$ (**6**) in a ratio of 1:3 produced the coordination polymer of the composition 2 $(Me_2Te)_2O(I)OH \cdot H_2O$ (**7**). An attempt at preparing an adduct of **3** with iodine failed but provided co-crystals of (*p*-$MeOC_6H_4)_2TeI_2 \cdot \frac{1}{2}I_2$ (**1a**). The supramolecular structures of **1a**, **3**, **5**, **7** and **9** are dominated by structurally directing secondary Te···I interactions.

Keywords: Tellurium; Secondary bonding; Supramolecular structure

1. Introduction

The coordination chemistry of organotellurium compounds has attracted considerable attention in recent years due to a fascinating wealth of molecular and supramolecular structures [1]. The diversity encountered within these structures can be attributed to the fact that tellurium can adopt different equally stable valence states and coordination modes, which are often closely associated with hypervalent and/or secondary bonding. Interactions between tellurium and iodine are of particular interest as the electronegativity and size difference of these elements are only marginal. The organotellurenyl group has even substantial pseudohalide character and is interchangeable with iodine in many structures (e.g. I_2 vs. RTeI, $RTeI \cdot I_2$; ICl vs. RTeCl; I_3^- vs. $RTeI_2^-$, $(RTe)_3^-$) [2]. Organotellurium(IV) iodides were extensively investigated by variation of the number and size of the organic substituents and the supramolecular motifs observed were rationalized by the concepts of crystal engineering [3].

In preceding work we were interested in the structure [4] and reactivity of telluroxanes [5]. In this context we have now structurally investigated two tetraorganoditelluroxane diiodides and three related compounds showing a number of structurally directing secondary Te···I interactions.

2. Discussion

The redistribution reaction of equimolar amounts of (*p*-$MeOC_6H_4)_2TeI_2$ (**1**) and (*p*-$MeOC_6H_4)_2TeO$ (**2**) produced the tetraorganoditelluroxane diiodide [(*p*-$MeOC_6H_4)_2Te]_2OI_2$ (**3**) in almost quantitative yield as orange crystalline solid

$$\underset{\mathbf{1}}{(p\text{-MeOC}_6\text{H}_4)_2\text{TeI}_2} + \underset{\mathbf{2}}{(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}} \rightarrow \underset{\mathbf{3}}{[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}]_2\text{OI}_2} \qquad (1)$$

The molecular structure of [(*p*-$MeOC_6H_4)_2Te]_2OI_2$ (**3**) is shown in Fig. 1. Selected bond parameters and crystal and refinement data are collected in the caption of Fig. 1

---

[*] Corresponding author.
E-mail address: beckmann@chemie.fu-berlin.de (J. Beckmann).

0022-328X/$ - see front matter
doi:10.1016/j.jorganchem.2007.12.006

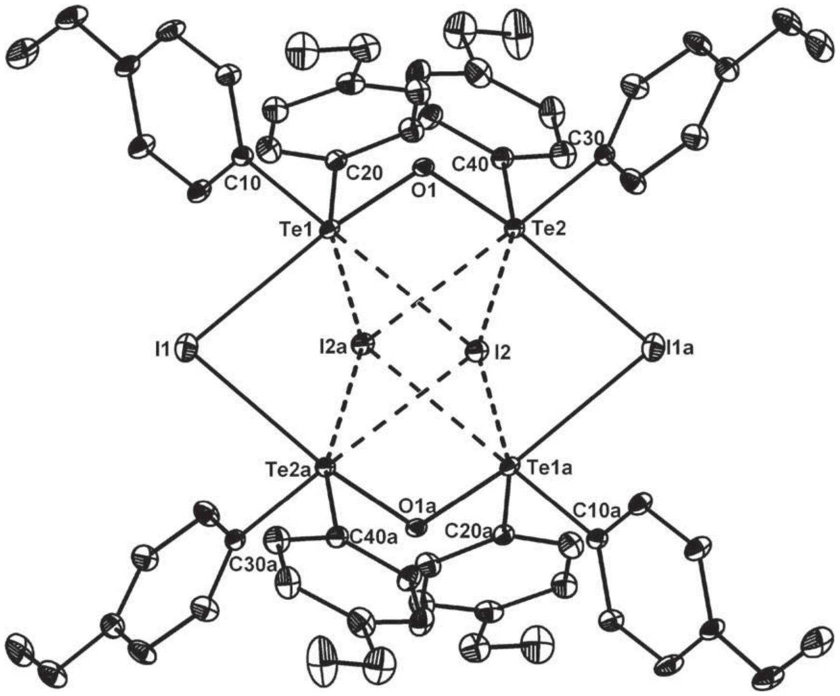


Fig. 1. Molecular structure and supramolecular association of $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}]_2\text{OI}_2$ (**3**) showing 30% probability ellipsoids and the crystallographic numbering scheme. The CHCl_3 molecules have been omitted for clarity. Symmetry code used to generate equivalent atoms: $a = 1 - x,\ 1 - y,\ 1 - z$. Selected bond parameters [Å, °]: Te1–C10 2.107(7), Te1–C20 2.102(7), Te1–I1 3.294(2), Te1···I2 3.499(2), Te1···I2a 3.696(1), Te1–O1 1.989(6), Te2–C30 2.116(8), Te2–C40 2.119(8), Te2–I1a 3.262(2), Te2···I2 3.740(2), Te2···I2a 3.513(2), Te2–O1 1.982(6); O1–Te1–I1 174.2(2), O1–Te2–I1a 173.4(2), Te1–O1–Te2 118.8(2).

and Table 1, respectively. The structure of **3** can be described as two centrosymmetric $\text{R}_2\text{TeOTeR}_2$ units that are linked by four iodine atoms. Taking into account the stereochemically active lone pair, the spatial arrangement around the Te atoms is trigonal biyramidal with a C_2IO donor set and the expected ligand occupancies. The average axial Te–I bond lengths of 3.278(2) Å are considerably longer than those of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeI}_2$ (**1**) being 2.9234(8) Å [6]. In turn, The Te–O bond lengths of 1.986(6) Å are somewhat shorter than the Te–O 'single bonds' of the polymeric parent $[(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}]_n$ (**2**) being 2.063(2) Å [4]. Thus, unlike the two starting materials **1** and **2**, the axial coordination of **3** is somewhat asymmetric. A similar observation was made for related trigonal bipyramidal triorganostannate anions having two unequal axial ligands [7]. In addition to the two axial I atoms (I1, I1a), there are two I atoms (I2, I2a) associated with the Te atoms *via* longer secondary interactions of average 3.612(2) Å. In this way, the overall crystal structure of **3** closely resembles that of the tetraorganoditelluroxane ditriflate $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}]_2\text{O}(\text{O}_3\text{SCF}_3)_2$ [8]. The Te–O–Te angle of **3** being 118.8(2)° compares well with the corresponding angle in $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}]_2\text{O}(\text{O}_3\text{SCF}_3)_2$ (120.2(3)°) and related tetraorganoditelluroxanes [8]. The primary coordination sphere of **3** is also reminiscent of the molecular structure of hexaphenyldistiboxane diiodide $(\text{Ph}_3\text{Sb})_2\text{OI}_2$ [9]. In solution **3** was characterized by ^{1}H and ^{13}C NMR spectroscopy (Section 3), however, all attempts at obtaining a ^{125}Te NMR signal failed. A similar observation was made previously for $[(p\text{-MeOC}_6\text{H}_4)_2\text{TeO}]_n$ (**2**) [4].

The hexaphenyldistiboxane diiodide $(\text{Ph}_3\text{Sb})_2\text{OI}_2$ is known to form an adduct with molecular iodine in the solid state, namely $(\text{Ph}_3\text{Sb})_2\text{OI}_2 \cdot \frac{1}{4}\text{I}_2$ [10]. When we attempted the preparation of a similar complex of $[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}]_2\text{OI}_2$ (**3**) and iodine, we surprisingly obtained co-crystals of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeI}_2 \cdot \frac{1}{2}\text{I}_2$ (**1a**) in about 30% yield as black crystals. The same material was obtained nearly quantitatively when stoichiometric amounts of **1** and iodine were co-crystallized. To the best of our knowledge, there are only three adducts of dialkyltellurium diiodides with iodine, namely $\text{Me}_2\text{TeI}_2 \cdot \text{I}_2$ [11], $\text{C}_5\text{H}_{10}\text{TeI}_2 \cdot \text{I}_2$, $\text{C}_4\text{H}_8\text{TeI}_2 \cdot \frac{1}{2}\text{I}_2$ [12]. The crystal structure of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeI}_2 \cdot \frac{1}{2}\text{I}_2$ (**1a**) is shown in Fig. 2. Selected bond parameters and crystal and refinement data are collected in the caption of Fig. 2 and Table 1, respectively. The crystal structure of **1a** consists of a centrosymmetric tetramer made of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeI}_2$ molecules, which are associated *via* secondary Te···I interactions. The bond parameters and the supramolecular arrangement of the tetramer are virtually identical with those of the two known polymorphs of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeI}_2$ (**1**) [6]. The iodine molecule of **1a** links adjacent tetramers in the crystal lattice *via* I···I contacts of average 3.360(1) Å. The primary I–I bond lengths of 2.743(1) Å is similar to those of other iodine adducts, such as $\text{Me}_2\text{TeI}_2 \cdot \text{I}_2$ (2.756(2) Å) [11], $\text{C}_5\text{H}_{10}\text{TeI}_2 \cdot \text{I}_2$ (2.744(1) Å), $\text{C}_4\text{H}_8\text{TeI}_2 \cdot \frac{1}{2}\text{I}_2$ (2.759(1) Å) [12] and $(\text{Ph}_3\text{Sb})_2\text{OI}_2 \cdot \frac{1}{4}\text{I}_2$ (2.732(3) Å) [10]. The motif

Table 1
Crystallographic data and refinement details for **3**, **1a**, **5**, **7** and **9**

	3	**1a**	**5**	**7**	**9**
Formula	$C_{28}H_{28}I_2O_5Te_2 \cdot CHCl_3$	$C_{28}H_{28}I_4O_4Te_2 \cdot I_2$	$C_4H_{12}I_2OTe_2$	$C_8H_{22}I_2O_4Te_4 \cdot H_2O$	$C_{12}H_{24}I_2O_2Te_3$
Formula weight	1072.87	1445.10	585.14	965.48	836.91
Crystal system	Triclinic	Triclinic	Orthorhombic	Orthorhombic	Orthorhombic
Crystal size (mm^3)	0.36 × 0.20 × 0.05	0.73 × 0.12 × 0.05	0.33 × 0.26 × 0.17	0.20 × 0.18 × 0.05	0.68 × 0.25 × 0.15
Temperature (K)	173	173	173	173	150
Space group	$P\bar{1}$	$P\bar{1}$	*Pbca*	*Pbca*	$P2_12_12_1$
a (Å)	10.828(5)	11.158(5)	16.041(4)	12.269(2)	9.712(4)
b (Å)	12.311(6)	13.552(5)	15.587(4)	14.131(3)	10.483(4)
c (Å)	14.229(7)	14.284(5)	21.001(5)	26.350(5)	20.230(8)
α (°)	70.935(10)	63.933(5)	90	90	90
β (°)	89.197(12)	85.830(5)	90	90	90
γ (°)	74.478(9)	77.065(5)	90	90	90
V (Å^3)	1721.7(14)	1890.2(13)	5251(2)	4568.3(14)	2059.8(14)
Z	2	2	16	8	4
D_c (g cm^{-3})	2.069	2.539	2.961	2.805	2.699
F(000)	1008	1300	4064	3408	1496
μ (Mo Kα, mm^{-1})	3.755	6.472	9.101	7.770	7.216
Index ranges	$-11 \leqslant k \leqslant 15$, $-17 \leqslant l \leqslant 17$, $-18 \leqslant h \leqslant 20$	$-15 \leqslant k \leqslant 15$, $-19 \leqslant l \leqslant 16$, $-20 \leqslant h \leqslant 19$	$-22 \leqslant k \leqslant 21$, $-18 \leqslant l \leqslant 22$, $-29 \leqslant h \leqslant 29$	$-17 \leqslant k \leqslant 14$, $-20 \leqslant l \leqslant 20$, $-37 \leqslant h \leqslant 26$	$-11 \leqslant k \leqslant 9$, $-12 \leqslant l \leqslant 9$, $-24 \leqslant h \leqslant 23$
Measured data	19680	23293	61885	53877	6628
2θ Range (°)	1.82–30.64	1.86–27.54	1.94–30.55	2.27–30.55	2.80–25.00
Completeness to θ_{max} (%)	95.1	96.5	99.3	99.2	99.4
Unique data	10129	11192	7992	6944	3563
($I \geqslant 2\theta(I)$)	7193	8239	6684	5860	3344
Number of refined parameters	370	361	163	176	172
Goodness-of-fit (F^2)	1.068	1.031	1.093	1.028	1.016
R, observed data; all data	0.0599; 0.0959	0.0327; 0.0556	0.0231; 0.0331	0.0276; 0.0369	0.0657; 0.0686
R_w, observed data; all data	0.1541; 0.1791	0.0692; 0.0781	0.0508; 0.0560	0.0666; 0.0722	0.1743; 0.1767
Largest diffraction peak/hole (e Å^{-3})	4.166/−2.354	1.382/−1.396	1.205/−1.577	2.351/−1.359	2.844/−2.390

$I1 \cdots I5–I6 \cdots I3$ is also strongly reminiscent of ‘classical’ tetraiodide (2^-) moieties found in numerous crystal structures. The Raman spectrum of solid (p-$MeOC_6H_4)_2TeI_2 \cdot \frac{1}{2}I_2$ (**1a**) reveals a band at $\tilde{\nu} = 176\ cm^{-1}$ for the I–I stretching vibration, that compares well with that of $(Ph_3Sb)_2OI_2 \cdot \frac{1}{4}I_2$ ($174\ cm^{-1}$) [10]. In molecular iodine the same vibration was observed in the solid state at $\tilde{\nu} = 184\ cm^{-1}$ and in the gas phase at $\tilde{\nu} = 213\ cm^{-1}$ [13].

In pioneering work, Vernon prepared an analogue of **3**, namely the tetraorganoditelluroxane $(Me_2Te)_2OI_2$ (**5**), by the partial hydrolysis of Me_2TeI_2 (**4**) in aqueous ammonia (Eq. (2)), or alternatively, by the redistribution reaction of Me_2TeI_2 (**4**) and $Me_2Te(OH)_2$ (**6**), which proceeds with condensation of the hydroxyl groups (Eq. (3)) [14]. Since compound **5** was not completely characterized at the time, we repeated its synthesis and now report on full structural details

$$\underset{\mathbf{4}}{2Me_2TeI_2} + H_2O + 2NH_3 \xrightarrow[-2NH_4I]{} \underset{\mathbf{5}}{(Me_2Te)_2OI_2} \tag{2}$$

$$\underset{\mathbf{4}}{Me_2TeI_2} + \underset{\mathbf{6}}{Me_2Te(OH)_2} \xrightarrow[-2H_2O]{} \underset{\mathbf{5}}{(Me_2Te)_2OI_2} \tag{3}$$

The crystal and molecular structure of $(Me_2Te)_2OI_2$ (**5**) is shown in Fig. 3. Selected bond parameters and crystal and refinement data are collected in the caption of Fig. 3 and Table 1, respectively. The structure contains two crystallographically independent molecules of **5**, which are associated *via* intermolecular secondary Te···I interactions giving rise to the formation of a coordination polymer. The spatial arrangement around the four independent Te atoms resembles the distorted trigonal bipyramid observed for **3**. The mean Te–I bond lengths 3.167(6) Å is significantly longer than those of Me_2TeI_2 (2.925(3) Å) [15]. The secondary Te···I contacts of average 3.740(3) Å connecting adjacent molecules are somewhat longer than those of **3**.

According to Vernon the redistribution reaction of Me_2TeI_2 (**4**) and $Me_2Te(OH)_2$ (**6**) in a ratio of 1:2 produced a different product, namely the hexaorganotritelluroxane $(Me_2Te)_3O_2I_2$ (**5a**) [14]. When we attempted to reproduce the preparation of **5a**, we obtained a crystalline product of the composition 2 $(Me_2Te)_2O(I)OH \cdot H_2O$ (**7**) in good yield, which has a melting point similar to **5a**. However, formally compound **7** is the product of a redistribution reaction between Me_2TeI_2 (**4**) and $Me_2Te(OH)_2$ (**6**) in a ratio of 1:3

$$\underset{\mathbf{4}}{Me_2TeI_2} + \underset{\mathbf{6}}{3Me_2Te(OH)_2} \underset{-H_2O}{\rightarrow} \underset{\mathbf{7}}{2(Me_2Te)_2O(I)OH \cdot H_2O} \tag{4}$$

The crystal structure of **7** and a perspective view along the crystallographic *b*-axis are shown in Figs. 4 and 5. Selected bond parameters and crystal and refinement data are collected in the caption of Fig. 4 and Table 1, respectively.

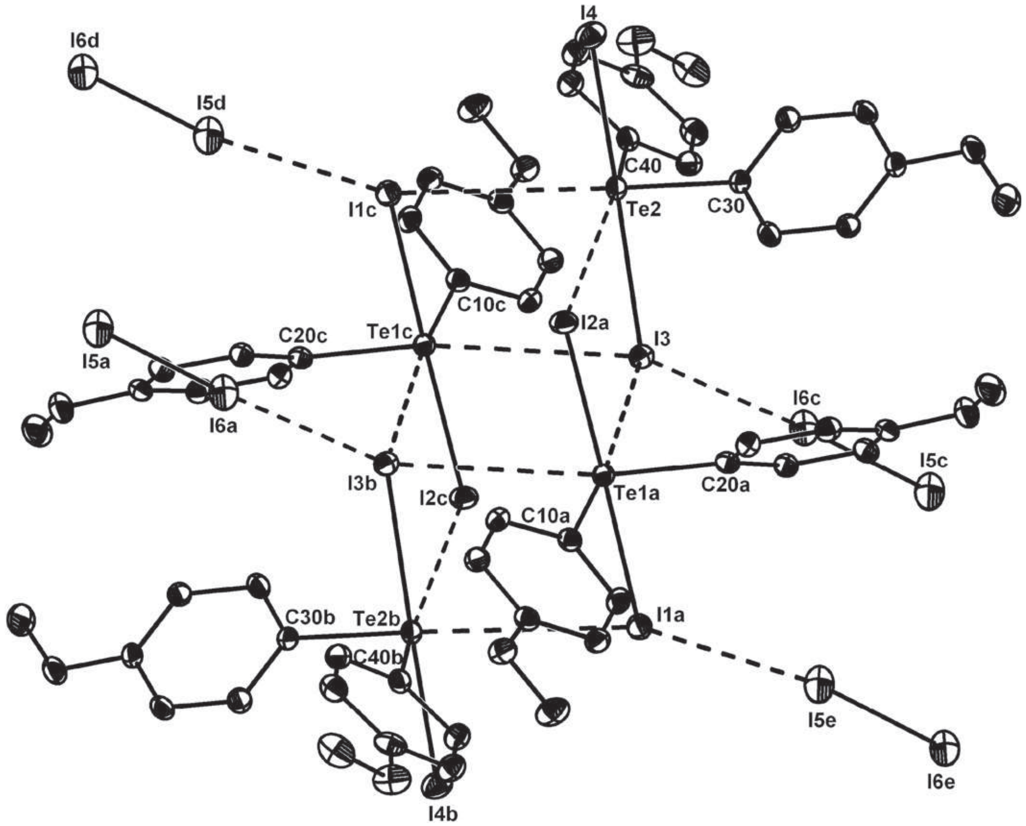


Fig. 2. Molecular structure and supramolecular association of $(p\text{-MeOC}_6\text{H}_4)_2\text{TeI}_2 \cdot \frac{1}{2}\text{I}_2$ (**1a**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Symmetry codes used to generate equivalent atoms: $a = 1 - x,\ 1 - y,\ 1 - z$, $b = -x,\ 1 - y,\ 1 - z$, $c = -1 + x,\ y,\ z$, $d = -1 + x,\ y, 1 + z$, $e = 1 - x,\ 1 - y,\ -z$. Selected bond parameters [Å, °]: Te1a–C10a 2.135(4), Te1a–C20a 2.134(4), Te1a–I1a 2.9818(8), Te1a–I2a 2.8964(7), Te1a···I3 3.678(1), Te1a···I3b 3.739(1), Te2–C30 2.115(4), Te2–C40 2.119(4), Te2–I3 3.0398(8), Te2–I4 2.8334(8), Te2···I1c 3.832(1), Te2···I2a 3.949(1), I1c···I5a 3.492(1), I3···I6c 3.360(1), I5a–I6a 2.743(1); I1–Te1–I2 174.74(1), I3–Te2–I4 176.56(1).

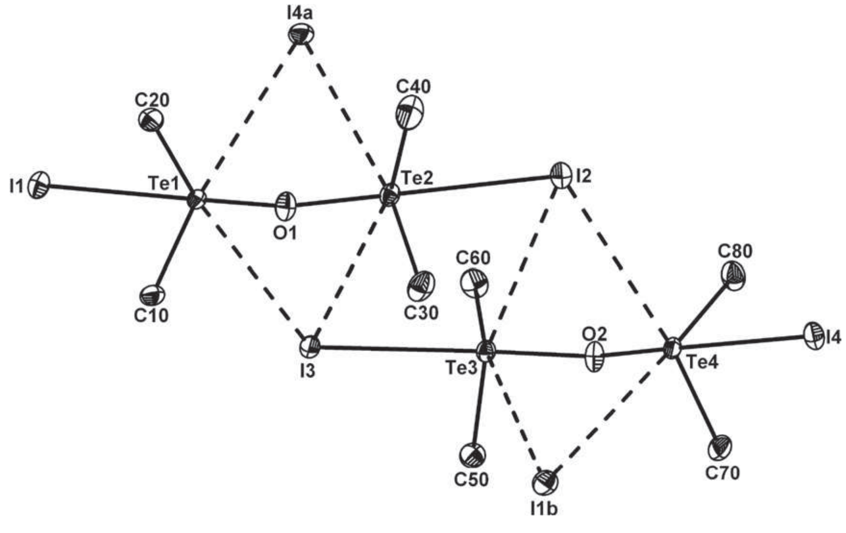


Fig. 3. Molecular structure and supramolecular association of $(\text{Me}_2\text{Te})_2\text{OI}_2$ (**5**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Symmetry code used to generate equivalent atoms: $a = x,\ 0.5 - y,\ -0.5 + z$, $b = 0.5 - x,\ 1 - y,\ -0.5 + z$. Selected bond parameters [Å, °]: Te1–C10 2.121(4), Te1–C20 2.107(4), Te1–I1 3.1854(7), Te1···I3 3.7083(7), Te1···I4a 3.6268(8), Te1–O1 1.976(3), Te2–C30 2.115(4), Te2–C40 2.108(5), Te2–I2 3.1692(6), Te2···I3 3.758(1), Te2···I4a 3.6066(8), Te2–O1 1.983(3), Te3–C50 2.105(4), Te3–C60 2.110(4), Te3–I3 3.1517(6), Te3···I2 3.7808(9), Te3···I1b 3.7756(8), Te3–O2 1.979(3), Te4–C70 2.115(4), Te4–C80 2.115(4), Te4–I4 3.1618(6), Te4···I1b 3.7503(9), Te4···I2 3.7503(9), Te4–O2 1.969(3), O1–Te1–I1 170.96(8); O1–Te2–I2 174.47(8), O2–Te3–I3 172.67(8), O2–Te4–I4 171.92(8), Te1–O1–Te2 123.5(1), Te3–O2–Te4 123.8(1).

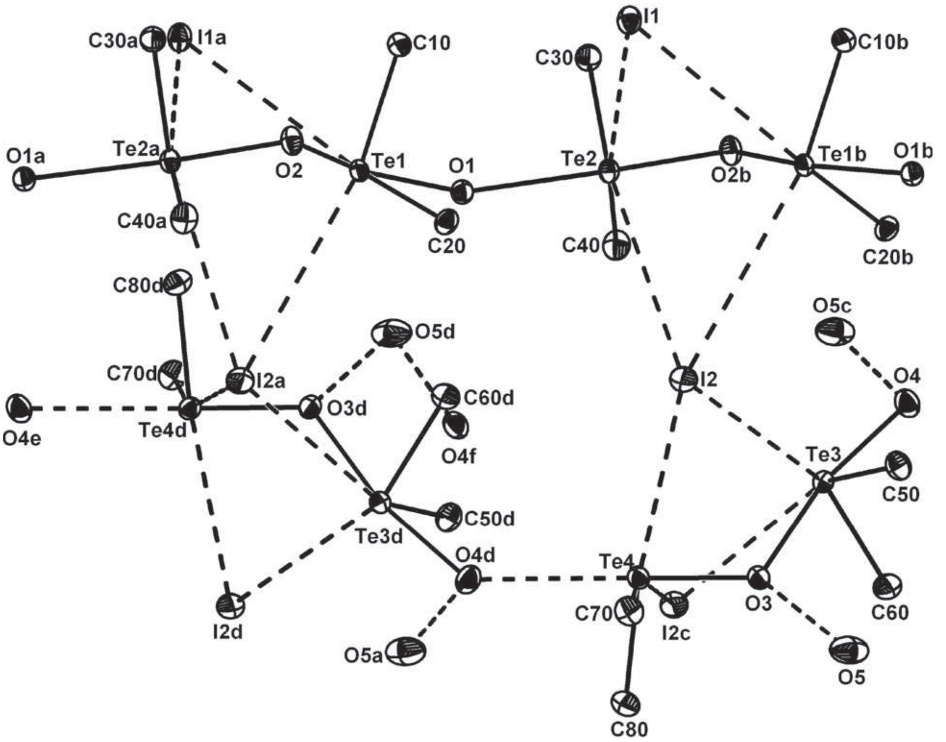


Fig. 4. Molecular structure and supramolecular association of 2 $(Me_2Te)_2O(I)OH \cdot H_2O$ (**7**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Symmetry codes used to generate equivalent atoms: $a = 0.5 - x, 0.5 + y, z$, $b = 0.5 - x - 0.5 + y, z$, $c = 0.5 + x, y, 0.5 - z$, $d = 1 - x, 0.5 + y, 0.5 - z$, $e = x, 1 + y, z$, $f = 1.5 - x, 0.5 + y, z$. Selected bond parameters [Å, °]: Te1–O1 2.179(3), Te1–O2 2.039(3), Te1···I1a 3.802(1), Te1···I2a 3.916(1), Te1–C10 2.105(4), Te1–C20 2.104(4), Te2–O1 2.373(3), Te2–O2b 1.965(3), Te2···I1 3.667(1), Te2···I2 3.808(1), Te2–C30 2.112(4), Te2–C40 2.108(5), Te3–O3 2.195(3), Te3–O4 2.063(3), Te3···I2 4.099(1), Te3···I2c 4.193(1), Te3–C50 2.102(5), Te3–C60 2.097(5), Te4–O3 1.913(3), Te4···O4d 2.715(3), Te4···I2 3.702(1), Te4···I2c 4.147(1), Te4–C70 2.109(5), Te4–C80 2.111(5), O3···O5 2.785(6), O4···O5c 2.792(6); O1–Te1–O2 163.0(1), O1–Te1–C10 84.9(2), O2–Te1–C20 81.8(1), O2–Te1–C10 87.0(2), O2–Te1–C20 84.8(2), C10–Te1–C20 100.2(2), O1, Te2–O2b 172.0(1), O1–Te2–C40 84.2(2), O1–Te2–C30 85.4(1), O2b–Te2–C30 89.6(2), O2b–Te2–C40 90.1(2), C30–Te2–C40 94.3(2), O3–Te3–O4 167.6(1), O3–Te3–C50 84.6(2), O3–Te3–C60 82.4(2), O4–Te3–C50 86.6(2), O4–Te3–C60 90.0(2), C50–Te3–C60 96.5(2), O3–Te4–O4d 177.7(1), O3–Te4–C70 95.25(17), O3–Te4–C80 95.23(16), O4d–Te4–C70 82.5(2), O4d–Te4–C80 84.9(1), C70–Te4–C80 91.9(2), Te1–O1–Te2 131.1(1), Te1–O2–Te2a 120.8(2), Te3–O3–Te4 118.7(1), Te3–O4d–Te3d 130.3(1).

The structure is complex and essentially contains two 1D polymers with a Te–O backbone. The first polymer string (Te1, O1, and Te2) can be regarded as $(Me_2TeO)_n$ polymer, similar as the polymeric structure of $[(p\text{-}MeOC_6H_4)_2TeO]_n$ (**2**) [4]. The average Te–O bond length and the Te–O–Te angle are 2.139(3) Å and 126.0(2)° and compare well with the related values of **2** being 2.063(2) Å and 126.0(1)° [4]. Notably, the structures of $Me_2Te(OH)_2$ (**6**) and potential condensation products, such as $(Me_2TeO)_n$ (**6a**) are still unknown. The second polymer string (Te3, O3, Te4, and O4) comprises $R_2Te(OH)TeR_2(OH)$ units that are associated by short secondary Te···O(H) interactions of 2.373(3) Å. The short Te–O(H) bonds within the $R_2Te(OH)TeR_2(OH)$ units are with average 2.058(3) Å comparable with other 'Te–O' single bonds [4,5]. The two crystallographically independent iodide ions are surprisingly not involved in primary bonding to the Te atoms. However, they appear to play an integral role for the supramolecular association as they form secondary bonds to all Te atoms. The supramolecular arrangement of **7** is shown in Fig. 4. The lengths of secondary Te···I bonds vary between 3.667(1) and 4.193(1) Å. The latter value is slightly larger than the sum of van-der Waals radii (4.04 Å), however, the directionality of the bonds suggests this to be an attractive interaction. The structural directing effect of the iodide ions is reminiscent of the recently reported dodecanuclear isopropyltellurium(IV)oxo cluster $[Li(THF)_4][\{(i\text{-}PrTe)_{12}O_{16}Br_4\{Li(THF)Br\}_4\}Br] \cdot 2\ THF$, in which 8 Te atoms are situated around a structurally directing bromide ion [16]. The water molecule (O5) of **7** acts twice as acceptor for hydrogen bonds with the hydroxyl groups (O3, O4). The mean O···O distance of 2.788(6) is indicative for medium strength hydrogen bonding [17]. The IR spectrum of **7** confirms the presence of different hydroxy groups being involved in hydrogen bonding by showing three OH stretching vibrations at $\tilde{\nu} = 3433, 3302, 3221\ cm^{-1}$. Once isolated from aqueous solution, the solubility of **5** and **7** in water is very poor. The ^1H NMR spectra (D_2O) of **5** and **7** exhibit a signal resonance at δ 2.62 and 2.50 with tellurium satellites ($^2J(^1H\text{–}^{125}Te) = 26$ and 25 Hz). The simplicity of the ^1H NMR spectra suggests that the Te atoms are equal in solution, presumably due to electrolytic dissociation of **5** and **7**. In organic solvents **5** and **7** are virtually insoluble. It should be noted that an alternative (formal) description of 2 $(Me_2Te)_2O(I)OH \cdot H_2O$ (**7**) may be $Me_2TeO \cdot [Me_2(I)TeOTe(OH)] \cdot [H_3O]I$, however, the

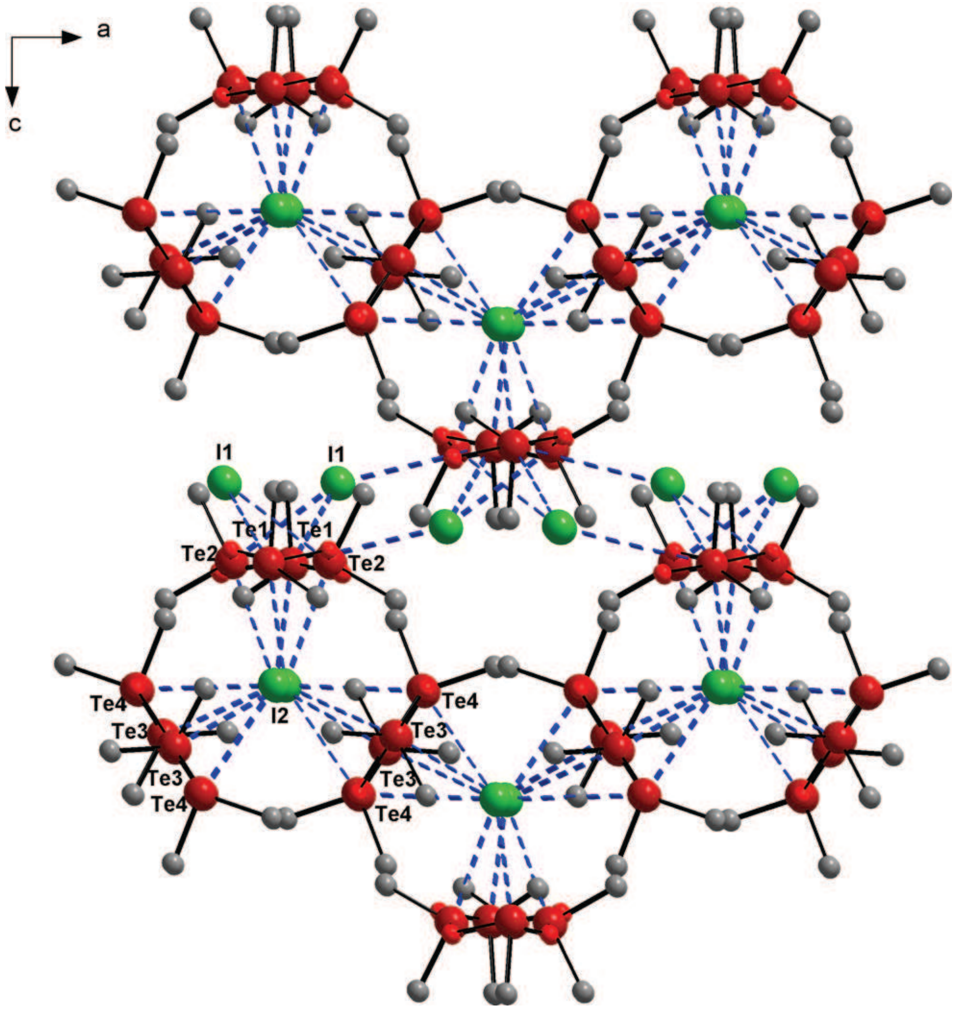


Fig. 5. Perspective view along the crystallographic *b*-axis of 2 $(Me_2Te)_2O(I)OH \cdot H_2O$ (**7**) showing the association of the 2D-polymer strings by secondary Te···I interactions (blue broken bonds).

aqueous solution of **7** reacts basic, which makes the presence of hydroxonium ions improbable.

The base hydrolysis of $C_4H_8TeI_2$ (**8**) with an excess of aqueous NaOH solution afforded the tritelluroxane diiodide $(C_4H_8Te)_3O_2I_2$ (**9**) in excellent yield as colourless crystals

$$\underset{\mathbf{8}}{3C_4H_8TeI_2} + 4NaOH \underset{\substack{-2H_2O\\-4NaI}}{\rightarrow} \underset{\mathbf{9}}{(C_4H_8Te)_3O_2I_2} \qquad (5)$$

The molecular structure and supramolecular association of **9** is shown in Fig. 6. Selected bond parameters and crystal and refinement data are collected in the caption of Fig. 6 and Table 1, respectively. Again, the spatial arrangement around the Te atoms is trigonal bipyramidal. Like in compounds **3** and **5**, the coordination of the terminal Te atoms (Te1 and Te3) is distorted. The average Te–O bond length of Te1 and Te2 (1.94(1) Å) is shorter than the average Te–O bond length of Te2 (2.11(1) Å). The average Te–I bond lengths of 3.322(2) Å is longer than in $C_4H_8TeI_2$ (**8**) being 2.925(1) Å [12] and resembles that of **3** and **5**. Besides the primary Te-I bonds, there are a number of secondary Te···I contracts ranging from 3.636(2) to 4.021(2) Å that connect adjacent molecules in the crystal lattice. Thus, Te1 is involved in one secondary contact, whereas Te2 and Te3 reveal two such contacts. Once crystallized from the mother liquor, the tritelluroxane **9** is virtually insoluble in all solvents, with the exception of methanol where it is sparingly soluble. The ^1H NMR spectrum of **9** reveals two equally intense signals at δ 2.86 and 2.40, which suggest that all C_4H_8Te moieties are magnetically equivalent in solution. Presumably electrolytic dissociation takes place upon dissolution in methanol.

3. Experimental

3.1. General

The diorganotellurium compounds R_2TeI_2 (**1**, R = *p*-$MeOC_6H_4$ [18]; **4**, R = Me [19]), (*p*-$MeOC_6H_4)_2TeO$ (**2**) [4], $Me_2Te(OH)_2$ (**6**) [19], $C_4H_8TeI_2$ (**8**) [20] have been prepared according to literature procedures. The ^1H and ^{13}C NMR spectra were recorded using Jeol GX 270 and Varian

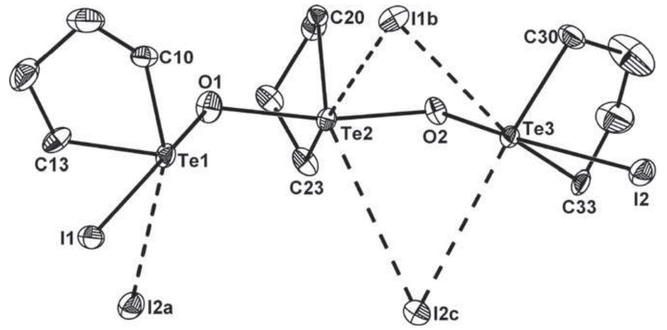


Fig. 6. Molecular structure and supramolecular association of $(C_4H_8Te)_3O_2I_2$ (**9**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Symmetry codes used to generate equivalent atoms: $a = x,\ 1 + y,\ z,\ b = 1 - x,\ -0.5 + y,\ 1.5 - z,\ c = 2 - x,\ 0.5 + y,\ 1.5 - z$. Selected bond parameters [Å, °]: Te1–O1 1.93(1), Te1–I1 3.303(2), Te1···I2a 4.021(2), Te1–C10 2.14(2), Te1–C13 2.13(2), Te2–O1 2.16(1), Te2–O2 2.06(1), Te2···I1b 3.662(2), Te2···I2c 3.918(2), Te2–C20 2.11(1), Te2–C23 2.13(2), Te3–O2 1.95(1), Te3–I2 3.341(2), Te3···I1b 3.687(2), Te3···I2c 3.636(2), Te3–C30 2.18(2), Te3–C33 2.14(2); O1–Te1–I1 179.2(4), O1–Te1–C10 93.9(6), O1–Te1–C13 92.7(7), I1–Te1–C10 85.3(5), I1–Te1–C13 87.4(5), C10–Te1–C13 83.6(7), O1–Te2–O2 165.7(5), O1–Te2–C20 82.2(6), O1–Te2–C23 86.4(6), O2–Te2–C20 84.2(6), O2–Te2–C23 88.2(6), C20–Te2–C23 85.5(7), O2–Te3–I2 176.5(4), O2–Te3–C30 92.4(6), O2–Te3–C33 92.0(6), I2–Te3–C30 84.2(5), I2–Te3–C33 87.3(5), C30–Te3–C33 84.4(8), Te1–O1–Te2 115.2(6), Te2–O2–Te3 118.0(6).

300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^1H, ^{13}C). Microanalyses were obtained from a Vario EL elemental analyzer. Infrared spectra were recorded using Nexus FT-IR spectrometer with a Smart DuraSamplIR. Raman spectra were recorded using a Bruker RFS 100/S spectrometer with a Nd:YAG laser.

3.2. Synthesis of $[(p\text{-}MeOC_6H_4)_2Te]_2OI_2$ (3)

A mixture of (p-$MeOC_6H_4)_2TeO$ (0.18 g, 0.5 mmol) and (p-$MeOC_6H_4)_2TeI_2$ (0.30 g, 0.5 mmol) was dissolved in THF (20 mL) and stirred for 1 h. With a minimum of convection, a layer of hexane (30 mL) was carefully place over this solution. Overnight crystallisation at the layer interface afforded orange crystals of **3** (0.44 g, 0.46 mmol, 92%; m.p. 200–201 °C). ^1H NMR ($CDCl_3$): $\delta = 7.84$ (d, 8H, p-$O_oMeC_6H_4$), 6.76 (d, 8H, p-$O_mMeC_6H_4$), 3.75 (s, 12 H, OCH_3). ^{13}C NMR ($CDCl_3$): $\delta = 161.3$ (p-$O_pMeC_6H_4$), 136.8 (p-$O_oMeC_6H_4$); 116.1 (p-$O_iMeC_6H_4$), 114.7 (p-$O_oMeC_6H_4$), 55.3 (OCH_3). Raman: $\tilde{\nu} = 3065$w, 3050w, 3015w, 2962w, 2935w, 1583m, 1565w, 1453w, 1433w, 1401w, 1308w, 1254w, 1183w, 1060w, 1000w, 825w, 790s, 702w, 627m, 600s, 590s, 519w, 454s cm^{-1}. Anal. Calc. for $C_{28}H_{28}I_2O_5Te_2$ (953.53): C, 35.27; H, 2.96. Found: C, 35.33; H, 2.57%.

3.3. Synthesis of $[(Me)_2Te]_2OI_2$ (5)

Solid Me_2TeI_2 (0.41 g, 1 mmol) was dissolved in conc. NH_3 solution (5 mL). Vacuum suction was applied to remove most of the excess NH_3. Slow evaporation of the water produced colourless crystals of **5** that slowly turned orange red upon standing at air (0.22 g, 0.38 mmol, 76%; m.p.: 100–102 °C (decomp.)). ^1H NMR (D_2O): $\delta = 2.62$ (s, 6H, $^2J(^1H\text{–}^{125}Te)$ 26 Hz). Raman: $\tilde{\nu} = 3010$w, 2916m, 1400vw, br, 1231m, 1216w, 849vw, br, 654m, 546sh, 536vs, 426vs, 249w, 211sh, 185m, 143m, 115m cm^{-1}. Anal. Calc. for $C_4H_{12}I_2OTe_2$ (581.15): C, 8.21; H, 2.07. Found: C, 8.21; H, 1.68%.

3.4. Synthesis of 2 $(Me_2Te)_2O(I)OH \cdot H_2O$ (7)

To a solution of $Me_2Te(OH)_2$ (prepared *in situ* from Me_2TeI_2 (1.7 g, 4 mmol)) [19] in water (20 mL) solid Me_2TeI_2 (0.41 g, 1 mmol) was added. Slow evaporation of the water afforded clear crystals of **7** (310 mg, 0.64 mmol, 64%; m.p. 144–145 °C). ^1H NMR (D_2O): $\delta = 2.50$ (s, 6H, $^2J(^1H\text{–}^{125}Te)$ 25 Hz). Raman: $\tilde{\nu} =$ 3028sh, 3009w, 2919m, 1408vw, br, 1237w, 1223w,1212w, 1016w, 650m, 556s, 546s, 535s, 499m, 470m,437m, 266m, 219m, 119s cm^{-1}. IR $\tilde{\nu} = 3433$m, 3302s, 3221sh, 3032sh, 3005m 2936sh, 2912m, 1641m, 1402m, 1233m, 1219m,1209m, 1101m, br, 1015m, 886m, 874sh, 858m, 827m,811m, 652s, 564m, 546m, 534m cm^{-1}. Anal. Calc. for $C_4H_{13}IO_2$-$Te_2 \cdot \frac{1}{2}H_2O$ (486.26): C, 9.92; H, 2.91. Found: C, 9.92; H, 2.52%.

3.5. Synthesis of $(C_4H_8Te)_3O_2I_2$ (9)

Solid $C_4H_8TeI_2$ (0.72 g, 1.65 mmol) was suspended in methanol (50 ml) and 4 ml of NaOH (5 M) was added. The coloured solution became clear and the remaining iodide dissolved. The reaction mixture was filtrated and another portion of the NaOH (2 ml) was added. Slow evaporation of the solvent produced colourless crystals of **9**. (0.42 g, 0.5 mmol, 91%; m.p. 185 °C) decomp. ^1H NMR(CD_3OD): $\delta = 2.86$ (m, 2H), 2.40 (m, 2H). IR: $\tilde{\nu} = 3422$s, br 3010w, 2989w, 2944m, sh, 2921m, 2854m, 1620m, br, 1449w, 1436m, 1399m, 1389m, 1326vw, 1301m, 1237m, 1230m, sh, 1182m, 1150w, 1140w, 1086m,1079m, sh, 1041m, sh, 1033m, 957w, 943m, 871w, 853m, 824w, 802m, 756m, 736m, 668s, 599vs br, 563s, 552s, 532s. Anal. Calc. for $(C_4H_8Te)_3O_2I_2$ (836.93): C, 17.22; H, 2.89. Found: C, 17.18; H, 2.50%.

3.6. X-ray crystallography

Intensity data were collected on a Bruker SMART 1000 area detector (**3**, **1a**, **5**, **7**) or a STOE IPDS 2T area detector (**9**) with graphite-monochromated Mo Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the programs SAINT and SADABS [21]. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WINGX 2002[22]. Full-matrix least-squares refinements on F^2, using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically. For **7**, the hydrogen atom H4 attached to O4 was located during the refinement and was also refined isotropically. The absolute configuration of **9** was determined by examination of the Flack parameter 0.00(14). Figures were created using DIAMOND [23].

Acknowledgements

Mrs. Irene Brüdgam (Freie Universität Berlin) is thanked for the X-ray data collection. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Appendix A. Supplementary material

CCDC 671469, 671470, 671471, 671472 and 671473 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.12.006.

References

[1] (a) J. Zuckerman-Schpector, I. Haiduc, Phosphorus, Sulfur, Silicon 171 (2001) 73;
(b) I. Haiduc, J. Zuckerman-Schpector, Phosphorus, Sulfur, Silicon 171 (2001) 171;
(c) W.-W. du Mont, C.G. Hrib, Handbook of Chalcogen Chemistry (2007) 833;
(d) M.C. Aragoni, M. Arca, F.A. Devillanova, A. Garau, F. Isaia, V. Lippolis, A. Mancini, Bioinorg. Chem. Appl. (2007) 1.

[2] (a) W.-W. du Mont, H.U. Meyer, S. Kubinoik, S. Pohl, W. Saak, Chem. Ber. 125 (1992) 761;
(b) A.C. Hillier, S.-Y. Liu, A. Sella, M.R.J. Elsegood, Angew. Chem., Int. Ed. 38 (1999) 2745;
(c) D. Witthaut, K. Kirschbaum, O. Conrad, D.M. Giolando, Organometallics 19 (2000) 5238;
(d) H.T.M. Fischer, D. Naumann, W. Tyrra, Chem. Eur. J. 12 (2006) 2515;
(e) J. Beckmann, S. Heitz, M. Hesse, Inorg. Chem. 46 (2007) 3275;
(f) J. Beckmann, M. Hesse, H. Poleschner, K. Seppelt, Angew. Chem., Int. Ed. 46 (2007) 8277.

[3] (a) E.S. Lang, R.M. Fernandes Jr., E.T. Silveira, U. Abram, E.M. Vázquez-López, Z. Anorg. Chem. 625 (1999) 1401;
(b) P.D. Bolye, W.I. Cross, S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, S. Sarward, J.M. Sheffield, Angew. Chem., Int. Ed. 39 (2000) 1796;
(c) E.S. Lang, G. Manzoni de Oliveira, R.M. Fernandes Jr., E.M. Vázquez-López, Inorg. Chem. Comm. 6 (2003) 869;
(d) D.B. Werz, R. Gleiter, F. Rominger, J. Organomet. Chem. 689 (2004) 627;
(e) G.N. Ledesma, E.S. Lang, U. Abram, J. Organomet. Chem. 689 (2004) 2092;
(f) E.S. Lang, G. Manzoni de Oliveira, G.N. Ledesma, Z. Anorg. Allg. Chem. 631 (2005) 1524;
(g) J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, M. Schürmann, Aust. J. Chem. 58 (2005) 119;
(h) J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, Acta Crystallogr., Sect. E61 (2005) o986;
(i) G. Manzoni de Oliveira, E. Faoro, E.S. Lang, G.A. Casagrande, Z. Anorg. Allg. Chem. 632 (2006) 659;
(j) E.S. Lang, G. Manzoni de Oliveira, G.A. Casagrande, J. Organomet. Chem. 691 (2006) 59;
(k) E. Faoro, G. Manzoni de Oliveira, E.S. Lang, J. Organomet. Chem. 691 (2006) 5867;
(l) E.S. Lang, G.A. Casagrande, G. Manzoni de Oliveira, G.N. Ledesma, S.S. Lemos, E.E. Castellano, U. Abram, Eur. J. Inorg. Chem. (2006) 958.

[4] J. Beckmann, D. Dakternieks, A. Duthie, F. Ribot, M. Schürmann, N.A. Lewcenko, Organometallics 22 (2003) 3257.

[5] (a) J. Beckmann, D. Dakternieks, A. Duthie, N.A. Lewcenko, C. Mitchell, Angew. Chem., Int. Ed. 43 (2004) 6683;
(b) J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, Dalton Trans. (2005) 1563;
(c) J. Beckmann, J. Bolsinger, Organometallics 26 (2007) 3601;
(d) J. Beckmann, J. Bolsinger, A. Duthie, Austr. J. Chem., submitted for publication.

[6] J. Farran, A. Alvarez-Larena, M.V. Capparelli, J.F. Piniella, G. Germain, L. Torres-Castellanos, Acta Crystallogr., Sect. C 54 (1998) 995.

[7] M. Suzuki, I.-H. Son, R. Noyori, H. Masuda, Organometallics 9 (1990) 3043.

[8] J. Beckmann, D. Dakternieks, A. Duthie, N.A. Lewcenko, C. Mitchell, M. Schürmann, Z. Anorg. Allg. Chem. 631 (2005) 1856.

[9] M.J. Taylor, L.-J. Baker, C.E.F. Rickard, P.W.J. Surman, J. Organomet. Chem. 498 (1995) C14.

[10] M.J. Almond, M.G.B. Drew, D.A. Rice, G. Salisbury, M.J. Taylor, J. Organomet. Chem. 522 (1996) 265.

[11] H. Pritzkow, Inorg. Chem. 18 (1979) 311.

[12] (a) P.C. Srivastava, S. Bajpai, S. Bajpai, C. Ram, R. Kumar, J.P. Jasinski, R.J. Butcher, J. Organomet. Chem. 689 (2004) 194;
(b) P.C. Srivastava, S. Bajpai, R. Lath, R.J. Butcher, J. Organomet. Chem. 608 (2000) 96.

[13] (a) W. Holzer, W.F. Murphy, H.J. Bernstein, J. Chem. Phys. 52 (1970) 399;
(b) A. Anderson, T.S. Sun, Chem. Phys. Lett. 6 (1970) 611.

[14] (a) R.H. Vernon, J. Chem. Soc. 117 (1920) 889;
(b) R.H. Vernon, J. Chem. Soc. 119 (1921) 687.

[15] L.Y.Y. Chan, F.W.B. Einstein, J. Chem. Soc., Dalton Trans. (1972) 316.

[16] H. Citeau, K. Kirschbaum, O. Conrad, d.M. Giolando, Chem. Commun. (2001) 2006.

[17] T. Steiner, Angew. Chem., Int. Ed. 41 (2002) 48.

[18] K. Lederer, Chem. Ber. 49 (1916) 1076.

[19] (a) R.H. Vernon, J. Chem. Soc. (1920) 86;
(b) P.C. Srivastava, S. Bajpai, C. Ram, R. Kumar, R.J. Butcher, J. Organomet. Chem. 692 (2007) 2482.

[20] G.T. Morgan, F.H. Burstall, J. Chem. Soc. (1931) 180.

[21] SMART, SAINT and SADABS, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1999.

[22] L.J. Farrugia, J. Appl. Cryst. 32 (1999) 837–838.

[23] DIAMOND V3.1d, Crystal Impact GbR, K. Brandenburg, H. Putz, 2006.

MANUSCRIPT III

5 A New Series of Intramolecularly Coordinated Diaryltellurium Compounds. Rational Synthesis of the Diarylhydroxytelluronium Triflate [(8-$Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$

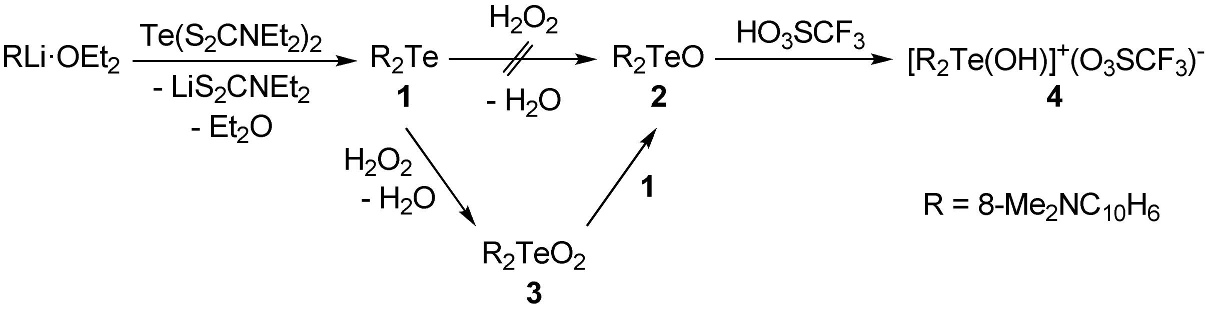
Jens Beckmann, Jens Bolsinger, Pamela Finke and Andrew Duthie, *Organometallics,*

received

5.1 SYNOPSIS

Aside from the intermolecular interactions concerning organotellurium compounds especially the reactivity and the influence of intramolecularly coordinating ligands were of interest.

In the course of this work the diaryltelluride (8-$Me_2NC_{10}H_6)_2Te$, the diaryltellurium(IV) oxide (8-$Me_2NC_{10}H_6)_2TeO$, the diaryltellurium(VI) dioxide (8-$Me_2NC_{10}H_6)_2TeO_2$ and the diarylhydroxytelluronium triflate [(8-$Me_2NC_{10}H_6)_2TeOH](O_3SCF_3)$, featuring the [(8-$Me_2NC_{10}H_6)_2TeOH]^+$ cation were prepared (Scheme 7).



Scheme 7: Synthesis of bis(8-dimethylaminonaphthyl)tellurium compounds

The synthesis of the bis(8-dimethylaminonaphthyl)telluride, (8-$Me_2NC_{10}H_6)_2Te$, was achieved by the reaction of 8-dimethylaminonaphthyllithium etherate with tellurium(II) bis(dithiocarbamate) in acetonitrile, which is essential since different solvents provided only the mono-substituted product 8-$Me_2NC_{10}H_6TeS_2CNEt_2$[70].

Notably, the reaction of the diaryltelluride (8-$Me_2NC_{10}H_6)_2Te$ with an excess of H_2O_2 did not afford the expected diaryltellurium(IV) oxide (8-$Me_2NC_{10}H_6)_2TeO$, but the diaryltellurium(VI) dioxide (8-$Me_2NC_{10}H_6)_2TeO_2$, which is unusual. The oxidation of other known diaryltellurides with most oxidizing agents either stops at the stage of diaryltellurium(IV) oxides or produces ill-defined product mixtures[28]. This compound is only the second example of this compound class. The first fully characterized monomeric diaryltellurium(VI) dioxide (2,4,6-*i*-$Pr_3C_6H_2)_2TeO_2$ was obtained recently, using the kinetic stabilization of a bulky organic substituent[27].

The organic substituents are situated in distorted *trans*-position, whereas the O and N atoms occupy mutually *cis*-positions. Despite the increase of the oxidation state and the coordination number, the (average) Te···N bond lengths of (8-$Me_2NC_{10}H_6)_2TeO_2$ decreases only marginally upon oxidation of (8-$Me_2NC_{10}H_6)_2Te$.

However, the synthesis of bis(8-dimethylaminonaphthyl)tellurium oxide, (8-$Me_2NC_{10}H_6)_2TeO$, was achieved by the comproportionation reaction of (8-$Me_2NC_{10}H_6)_2Te$ and (8-$Me_2NC_{10}H_6)_2TeO_2$. In solution and in the solid state the tellurium oxide is sensitive to air oxidation and slowly turns into the tellurium dioxide. This reactivity is highly unusual as all previously known diaryltellurium oxides are air-stable and rather difficult to oxidize[28].

All attempts at obtaining single crystals of the oxide suitable for X-ray crystallography failed, however, the much higher melting point of the diaryltellurium oxide compared to those of the starting material points to a polymeric structure in the solid state, similar to that of (4-$MeOC_6H_4)_2TeO$[19]. This assumption is further supported by the observation that the solubility of the tellurium oxide is drastically reduced once isolated from the mother liquor. The IR spectrum is inconclusive with respect to asymmetric and symmetric Te-O stretching vibration and shows no evidence for O-H stretching vibrations.

The ^{125}Te NMR spectrum (D_3COD, r.t.) of the tellurium oxide exhibits broad signals in all solvents ($CDCl_3$, d_6-DMSO, D_3COD) at all temperatures measured. Therefore, it is proposed that the tellurium oxide exists as mixture of oligomers $R_2Te(OTeR_2)_nO$ with Te-O single bonds in solution rather than a discrete monomer containing a (formal) Te-O double as found for the related (2-$MeNCH_2C_6H_4)_2TeO$[25].

The intramolecular coordination of the N donor ligand allows an isolation of the bis(8-dimethylaminonaphthyl)hydroxytelluronium triflate, [(8-$Me_2NC_{10}H_6)_2TeOH](O_3SCF_3)$, featuring the [(8-$Me_2NC_{10}H_6)_2TeOH]^+$ cation and triflat ions that are associated by medium strength hydrogen bonding[71]. The protonation of a diaryltellurium(IV) oxide lacking intramolecularly coordination, namely (4-$MeOC_6H_4)_2TeO$ with triflic acid produced the diarylhydroxytelluronium(IV) cation $[(4\text{-}MeOC_6H_4)_2TeOH]^+$ and triflate anions only in solution[22]. All attempts at isolating the cation lead to a condensation reaction and the formation of the tetraarylditelluroxane $[(4\text{-}MeOC_6H_4)_2Te]_2O(O_3SCF_3)_2$[22].

It is notable that the axial Te1···N1 bond is considerably shorter than the equatorial Te1···N2 bond – contradicting Bent's rule –, which points to a strong attractive interaction of one intramolecularly coordinating ligand with the Te atom.

The ^1H and ^{13}C NMR spectra ($CDCl_3$, –35℃) show two sets of signals for the magnetically inequivalent 8-dimethylaminonaphthyl substituents. The four N-methyl groups give rise to four singulets (^1H) as well as (^{13}C), respectively, which suggests that the trigonal bipyramidal structure is retained in solution and configurationally stable at –35℃. However, at room temperature the configurational stability might be compromised as the ^1H and ^{125}Te NMR signals are somewhat broad.

DFT calculations

The geometries and Hirshfeld charges of the compounds R_2Te, R_2TeO, R_2TeO_2, $[R_2TeOH]^+$ and $R_2Te(OH)_2$ were calculated, whereby the organic substituent was R= $8\text{-}Me_2NC_{10}H_6$, respectively R = Ph.

Due to the lack of an experimentally established molecular structure of $(8\text{-}Me_2NC_{10}H_6)_2TeO$, the calculated geometry in the gas phase was examined closely. The spatial arrangement is best described as distorted trigonal bipyramidal. The calculated Te-O bond length is in the typical range of a (formal) Te-O double bond and very good comparable with the experimental value of $(2\text{-}Me_2NCH_2C_6H_4)_2TeO$[25]. The intramolecular Te···N bonds differ in their lengths, whereas the longer Te···N bond is situated in *trans*-position in respect to the (formal) Te-O double bond.

The formation of all neutral oxidation products is increasingly exothermic when going from the lowest to the highest oxidation states regardless of the organic substituent.

Notably, the energy difference between the respective diarylhydroxytelluronium ions $[R_2Te(OH)]^+$ is much larger than those for the neutral compound classes, which is attributed to the intramolecularly coordinating 8-dimethylaminonaphthyl substituents, which compensate the positive charge of diarylhydroxytelluronium ions $[R_2Te(OH)]^+$.

The Hirshfeld charges situated at the N atoms of $(8\text{-}Me_2NC_{10}H_6)_2TeO$ and $[(8\text{-}Me_2NC_{10}H_8)_2Te(OH)]^+$ reveals that the axial N donor substituent being situated in *trans*-position to the hydroxyl group underwent a larger change than the equatorial N donor substituent upon protonation. In fact, the axial N atom of $[(8\text{-}Me_2NC_{10}H_8)_2Te(OH)]^+$ possesses the smallest negative charge of all species under consideration. Therefore the axial N atom appears to be deeper involved in the charge compensation than the equatorial N atom, which is consistent with the fact that the axial Te···N bond length is shorter than the equatorial Te···N bond lengths.

5.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann and Pamela Finke.

X-Ray Crystallography: Prof. Dr. Jens Beckmann
^{125}Te MAS-NMR spectra and analysis thereof: Dr. Andrew Duthie
The DFT-calculations were carried out by Pamela Finke
.

Organometallics - Full Paper

A New Series of Intramolecularly Coordinated Diaryltellurium Compounds. Rational Synthesis of the Diarylhydroxytelluronium Triflate $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$

Jens Beckmann,[a,b] * Jens Bolsinger,[a] Andrew Duthie,[c] Pamela Finke[a,b]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstr. 34/36, 14195 Berlin, Germany*

[b] *Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Str., 28359 Bremen, Germany*

[c] *School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia*

Received

Abstract

The reaction of 8-dimethylaminonaphthyllithium etherate with the tellurium(II) bis(dithiocarbamate), $Te(S_2CNEt_2)_2$, provided the diaryltelluride $(8\text{-}Me_2NC_{10}H_6)_2Te$ (**1**). The oxidation of **1** with an excess of H_2O_2 did not afford the expected diaryltellurium(IV) oxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$ (**2**), but the diaryltellurium(VI) dioxide $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$ (**3**). The preparation of **2** was achieved by the comproportionation reaction of **1** and **3**. The protonation of **2** using triflic acid gave rise to the formation of diarylhydroxytelluronium triflate $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$ (**4**), which features the protonated diaryltellurium oxide $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]^+$ (**4a**). Compounds **1**, **3** · H_2O · H_2O_2, **3** · 2 H_2O and **4** were characterized by X-ray crystallography. The experimentally obtained molecular structures

---

* Correspondence to Jens Beckmann: Fax ++49(0)421 218 9863160, E-mail: j.beckmann@uni-bremen.de

were compared to those calculated for **1** - **3**, **4a** and $(8\text{-}Me_2NC_{10}H_6)_2Te(OH)_2$ (**5**) as well as the related diphenyltellurium compounds Ph_2Te (**6**), Ph_2TeO (**7**), Ph_2TeO_2 (**8**), $[Ph_2Te(OH)]^+$ (**9a**) and $Ph_2Te(OH)_2$ (**10**) at the DFT/B3PW91 level of theory.

Introduction

Diaryltellurium(IV) oxides, R_2TeO (e.g. R = Ph, $4\text{-}MeOC_6H_4$, $4\text{-}Me_2NC_6H_4$, Mes), containing reactive, polar (formal) Te-O double bonds have attracted considerable interest as mild oxygen transfer reagents in organic[1] and organometallic[2] syntheses and for their antioxidant activity.[3] However, diaryltellurium(IV) oxides have also received attention for their own sake. In the solid-state, most diaryltellurium(IV) oxides are aggregated. For instance, crystalline Ph_2TeO contains two conformers with somewhat elongated Te-O double bonds that are associated by short secondary Te···O bonds giving rise to asymmetric dimers.[4] The closely related $(4\text{-}MeOC_6H_4)_2TeO$ comprises a one-dimensional polymer with two Te-O single bonds and lacks any secondary interactions.[5] Intramolecularly coordinated diaryltellurium(IV) oxides are rare. The first fully characterized example, namely $(2\text{-}Me_2NCH_2C_6H_4)_2TeO$ is a monomer that lacks any secondary Te···O bonds, which was attributed to the intramolecular coordination of both N-donor ligands.[6] By contrast, the very recently reported $(2\text{-}PhNNC_6H_4)_2TeO$ contains an asymmetric dimer in the solid-state, which is presumably due to the fact that only one of the two N-donor substitutions is involved in intramolecular coordination.[7]

In moist solvents, diaryltellurium(IV) oxides are slightly basic and appear to exist ‘hydrated’ as diaryltellurium(IV) dihydroxides, $R_2Te(OH)_2$, that partly undergo dissociation into diarylhydroxytelluronium(IV) ions $[R_2Te(OH)]^+$ and hydroxide ions.[8] Protonation of the diaryltellurium(IV) oxide $(4\text{-}MeOC_6H_4)_2TeO$ with triflic acid in acetonitrile, indeed produced the diarylhydroxytelluronium(IV) ion $[(4\text{-}MeOC_6H_4)_2TeOH]^+$ and triflate ions in solution, however, the attempted isolation lead to condensation and formation of the related tetraarylditelluroxane ditriflate $[(4\text{-}MeOC_6H_4)_2Te]_2O(SO_3CF_3)_2$.[9] Very recently, the molecular structure of an intramolecularly coordinated diarylhydroxytelluronium(IV) cation, namely, $[(2\text{-}MeNCH_2C_6H_4)_2TeOH]_2(SiF_6)$ was reported, which was obtained by the accidental hydrolysis of the diaryltellurium(IV) difluoride $(2\text{-}MeNCH_2C_6H_4)_2TeF_2$ in a glass vial.[10]

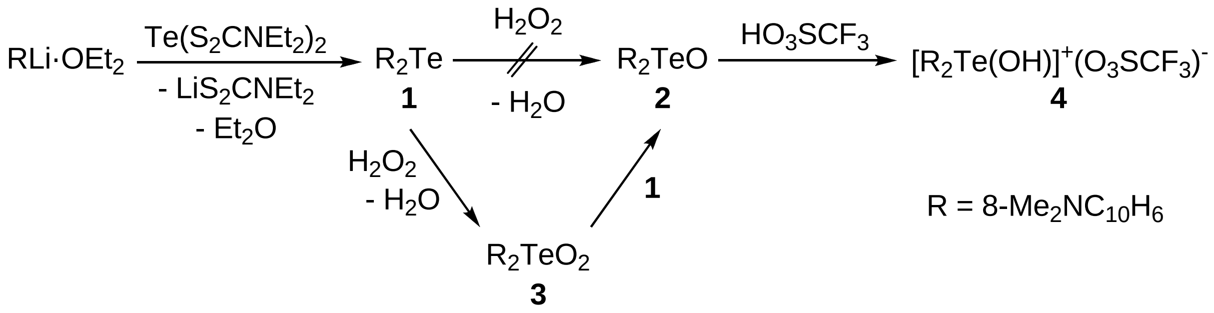
Most previously known diaryltellurium(VI) dioxides (also referred to as tellurones), R_2TeO_2 (e.g. R = $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$) are ill-defined compounds with presumably random polymeric structures.[11] The first fully characterized monomeric diaryltellurium(VI) dioxide $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2TeO_2$ was obtained recently using the kinetic stabilization of a bulky organic substituent.[12]

We have now prepared a new series of intramolecularly coordinated bis(8-dimethylaminonaphthyl)tellurium compounds, namely $(8\text{-}Me_2NC_{10}H_6)_2Te$ (**1**), $(8\text{-}Me_2NC_{10}H_6)_2TeO$ (**2**), $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$ (**3**). The latter compound is only the second example of this compound class. Protonation of **2** using triflic acid produced bis(8-dimethylaminonaphthyl)hydroxytelluronium triflate, $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$ (**4**) featuring the $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]^+$ (**4a**) ion. The structure and reactivity of **1 - 4** were studied and compared to those of previously known diaryltellurium compounds that lack intramolecular coordinating N-donor substituents.

Results and Discussion

The synthesis of bis(8-dimethylaminonaphthyl)telluride, $(8\text{-}Me_2NC_{10}H_6)_2Te$ (**1**), was achieved by the reaction of 8-dimethylaminonaphthyllithium etherate with tellurium(II) bis(dithiocarbamate), $Te(S_2CNEt_2)_2$, in 75% yield (Scheme 1).

Scheme 1. Synthesis of bis(8-dimethylaminonaphthyl)tellurium compounds **1 - 4**.



Compound **1** was obtained as bright orange crystalline solid. It is noteworthy that the use of acetonitrile as solvent is essential for high yields as previous attempts at preparing **1** in a similar way using different solvents provided only the mono-substituted product 8-$Me_2NC_{10}H_6TeS_2CNEt_2$.[13] The molecular structure of **1** is shown in Figure 1 and selected bond parameters are collected in the caption of the Figure. The spatial arrangement of the Te atom is distorted tetrahedral and defined by a C_2+N_2 donor set. The average Te-C bond length of **1** (2.163(3) Å) is somewhat longer than that of bis(1-naphthyl)telluride (2.119(2) Å),[14] presumably due to the intramolecular N-coordination. The C-Te-C angle of **1** (97.7(2)°) is very similar to the value observed for bis(1-naphthyl)telluride (96.32(9)°).[14] The two Te···N bond lengths of **1** (2.699(4), 2.827(4) Å) differ by 0.128(4) Å for no obvious reason, but the average (2.763(4) Å) resembles values found for bis(8-dimethylaminonaphthyl)ditelluride (2.699(5), 2.743(5) Å)[15] and bis(8-dimethylaminonaphthyl)tritelluride (2.66(1), 2.68(1) Å).[16] The ^{125}Te CP MAS NMR spectrum of **1** shows a signal at $\delta_{iso} = 701$ ppm whereas the ^{125}Te NMR spectrum ($CDCl_3$) of **1** reveals a signal at $\delta = 780.6$ ppm . Both values differ substantially from each other and even more from the ^{125}Te NMR chemical shift ($CDCl_3$) measured for bis(1-naphthyl)telluride ($\delta = 466.5$ ppm).[14] The ^{1}H and ^{13}C NMR spectra ($CDCl_3$) of **1** show one set of signals for the 8-dimethylaminonaphthyl substituents. The two N-methyl groups are magnetically equivalent and give rise to one singulet at $\delta = 2.73$ ppm (^{1}H) and 46.5 ppm (^{13}C), respectively.

The oxidation of a suspension of **1** in H_2O using an excess of H_2O_2 did not produce the expected (8-dimethylaminonaphthyl)tellurium oxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO$ (**2**), but rather the (8-dimethylaminonaphthyl)tellurium dioxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$ (**3**), in 83% yield (Scheme 1). The facile formation of **3** deserves a comment as the oxidation of other known diaryltellurides with most oxidizing agents either stops at the stage of diaryltellurium(IV) oxides or produces ill-defined product mixtures.[11] Compound **3** was initially obtained as brownish crystalline hydrate perhydrate **3** · H_2O · H_2O_2 (Caution!) and after recrystallisation from aqueous methanol as colorless crystalline dihydrate **3** · 2 H_2O. While (2,4,6-*i*-$Pr_3C_6H_2)_2TeO_2$ is a strong oxidizing agent, sufficiently strong to oxidize alcohols to carbonyl compounds,[11] the diaryltellurium(VI) dioxide **3** appears to show no oxidizing power towards alcohols under similar conditions. Removal of water molecules associated to **3** by drying in high vacuum was difficult and remained incomplete. Both crystals, **3** · H_2O · H_2O_2 and **3** · 2 H_2O, were investigated by X-ray crystallography giving rise to very similar conformers of **3** having nearly the same bond parameters. The molecular structure of **3** (crystallized as hydrate perhydrate, **3** · H_2O · H_2O_2) is shown in Figure 2 and selected bond parameters are collected in the caption of the Figure. The spatial arrangement of the Te atom is distorted octahedral and defined by a C_2O_2+N_2 donor set. The organic substituents are situated in distorted *trans*-position (C-Te-C 137.8(3)°), whereas the O and N atoms occupy mutually *cis*-positions. The average Te-O bond lengths of **3** (1.822(6) Å) is somewhat longer than that of (2,4,6-*i*-$Pr_3C_6H_2)_2TeO_2$ (1.802(3) Å),[11] presumably due to the fact that the O atoms of **3** act as hydrogen bond acceptors in the solid-state. The supramolecular association of **3** · H_2O · H_2O_2 and **3** · 2 H_2O by hydrogen bonding is shown in the *Supporting Information*. Despite the increase of the oxidation state and the coordination number, the (average) Te···N bond lengths of **3** (2.736(7) Å) decreases only marginally upon oxidation of **1** (2.763(4) Å). The ^{125}Te CP MAS NMR spectrum of **3** shows a signal at δ_{iso} = 1171 ppm. The ^{125}Te NMR spectrum (D_3COD, r.t.) reveals a very similar signal at δ = 1156.2 ppm.

The ^{1}H and ^{13}C NMR spectra (D_3COD, r.t.) of **3** each show one set of signals for the 8-dimethylaminonaphthyl substituents. The two N-methyl groups are magnetically inequivalent and give rise to two equally intense singulets at δ = 2.67 and 1.58 ppm (^{1}H) and δ = 51.1 and 46.5 ppm (^{13}C), respectively. The ^{125}Te NMR spectrum ($CDCl_3$, r.t.) of an analytically pure sample of **3** exhibits two signals at 1199.5 and 1137.4 ppm (1184.2 and 1120.5 ppm at –60 °C) with an integral ratio of 85:15. The ^{1}H and ^{13}C NMR spectra ($CDCl_3$, r.t.) of **3** each show one somewhat broad set of signals for the 8-dimethylaminonaphthyl substituents. Again, the two methyl groups are magnetically inequivalent and give rise to two equally intense singulets at δ = 2.69 and 1.45 ppm (^{1}H) and 50.4 and 46.7 ppm (^{13}C), respectively. The ^{1}H NMR spectrum ($CDCl_3$, –60 °C) of **3** reveals two sharp sets of signals for the 8-dimethylaminonaphthyl substituents with an integral ratio of 85:15. The major set of signals comprises two equally intense singulets for the methyl groups at δ = 2.69 and 1.45 ppm while the minor intense set of signals consists of four equally intense singulets for the N-methyl groups at δ = 3.34, 3.18, 2.91 and 2.09 ppm. The minor intense set of signals was tentatively assigned to a structural isomer **3a** with a lower symmetry being in equilibrium with **3** in $CDCl_3$ solution.

The synthesis of bis(8-dimethylaminonaphthyl)tellurium oxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO$ (**2**), was achieved by the comproportionation reaction of **1** and **3** in 67% yield (Scheme 1). In solution and in the solid-state, bis(8-dimethylaminonaphthyl)tellurium oxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO$ (**2**), is sensitive to air oxidation and slowly turns into the bis(8-dimethylaminonaphthyl)tellurium dioxide (**3**) as can be monitored by ^{1}H NMR spectroscopy. For instance, when a solution of **2** in THF was purged with air for 3 h, about 20% were converted into **3**. This reactivity is highly unusual as all previously known diaryltellurium oxides are air-stable and rather difficult to oxidize.[11] All attempts at obtaining single crystals suitable for X-ray crystallography failed. Interestingly, the melting point of **2** (dec. 202 – 203 °C) is much higher than those of the starting materials **1** (149-153 °C) and **3** (158-164 °C), which points to a polymeric structure similar to that of $(4\text{-MeOC}_6\text{H}_4)_2\text{TeO}$ in the solid state.[5] The IR spectrum of **2** is inconclusive with respect to asymmetric and symmetric Te-O stretching vibration and shows no evidence for O-H stretching vibrations. The assumption of a polymeric structure of **2** is further supported by the observation that the solubility of **2** is drastically reduced once isolated from the mother liquor. The ^{125}Te NMR spectrum (D_3COD, r.t.) of **2** exhibits a slightly broad signal at $\delta = 1255.2$ ppm, while the ^{125}Te NMR spectrum ($CDCl_3$, r.t.) of **2** shows a broad signal at $\delta = 1272.0$ ppm ($\delta = 1259.4$ ppm at –40 °C). Both ^{1}H NMR and ^{13}C NMR spectra of **2** show broad signals in all solvents ($CDCl_3$, d_6-DMSO, D_3COD) at all temperatures measured. With the data at hand we propose that the diaryltellurium oxide **2** exists as mixture of oligomers $R_2Te(OTeR_2)_nO$ with Te-O single bonds in solution rather than a discrete monomer containing a (formal) Te-O double bond as found for the related $(2\text{-MeNCH}_2\text{C}_6\text{H}_4)_2\text{TeO}$.[6] Solutions of **2** containing chlorinated solvents such as $CHCl_3$ and CH_2Cl_2 slowly decompose into species containing Te-Cl bonds.

The reaction of **2** with triflic acid in acetonitrile[17] produced the bis(8-dimethylaminonaphthyl)hydroxytelluronium triflate, $[(8\text{-Me}_2\text{NC}_{10}\text{H}_6)_2\text{Te(OH)}](\text{O}_3\text{SCF}_3)$ (**4**), in 70% yield (Scheme 1). Compound **4** was obtained as a colorless crystalline solid. The molecular structure of **4** is shown in Figure 3 and selected bond parameters are collected in the caption of the Figure. It possesses bis(8-dimethylaminonaphthyl)hydroxytelluronium ions, $[(8\text{-Me}_2\text{NC}_{10}\text{H}_6)_2\text{Te(OH)}]^+$ (**4a**), and triflate ions that are associated by medium strength hydrogen bonding as indicated by the O···O donor acceptor distance of 2.814(6) Å.[18] Consistently, the IR spectrum of **4** shows an absorption at $\tilde{\nu} = 3531\ \text{cm}^{-1}$, which is indicative for an O-H stretching vibration being involved in hydrogen bonding. The spatial arrangement of the Te atom is distorted trigonal bipyramidal and defined by a C_2O+N_2 donor set, whereby the equatorial positions are occupied by C10, C20 and N2, while N1 and O1 are situated in the axial positions. The Te1-O1 bond length of **4** (1.957(4) Å) compares well with $(4\text{-MeOC}_6\text{H}_4)_2\text{Te(OPh)OH}$ (1.9840(4) Å)[19] and accounts for a bond order of about 1.

Quite unexpected and contradicting Bent’s rule, the axial Te1···N1 bond (2.591(5) Å) is considerably shorter than the equatorial Te1···N2 bond (2.706(6) Å), which points to a strong attractive interaction to the Te atom. It is to note that even shorter Te···N bond lengths were observed in the aryltellurenyl chloride 8-$Me_2NC_{10}H_6TeCl$ (2.350(3) Å) and the aryltellurium trichloride 8-$Me_2NC_{10}H_6TeCl_3$ (2.420(3) Å) containing only one of the intramolecularly coordinating 8-dimethylaminonaphthyl substituents.[20] The ^{125}Te CP MAS NMR spectrum of **4** shows a signal at δ_{iso} = 1214 ppm. Compound **4** is only sparingly soluble in strongly polar solvents such as acetonitrile. The ^{125}Te NMR spectrum (D_3CCN) of **4** exhibits a slightly broad signal at δ = 1197.6 ppm at r.t. and a sharp signal at δ = 1176.3 ppm at –35 °C. The ^{1}H and ^{13}C NMR spectra ($CDCl_3$, –35 °C) of **4** show two sets of signals for the magnetically inequivalent 8-dimethylaminonaphthyl substituents. The four N-methyl groups give rise to four singulets at δ = 3.04, 2.96, 2.86 and 2.06 ppm (^{1}H) as well as 51.3, 47.3, 46.5 and 46.2 ppm (^{13}C), respectively, which suggests that the trigonal bipyramidal structure is retained in solution and configurationally stable at –35 °C. However, at r.t. the configurational stability might be compromised as the ^{1}H and ^{125}Te NMR signals are somewhat broaden.

DFT calculations

The geometries and Hirshfeld charges of the bis(8-dimethylaminonaphthyl)tellurium compounds (8-$Me_2NC_{10}H_6)_2Te$ (**1**), (8-$Me_2NC_{10}H_6)_2TeO$ (**2**), (8-$Me_2NC_{10}H_6)_2TeO_2$ (**3**), [(8-$Me_2NC_{10}H_6)_2Te(OH)]^+$ (**4a**) and (8-$Me_2NC_{10}H_6)_2Te(OH)_2$ (**5**) as well as those of the related diphenyltellurium compounds Ph_2Te (**6**), Ph_2TeO (**7**), Ph_2TeO_2 (**8**), $[Ph_2Te(OH)]^+$ (**9a**) and $Ph_2Te(OH)_2$ (**10**) were calculated in the gas phase and selected values collected in Table 1. The calculated geometries of **1** and **4a** closely resemble those found in the X-ray structure. The primary bond lengths and angles differ only marginally by 0.025 Å and 2.5°.

The intramolecularly coordinating ligands give rise to Te···N bond lengths that are identical to those found experimentally within 0.045 Å.

The calculated gas phase geometry of **3** is slightly different from the X-ray structure. Whilst the Te-C and Te-O bond lengths reasonably agree within 0.035Å, the average Te···N bond length of 3.005 Å are significantly longer than in the crystal structure (2.736(7) Å). Moreover, the octahedral coordination of **3** in the gas phase is more distorted than in the solid-state.[21] Since the molecular structure of **2** was not established experimentally, the geometry of **2** calculated in the gas phase is worth a closer look. The spatial arrangement of **2** is best described as distorted trigonal bipyramidal. The calculated Te-O bond length of **2** (1.824 Å) is in the typical range of a (formal) Te-O double bond and very close to the experimental value of $(2\text{-}Me_2NCH_2C_6H_4)_2TeO$ (1.829(1) Å).[6] The two intramolecular Te···N bonds of **2** (2.780 and 2.941Å) are different in lengths. The longer Te···N bond is situated in *trans*-position to the (formal) Te-O double bond. Due to the lower coordination numbers, the Te-C and Te-O bond lengths calculated for Ph_2Te (**6**), Ph_2TeO (**7**), Ph_2TeO_2 (**8**), $[Ph_2TeOH]^+$ (**9a**) and $Ph_2Te(OH)_2$ (**10**) in the gas phase are on average shorter by 0.03 Å and 0.04 Å than those of the related intramolecularly coordinated compounds **1**, **2**, **3**, **4a** and **5**. The relative energies of **1** - **10** (counterbalanced with H_2O_2, H_2O and OH^-) were calculated and are displayed in Figure 4. The energies for R_2Te (**1**, R = $8\text{-}Me_2NC_{10}H_6$; **6**, R = Ph) + 2 H_2O_2 were arbitrary set to 0 kJ mol^{-1} and used as references. Compared to these references the formation of all neutral oxidation products is increasingly exothermic when going from the lowest to the highest oxidation states regardless of the organic substituent R. Amongst the diaryltellurium(IV) species the diaryltellurium dihydroxides, $R_2Te(OH)_2$ (**5**, R = $8\text{-}Me_2NC_{10}H_6$; **10**, R = Ph), are by –14 and –56 KJ mol^{-1} more stable than the related diaryltellurium oxides, R_2TeO (**2**, R = $8\text{-}Me_2NC_{10}H_6$; **7**, R = Ph), and H_2O. As expected for isolated charged species in vacuo, the energies of the diarylhydroxytelluronium ions $[R_2Te(OH)]^+$ (**4a**, R = $8\text{-}Me_2NC_{10}H_6$; **8a**, R = Ph) counterbalanced with OH^- by +341 and +474 KJ mol^{-1} considerably higher than those of the neutral reference species.

The difference of the later two values (133 KJ mol^{-1}) is much larger than those for the neutral compound classes, which is attributed to the intramolecularly coordinating 8-dimethylaminonaphthyl substituents that compensate the positive charge of **4a**. Indeed, the Hirshfeld charge situated at the Te atom of $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]^+$ (**4a**, 0.716 e) is by 0.093 e significantly smaller than that of $[Ph_2Te(OH)]^+$ (**9a**, 0.809 e). With the exception of the elusive diaryltellurium dihydroxides, $R_2Te(OH)_2$ (**5**, R = $8\text{-}Me_2NC_{10}H_6$; **10**, R = Ph), the charge differences of the Te atoms are smaller for all other compound classes, e.g. 0.018 e for R_2Te (**1**, R = $8\text{-}Me_2NC_{10}H_6$; **6**, R = Ph), 0.021 e for R_2TeO (**2**, R = $8\text{-}Me_2NC_{10}H_8$; **7**, R = Ph) and 0.041 e for R_2TeO_2 (**3**, R = $8\text{-}Me_2NC_{10}H_8$; **8**, R = Ph), respectively. An inspection of the Hirshfeld charges situated at the N atoms of $(8\text{-}Me_2NC_{10}H_6)_2TeO$ (**2**, N1 –0.054 e; N2 –0.066 e) and $[(8\text{-}Me_2NC_{10}H_8)_2Te(OH)]^+$ (**4a**, N1 –0.040 e; N2 –0.064 e) reveals that the axial N donor substituent being situated in *trans*-position to the hydroxyl group underwent a larger change (0.014 e) than the equatorial N donor substituent (0.002 e) upon protonation. In fact, the axial N atom of **4a** possesses the smallest negative charge (–0.040 e) of all species under consideration. Therefore the axial N atom (N1) appears to be more deeply involved in the charge compensation of the equatorial N atom (N2), which is consistent with the fact that the axial Te···N bond length is shorter than the equatorial Te···N bond lengths (see above).

Conclusion

A series of intramolecularly coordinated bis(8-dimethylaminonaphthyl)tellurium compounds in the oxidation states II, IV and VI, namely, $(8\text{-}Me_2NC_{10}H_6)_2Te$ (**1**), $(8\text{-}Me_2NC_{10}H_6)_2TeO$ (**2**), $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$ (**3**), was prepared and fully characterized. The diaryltellurium dioxide **2** is only the second example of the compound class. Unlike the kinetically stabilized $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2TeO_2$,[12] **2** shows no oxidizing power towards alcohols. This difference in reactivity is tentatively attributed to the presence of the intramolecular N-donor substituents in the latter.

Quite unexpected for diaryltellurium oxides, **2** was readily oxidized by air under normal conditions to give **3**. Protonation of **2** using HO_3SCF_3 provided bis(8-dimethylaminonaphthyl)hydroxytelluronium triflate $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$ (**4**) featuring the $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]^+$ (**4a**) ion, a rare example of a protonated diaryltellurium oxide. By contrast, the reaction of $(4\text{-}MeOC_6H_4)_2TeO$ with HO_3SCF_3 gave the tetraarylditelluroxane $[(4\text{-}MeOC_6H_4)_2Te]_2O(O_3SCF_3)_2$, in which the triflates are involved in secondary Te···O interactions with the Te atoms.[9] The stabilization of the diarylhydroxytelluronium ion $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]^+$ (**4a**) is attributed to the charge compensation by the intramolecularly coordinating N donor substituents. A similar observation was recently made for the related arylhydroxystibonium triflate $[2,6\text{-}(Me_2NCH_2)_2C_6H_3Sb(OH)](O_3SCF_3)$ containing the 2,6-bis(dimethylaminomethyl)phenyl substituent (a NCN pincer type ligand).[22]

Experimental

General. The 8-dimethylaminonaphthyllithium etherate and $Te(S_2CNEt_2)_2$ were prepared according to literature procedures. The ^1H, ^{13}C and ^{125}Te NMR spectra were recorded using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^1H, ^{13}C) and Me_2Te (^{125}Te). The ^{125}Te CP MAS NMR spectra were obtained using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 8 and 10 kHz. A 4 s recycle delay was used and typically 5000 to 10000 transitions were accumulated to obtain adequate signal-to-noise ratios. The isotropic chemical shifts δ_{iso} were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced using solid $Te(OH)_6$ as the secondary reference (δ_{iso} 692.2 / 685.5 ppm). Infrared (IR) spectra were recorded using Nexus FT-IR spectrometer with a Smart DuraSamplIR. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of bis(8-dimethylaminonaphthyl)telluride (8-$Me_2NC_{10}H_6$)$_2$Te (1). To a solution of 8-dimethylaminonaphthyllithium etherate (4.10 g, 16.3 mmol) in THF (80 mL) solid Te(S_2CNEt_2)$_2$ (3.00 g, 7.07 mmol) was added and stirred overnight. The solvent was completely removed in vacuum and the oily residue stirred in acetonitrile (10 mL) for 30 min. The yellow solid was filtered off and washed with acetonitrile (20 mL). Recrystallization from acetonitrile and cooling to –20 °C afforded orange needles of **1** (Yield 2.85 g, 6.09 mmol, 86%; Mp. 149-153 °C).

^{1}H NMR ($CDCl_3$, r.t.): δ = 7.83 (dd, 2H), 7.62 (d, 4H), 7.40 (t, 2H), 7.32 (dd, 2H), 7.10 (t, 2H; Ar), 2.73 ppm (s, 6H; Me). ^{13}C NMR ($CDCl_3$, r.t.): δ = 151.6, 135.9, 135.4, 133.1, 126.5, 126.1, 125.8, 125.2, 121.6, 118.3 (Ar), 46.5 ppm (Me). ^{125}Te NMR ($CDCl_3$, r.t.): δ = 780.6 ppm. ^{125}Te CP MAS NMR: δ_{iso} = 701 ppm. Anal. Calcd. for **1**: $C_{24}H_{24}N_2Te$ (468.06): C 61.59, H 5.17; N 5.98. Found: C 61.35, H 5.07, N 5.86 %.

Synthesis of bis(8-dimethylaminonaphthyl)tellurium oxide (8-$Me_2NC_{10}H_6$)$_2$TeO (2). To a solution of **1** (702 mg, 1.50 mmol) in THF (100 mL), solid **3** · 2 H_2O (804 mg, 1.50 mmol) was added and stirred overnight. The solvent was reduced in vacuum and dry hexane (40 mL) was added. The yellow-greenish precipitate was separated by filtration and dried in vacuum to give **2** as yellow-greenish microcrystalline solid (973 mg, 2.01 mmol, 67 %; Mp. (dec.) 202-208 °C).

^{1}H NMR ($CDCl_3$, r.t.): δ = 7.89 (s, broad), 7.77 (d, broad), 7.55 - 7.44 (m, broad; Ar), 2.83 ppm (s, broad; Me). ^{1}H NMR ($CDCl_3$, very broad signals at –40 °C): δ = 8.80 (s, 1H, broad), 8.00 (s, 1H, broad), 7.83-7.35 (m, 8H, broad), 6.96 (s, 1H, broad), 6.73 (s, 1H, broad; Ar), 2.90-2.77 (m, 9H, broad); 2.00 ppm (s, 3H, broad; Me). ^{1}H NMR (d_6-DMSO, r.t.): δ = 8.08 (s, very broad), 7.96 (d, very broad), 7.77 (d, very broad), 7.64 (t, very broad; Ar), 2.77 ppm (s, very broad; Me). ^{1}H NMR (D_3COD, r.t.): δ = 8.28 (s, broad), 8.20 (s, broad), 7.95-7.86 (m, broad), 7.63 (s, broad), 7.09 (s, broad.), 6.79 (s, broad; Ar), 2.90-2.77 (m, broad), 2.00 ppm (s, broad; Me). ^{13}C NMR ($CDCl_3$, r.t.): δ = 149.9, 135.1, 134.7, 132.9, 132.3, 130.6, 126.91, 126.90, 126.1, 120.0 (broad; Ar), 48.3, 45.2 ppm (broad; Me). ^{125}Te NMR ($CDCl_3$, r.t.): δ = 1272.0 ppm (very broad). ^{125}Te NMR ($CDCl_3$, –40°C): δ =1259.3 ppm (broad). ^{125}Te NMR (D_3COD, r.t.): δ = 1255.2 ppm (slightly broad). Anal. Calcd. for **2**: $C_{24}H_{24}N_2OTe$ (484.06): C 59.55, H 5.00; N 5.79. Found: C 58.98, H 4.91, N 5.72 %.

Synthesis of bis(8-dimethylaminonaphthyl)tellurium dioxide $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$ (3). To a suspension of **1** (950 mg, 2.03 mmol) in water (10 mL), H_2O_2 (35%, 2 mL) was added and stirred for 3 h. The brownish solid (**3** · H_2O · H_2O_2) was filtered off and washed with water (20 mL) and dried in vacuum. Slow evaporation of the mother liquor yielded brownish prisms of **3** · H_2O · H_2O_2. Recrystallization of from aqueous methanol yielded colorless prisms of **3** · 2 H_2O (890 mg, 1.66 mmol, 82 %; Mp. (dec.) 158-164 °C).

^{1}H NMR ($CDCl_3$, r.t.): δ = 9.14 (d, very broad), 8.15 (d, very broad), 7.89-7.83 (m, very broad), 7.52 (t, very broad), 7.46 (d, very broad; Ar), 2.69 (s, very broad), 1.45 ppm (s, very broad; Me). ^{1}H NMR ($CDCl_3$, –60 °C): Major set of signals (integral 85%): δ = 9.05 (d, 1H), 8.19 (d, 1H), 7.89-7.83 (m, 2H), 7.59 (t, 1H), 7.53 (d, 1H; Ar), 2.68 (s, 3H), 1.46 ppm (s, 3H; Me). Minor set of signals (integral 15%): δ = 8.86 (d, 1H), 8.17 (m, 1H), 7.98 (d, 1H), 7.93 (d, 1H), 7.83 (m, 1H), 6.92 (d, 1H; Ar), 3.34 (s, 3H), 3.18 (s, 3H), 2.91(s, 3H), 2.09 ppm (s, 3H; Me). ^{1}H NMR (CD_3OD, r.t.): δ = 8.90 (dd, 1H), 8.41 (dd, 1H), 8.05 (dd, 1H), 8.03 (t, 1H), 7.77 (dd, 1H), 7.70 (t, 1H; Ar), 2.67 (s, 3H), 1.58 ppm (s, 3H; Me). ^{13}C NMR ($CDCl_3$, r.t.): δ = 148.0, 136.1, 135.2, 133.0, 132.2, 130.1, 127.2, 126.9, 126.7, 120.9 (broad; Ar), 50.4, 46.7 ppm (broad; Me). ^{13}C NMR ($CDCl_3$, –60 °C): δ = 146.8, 134.7, 134.5, 133.0, 129.1, 127.1, 126.9, 126.4, 126.2, 121.1 (Ar), 50.1, 46.8 ppm (Me). ^{13}C NMR (D_3COD, r.t.): δ = 147.9, 136.6, 135.9, 135.2, 130.1, 129.3, 128.5, 128.0, 127.2, 123.1 (Ar), 51.1, 47.4 ppm (Me). ^{125}Te NMR ($CDCl_3$, r.t.): δ = 1199.5 (integral 85%) and 1137.4 ppm (integral 15%). ^{125}Te NMR ($CDCl_3$ –60 °C): δ = 1184.2 (integral 85%) and 1120.5 ppm (integral 15%). ^{125}Te NMR (CD_3OD): δ = 1156.2 ppm. ^{125}Te NMR (CD_3OD, –90 °C): δ = 1125.9 ppm. ^{125}Te CP MAS NMR: δ_{iso} = 1170.9 ppm. Anal. Calcd. for **3** · H_2O · H_2O_2: $C_{24}H_{28}N_2O_5Te$ (552.09): C 52.21, H 5.11; N 5.07. Found: C 52.78, H 4.92, N 4.94 %. **3**· H_2O: IR: $\tilde{\nu}$ (H_2O) = 3426 cm^{-1}. Anal. Calcd. for **3** · 2 H_2O: $C_{24}H_{28}N_2O_4Te$ (536.09): C 53.77, H 5.26; N 5.23. Found: C 53.40, H 4.96, N 4.99 %.

Synthesis of bis(8-dimethylaminonaphthyl)hydroxytelluronium triflate [(8-$Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$ (4). To a suspension of **2** (242 mg, 0.50 mmol) in MeCN (20 mL), a solution of HO_3SCF_3 (75 mg, 0.53 mmol) in MeCN (10 mL) was added. The dark red solution was reduced to approximately 5 mL and hexane (5 mL) was added. Cooling of the solution to –20 °C provided **4** as colorless crystals (223 mg, 0.35 mmol, 70 %; Mp. (dec.) 219-225 °C).

^{1}H NMR (D_3CCN, r.t.): δ = 8.48 (s, broad), 8.32 (s, broad), 8.01 (s, broad), 7.63 (s, broad), 7.91 (m, broad), 7.71 (m, broad), 7.22 (t, broad), 6.87 (d, broad; Ar), 2.90-2.77 (m, broad), 2.00 ppm (s, broad; NCH_3). ^{1}H NMR (D_3CCN, –35 °C): δ = 8.49 (dd, 1H,), 8.30 (dd, 1H), 8.07 (m, 2H), 7.96-7.88 (m, 3H), 7.75-7.67 (m, 3H), 7.18 (t, 1H), 6.82 (d, 1H; Ar), 5.82 (s, 1H; OH), 3.04 (s, 3H), 2.96 (s, 3H), 2.86 (s, 3H), 2.06 ppm (s, 3H; Me). ^{13}C NMR (D_3CCN, –35 °C): δ = 149.4, 147.9, 135.4, 135.1, 134.5, 133.4, 133.3, 132.4, 132.2, 132.1, 129.6, 129.1, 128.7, 128.6, 127.6, 127.2, 126.8, 126.1, 122.2, 120.5 (Ar), 51.3, 47.28, 46.5, 46.2 ppm (Me). ^{19}F NMR (D_3CCN): δ = –79.0 ppm. ^{125}Te NMR (D_3CCN): δ = 1197.6 ppm. ^{125}Te NMR (D_3CCN, –35 °C): δ = 1176.3 ppm. ^{125}Te CP MAS NMR: δ_{iso} = 1213.4 ppm. IR: $\tilde{\nu}$ (OH) =

3531 cm^{-1}. Anal. Calcd. for **4**: $C_{25}H_{25}F_3N_2O_4STe$ (625.14): C 48.03, H 4.03; N 4.48; S 5.13. Found: C 46.83, H 3.92, N 4.21, S: 5.25 %.

X-ray crystallography. Intensity data were collected on a STOE IPDS 2T diffractometer at 150 K with graphite-monochromated Mo-Kα (0.7107 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 and SHELXL-97 implemented in the program WinGX 2002.[23] Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model (including free rotation about C-C) and were refined isotropically. The hydrogen atom H1 attached to the oxygen atom O1 of **4** was located in the last refinement cycle. Crystal and refinement data are collected in Table 2. Figures were created using DIAMOND.[24] Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Computational Methodology. Calculations were carried out using the Gaussian 03 and Gaussian 09 suite of programs using the physical constants default for Gaussian 03.[25, 26] All geometries were fully optimized at the DFT/B3PW91[27] level of theory using a large-core quasi-relativistic effective core potential[28] with the appropriate cc-pVTZ basis set[29] for tellurium and the split-valence 6-311+G(2df,p) basis set for all other atoms. The geometries were optimized without any symmetry constraints except for **1** (C_2), **5** (C_2), **7** (C_s) and **10** (C_2). Stationary points were characterized as true minima by frequency calculations. The energies have been corrected for zero point vibrational energies.

Acknowledgements

The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support. Dr. Malte Hesse is thanked for the X-ray data collection.

Supporting Information available. Cif files of **1**, of **3** · H_2O · H_2O_2 and **3** · 2 H_2O and **4**. Bond parameters of **3** · 2 H_2O. The supramolecular association of **3** · H_2O · H_2O_2 and **3** · 2 H_2O by hydrogen. The optimized geometries of **1-10** as well as the absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

References

[1] (a) Barton, D. H. R.; Ley, S. V.; Meerholz, C. A. *J. Chem. Soc., Chem. Commun.* **1979**, 755-756. (b) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron Lett.* **1980**, *21*, 1785-1788. (c) Engman, L.; Cava, M. P. *Tetrahedron Lett.* **1981**, *22*, 5251-5252. (d) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron, Suppl.* **1981**, 213-223. (e) Akiba, M.; Lakshimikantham, M. V.; Jen, K.-Y.; Cava, M. P. *J. Org. Chem*. **1984**, *49*, 4819-4821. (f) Oba, M.; Endo, M.; Nishiyama, K.; Ouchi, A.; Ando, W. *Chem. Commun*. **2004**, 1672-1673. (g) Oba, M.; Okada, Y.; Nishiyama, K.; Ando, W. *Org. Lett*. **2009**, *11*, 1879-1881.

[2] (a) Shen, J. K.; Gao, Y.; Shi, Q.; Rheingold, A. L.; Basolo, F. *Inorg. Chem.* **1991**, *30*, 1868-1873. (b) Xue, M.; Gao, Y. C.; Shen, J. K.; Shi, Q. Z.; Basolo, F. *Inorg. Chim. Acta* **1993**, *207*, 207-212. (c) Liu, X.; Gao, Y. C.; Su, Z. X.; Wang, Y. Y.; Shi, Q. Z. *Trans. Met. Chem.* **1999**, *24*, 666-668. (d) Song, L. C.; Li, Q. S.; Hu, Q. M.; Dong, Y. B. *J. Organomet. Chem.* **2001**, *619*, 194-203. (e) Okada, Y.; Oba, M.; Arai, A.; Tanaka, K.; Nishiyama, K.; Ando, W. *Inorg. Chem*. **2010**, *49*, 383-385.

[3] (a) Kanda, T.; Engman, L.; Cotgreave, I. A.; Powis, G. *J. Org. Chem*. **1999**, *64*, 8161-8169. (b) You, Y.; Ahsan, K.; Detty, M. R. *J. Am. Chem. Soc*. **2003**, *125*, 4918-4927.

[4] Alcock, N. W.; Harrison, W. D. *J. Chem. Soc., Dalton Trans.* **1982**, 709-712.

[5] Beckmann, J.; Dakternieks, D.; Duthie, A.; Ribot, F.; Schürmann, M.; Lewcenko, N. A. *Organometallics* **2003**, *22*, 3257-3261.

[6] Klapöke, T. M.; Krumm, B.; Scherr, M. *Phosphorous Sulfur Silicon* **2009**, *184*, 1347-1354.

[7] Srivastava, K.; Shah, P.; Singh, H.; Butcher, R. J. *Organometallics* **2011**, *30*, 534-546.

[8] Engman, L.; Lind, J.; Merényi, G. *J. Phys. Chem*. **1994**, *98*, 3174-3182.

[9] Beckmann, J.; Dakternieks, D.; Duthie, A.; Lewcenko, N. A.; Mitchell, C.; Schürmann, M. *Z. Anorg. Allg. Chem*. **2005**, *631*, 1856-1862.

[10] Klapöke, T. M.; Krumm, B.; Scherr, M. *Acta Cryst*. **2007**, *E63*, o4189.

[11] (a) Engman, L.; Cava, M. P. *J. Chem. Soc. Chem. Commun*. **1982**, 164-165.

[12] (a) Oba, M.; Okada, Y.; Nishiyama, K.; Shimada, S.; Ando, W. *Chem. Commun*. **2008**, 5378-5380. (b) Oba, M.; Okada, Y.; Endo, M.; Tanaka, K.; Nishiyama, K.; Shimada, S.; Ando, W. *Inorg. Chem*. **2010**, *49*, 10680-10686.

[13] Panda, A.; Mugesh, G.; Singh, H. B.; Butcher, R. J. *Organometallics* **1999**, *18*, 1986-1993.

[14] Chauhan, A. K. S.; Anamika; Srivastava, R. C.; Duthie, A. *Acta Cryst*. **2007**, *E63*, o4386.

[15] Menon, S. C.; Singh, H. B.; Jasinksi, J. M. Jasinski, J. P.; Butcher, R. J. *Organometallics* **1996**, *15*, 1707-1712.

[16] Beckmann, J.; Bolsinger, J.; Duthie, A. *Organometallics* **2009**, *28*, 4610-4612.

[17] In the absence of triflic acid compound **2** reversibly reacts with acetonitrile to give bis(8-dimethylaminonaphthyl)tellurium(IV) acetimidate, (8-$Me_2NC_{10}H_6)_2TeNC(O)CH_3$, the structure of which will be described in a forthcoming paper.

[18] Steiner, T. *Angew. Chem.* **2002**, *114*, 50-80. *Angew. Chem. Int. Ed.* **2002**, *41*, 48-76.

[19] Beckmann, J.; Bolsinger, J.; Duthie, A. *Aust. J. Chem.* **2008**, *61*, 172-182.

[20] Beckmann, J.; Bolsinger, J. Duthie, A. *Chem. Eur. J.* **2011**, *17*, 930-940.

[21] Preliminary attempts to optimize the geometry of **3** at the DFT/M05, DFT/M05-2X and MP2 level of theory also revealed no resemblance with the X-ray structure.

[22] Fridrichová, A.; Svoboda, T.; Jambor, R.; Padělková, Z.; Růžička A.; Erben, M.; Jirásko, R.; Dostál, L. *Organometallics* **2009**, *28*, 5522-5528.

[23] Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837-838.

[24] DIAMOND V2.1d, Crystal Impact, K. Brandenburg & M. Berndt GbR, **2002**.

[25] Gaussian 03, Revision B.04-E.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, **2004**.

[26] Gaussian 09, Revision A.2, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth,

G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

[27] a) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671-6687. b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

[28] Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408-3420.

[29] Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431-1441.

Table 1. Selected bond lengths [Å] and Hirshfeld charges [e] calculated for R_2Te, R_2TeO, $[R_2Te(OH)]^+$, $R_2Te(OH)_2$ and R_2TeO_2 (R = 8-$Me_2NC_{10}H_6$, R = Ph (values in brackets)).

		R_2Te	R_2TeO	$[R_2Te(OH)]^+$	$R_2Te(OH)_2$	R_2TeO_2
Bond lengths	Te-C1	2.148 (2.112)	2.161 (2.135)	2.121 (2.091)	2.147 (2.130)	2.135 (2.106)
	Te-C2	2.148 (2.112)	2.168 (2.135)	2.109 (2.079)	2.147 (2.130)	2.135 (2.106)
	Te···N1	2.846	2.780[b]	2.583[a]	2.927	3.004
	Te···N2	2.846	2.941	2.750[b]	2.927	3.005
	Te-O1		1.824 (1.815)	1.972 (1.927)	2.074 (2.069)	1.800 (1.795)
	Te-O2				2.074 (2.069)	1.800 (1.795)
Hirshfeld Charges	q(Te)	0.218 (0.200)	0.632 (0.653)	0.716 (0.809)	0.435 (0.681)	0.893 (0.934)
	q(O1), q(O1H)		-0.511 (-0.494)	-0.313 (-0.271) -0.159 (-0.085)	-0.372 (-0.362) -0.266 (-0.242)	-0.478 (-0.477)
	q(O2), q(O2H)				-0.372 (-0.362) -0.266 (-0.242)	-0.478 (-0.477)
	q(N1)	-0.058	-0.054[b]	-0.040	-0.076	-0.064
	q(N2)	-0.058	-0.066[a]	-0.064	-0.076	-0.064

[a] axial position, [b] equatorial position

Table 2. Crystal data and structure refinement of **1 - 4**.

	1	**3**$\cdot H_2O\cdot H_2O_2$	**3**$\cdot 2\ H_2O$	**4**
Formula	$C_{24}H_{24}N_2Te$	$C_{24}H_{28}N_2O_5Te$	$C_{24}H_{28}N_2O_4Te$	$C_{25}H_{25}F_3N_2O_4STe$
Formula weight. g mol^{-1}	468.06	552.09	536.09	634.13
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Crystal size. mm	0.43×0.26×0.06	0.10×0.06×0.01	0.27×0.16×0.01	0.36 × 0.23 × 0.12
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a. Å	13.5319(16)	9.577(7)	9.566(2)	9.982(5)
b. Å	9.1853(7)	23.245(9)	23.122(3)	9.237(9)
c. Å	17.734(2)	10.460(6)	10.433(2)	28.56(2)
α. °	90	90	90	90
β. °	110.168(9)	106.92(5)	106.51(1)	107.19(5)
γ. °	90	90	90	90
V. Å^3	2069.1(4)	2228(2)	2212.5(6)	2516(3)
Z	4	4	4	4
ρ_{calcd}. Mg m^{-3}	1.503	1.646	1.609	1.674
μ (Mo $K\alpha$). mm^{-1}	1.448	1.374	1.378	1.323
$F(000)$	936	1112	1080	1264
θ range. deg	2.76 to 29.17	1.75 to 29.20	1.76 to 29.23	2.14 to 29.35
Index ranges	$-18 \le h \le 18$	$-13 \le h \le 13$	$-13 \le h \le 12$	$-13 \le h \le 13$
	$-12 \le k \le 10$	$-31 \le k \le 30$	$-30 \le k \le 31$	$-12 \le k \le 12$
	$-24 \le l \le 24$	$-14 \le l \le 11$	$-13 \le l \le 14$	$-37 \le l \le 37$
No. of reflns collected	14317	15761	15683	28795
Completeness to $\theta_{\max}$	98.4%	98.8%	98.7%	98.4%
No. indep. Reflns	5506	5962	5925	6804
No. obsd reflns with $(I>2\sigma(I))$	3286	1808	2987	3557
No. refined params	244	289	280	325
GooF (F^2)	0.812	0.862	0.876	0.859
R_1 (F) ($I > 2\sigma(I)$)	0.0277	0.0457	0.0528	0.0536
wR_2 (F^2) (all data)	0.0579	0.1069	0.1238	0.1171
Largest diff peak/hole. e Å^{-3}	0.319 / –0.503	0.757 / –1.150	0.699 / –1.635	0.542 / –0.843
CCDC number	**000000**	**000000**	**000000**	**000000**

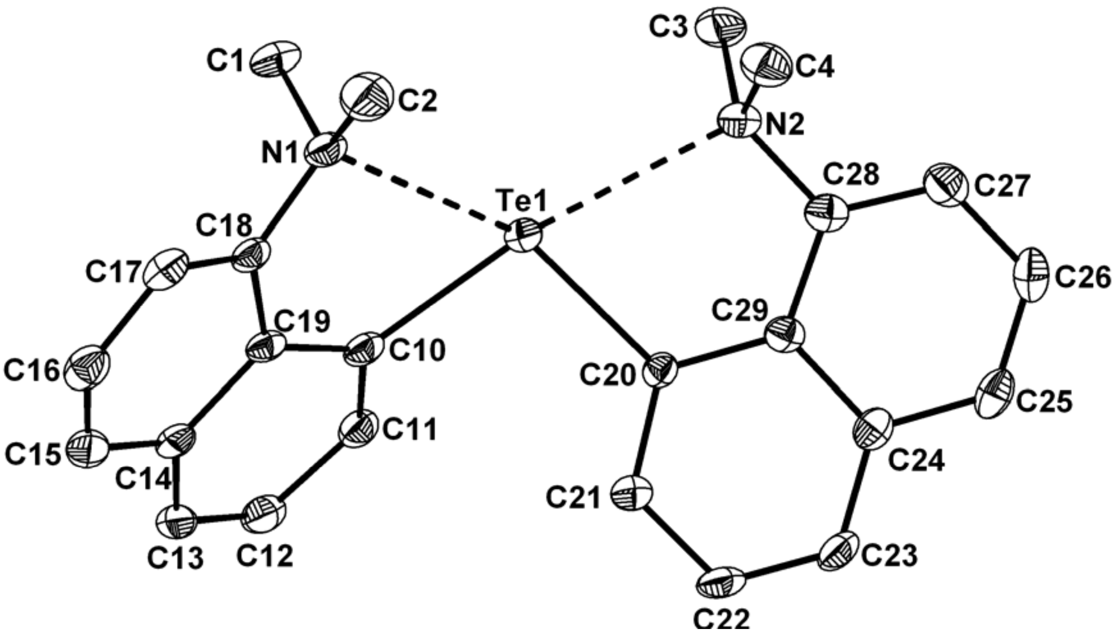

C1
C2
N1
C18
C17
C19
C10
C16
C15
C14
C13
C12
C11
Te1
C3
C4
N2
C28
C27
C26
C29
C20
C25
C24
C21
C23
C22

Figure 1

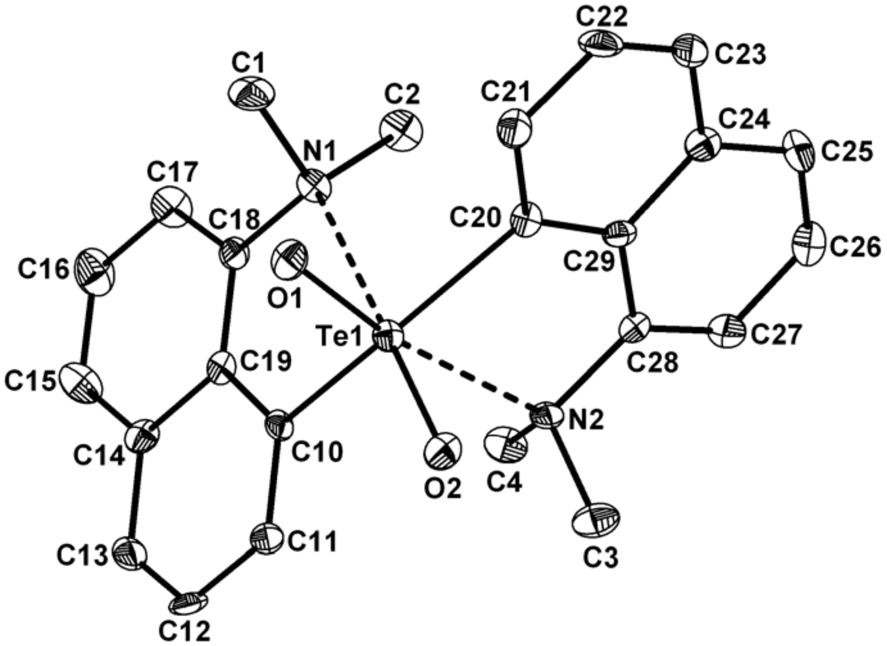

C22
C23
C1
C2
C21
C24
C25
N1
C17
C20
C18
C29
C26
C16
O1
Te1
C27
C15
C19
C28
N2
C14
C10
C4
O2
C3
C13
C11
C12

Figure 2

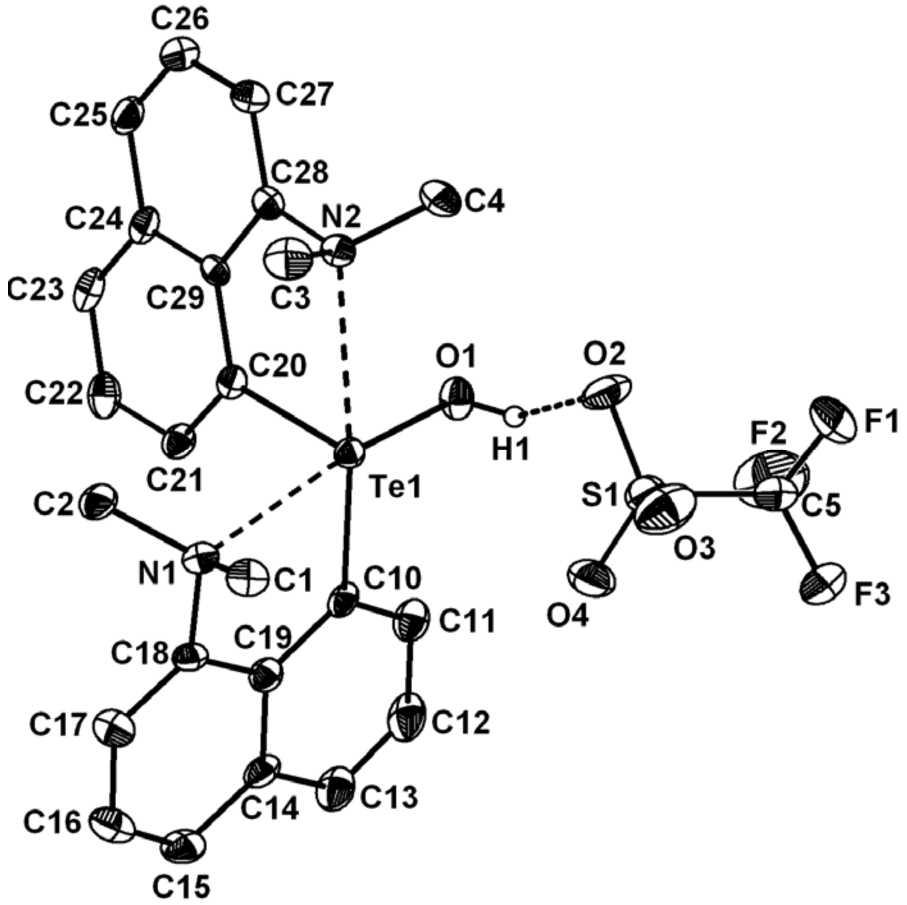

C26
C27
C25
C28
C4
N2
C24
C23
C29
C3
O1
O2
C20
C22
F2
F1
H1
Te1
C21
S1
C5
C2
O3
N1
C1
C10
F3
C11
O4
C18
C19
C17
C12
C14
C13
C16
C15

Figure 3

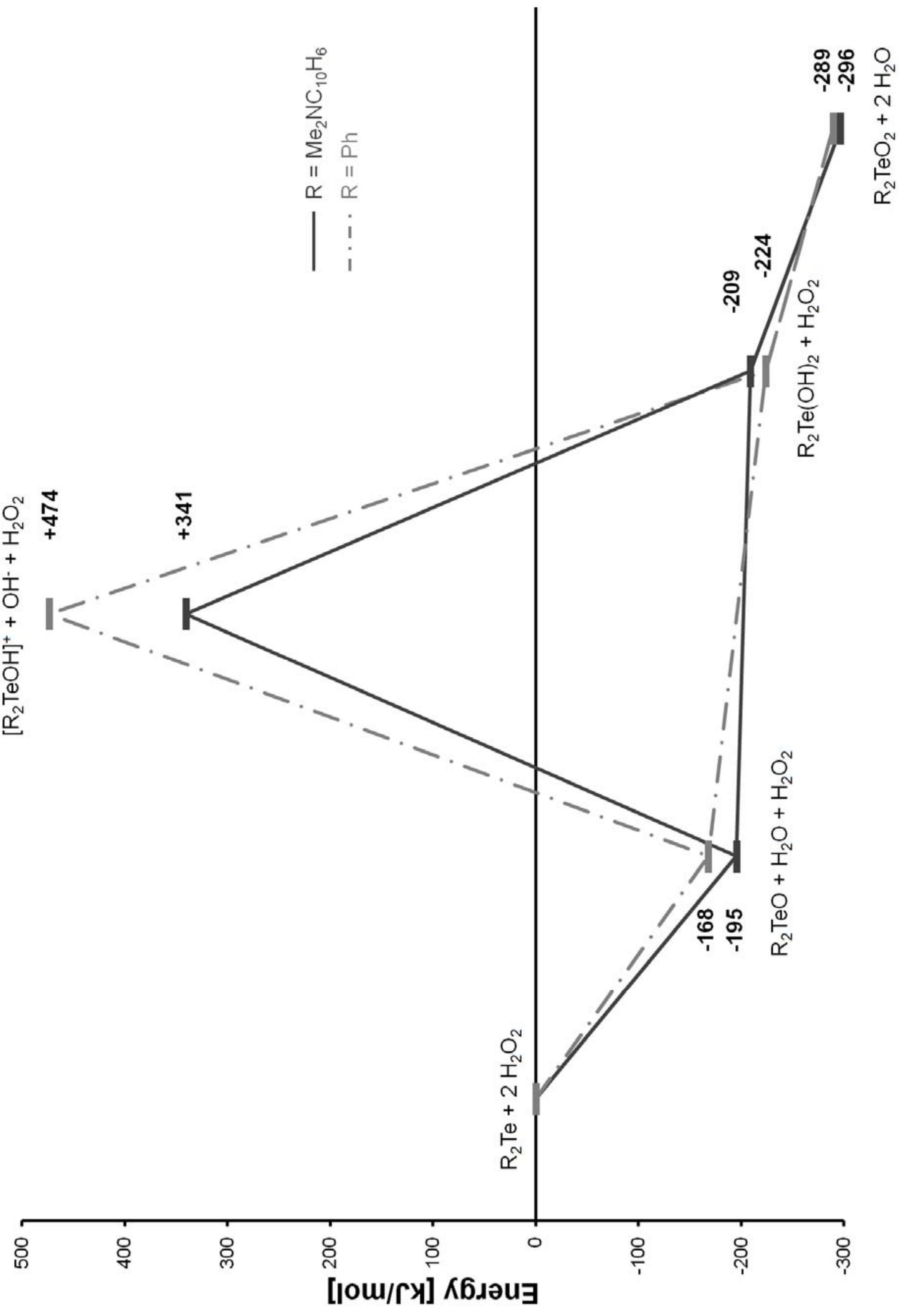

Energy [kJ/mol]
500
400
300
200
100
0
-100
-200
-300
R = Me$_2$NC$_{10}$H$_6$
R = Ph
R$_2$Te + 2 H$_2$O$_2$
R$_2$TeO + H$_2$O + H$_2$O$_2$
-168
-195
[R$_2$TeOH]$^+$ + OH$^-$ + H$_2$O$_2$
+474
+341
R$_2$Te(OH)$_2$ + H$_2$O$_2$
-209
-224
R$_2$TeO$_2$ + 2 H$_2$O
-289
-296

Figure 4

Caption of Figures

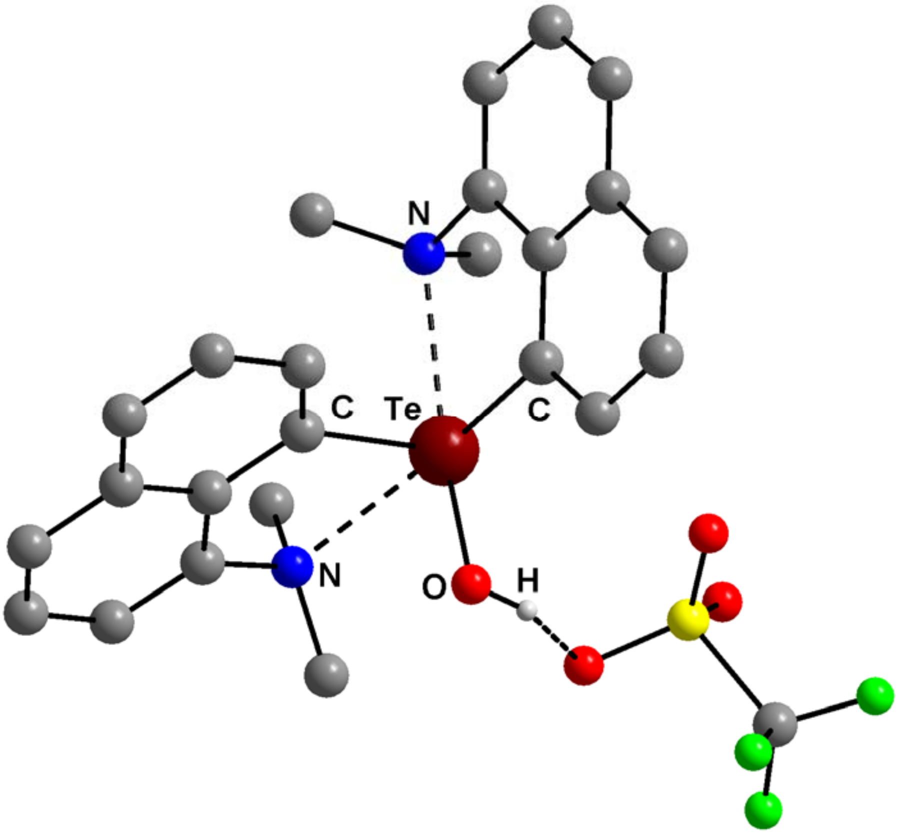
Figure 1. Molecular structure of **1** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, º]: Te1-C10 2.171(3), Te1-C20 1 2.155(2), Te1···N1 2.827(4), Te1···N2 2.699(4), C10-Te1-C20 97.7(2).

Figure 2. Molecular structure of **3** showing 30% probability ellipsoids and the crystallographic numbering scheme. Co-crystallized H_2O and H_2O_2 molecules are not shown. Selected bond parameters [Å, º]: Te1-O1 1.811(5), Te1-O2 1.832(6), Te1-C10 2.103(7), Te1-C20 2.119(7), Te1···N1 2.709(7), Te1···N2 2.762(7), O1-Te1-O2 104.5(3), O1-Te1-C10 103.8(3), O2-Te1-C10 101.8(3), O1-Te1-C20 101.4(3), O2-Te1-C20 104.1(3), C10-Te1-C20 137.8(3).

Figure 3. Molecular structure of **4** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, º]: Te1-O1 1.957(4), Te1-C10 2.139(6), Te1-C20 2.119(5), Te1···N1 2.591(5), Te1···N2 2.706(6), O1···O2 2.814(6), O1-Te1-C10 93.0(2), O1-Te1-C20 90.5(2), C10-Te1-C20 95.0(2).

Figure 4. Relative energies of the diaryltellurium species R_2Te, R_2TeO, $R_2Te(OH)_2$, $[R_2Te(OH)]^+$ and R_2TeO_2 (counterbalanced with H_2O_2, H_2O and OH^-; R = 8-$Me_2NC_{10}H_6$, R = Ph).

For table of contents use only.



Organometallics - Full Paper

A New Series of Intramolecularly Coordinated Diaryltellurium Compounds. Rational Synthesis of the Diarylhydroxytelluronium Triflate $[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$

Jens Beckmann,[a,b] * Jens Bolsinger,[a] Andrew Duthie,[c] Pamela Finke[a,b]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Fabebstr. 34/36, 14195 Berlin, Germany*

[b] *Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Str. 28359 Bremen, Germany.*

[c] *School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia*

Supporting Information

Figure S1. Molecular structure of **3**$\cdot$2 H_2O.

Figure S2. Supramolecular association of **3**$\cdot H_2O\cdot H_2O_2$.

Figure S3. Supramolecular association of **3**$\cdot$2 H_2O.

Optimized geometries of **1-10** as well as absolute energies.

---

[*] Correspondence to Jens Beckmann: Fax ++49(0)421 218 9863160, E-mail: j.beckmann@uni-bremen.de

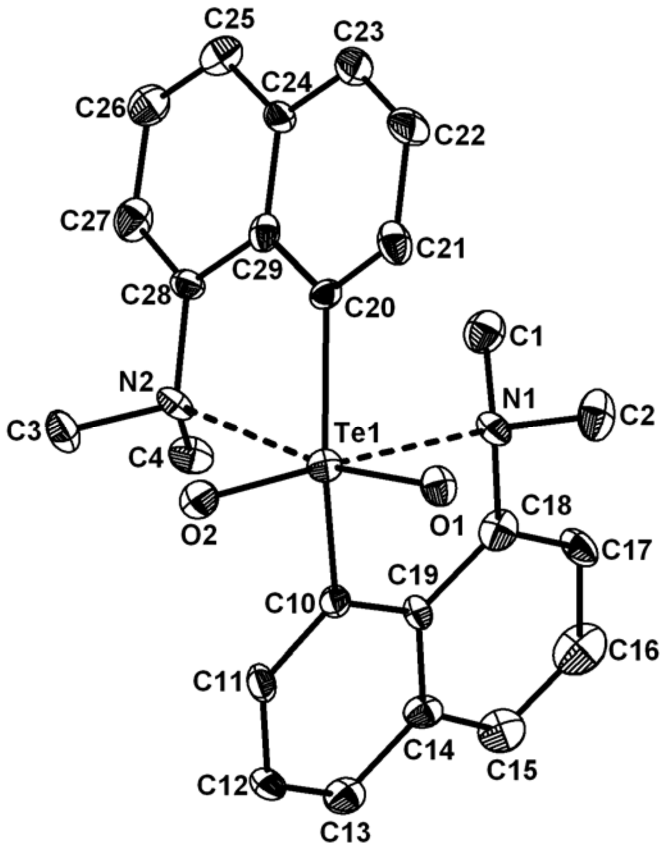


Figure S1. Molecular structure of **3** showing 30% probability ellipsoids and the crystallographic numbering scheme. Co-crystallized H_2O molecules are not shown. Selected bond parameters [Å, º]: Te1-O1 1.813(4), Te1-O2 1.835(5), Te1-C10 2.115(5), Te1-C20 2.093(6), Te1···N1 2.757(5), Te1···N2 2.787(5), O1-Te1-O2 106.2(2), O1-Te1-C10 103.9(2), O2-Te1-C10 101.2(2), O1-Te1-C20 101.2(2), O2-Te1-C20 106.2(2), C10-Te1-C20 135.6(2).

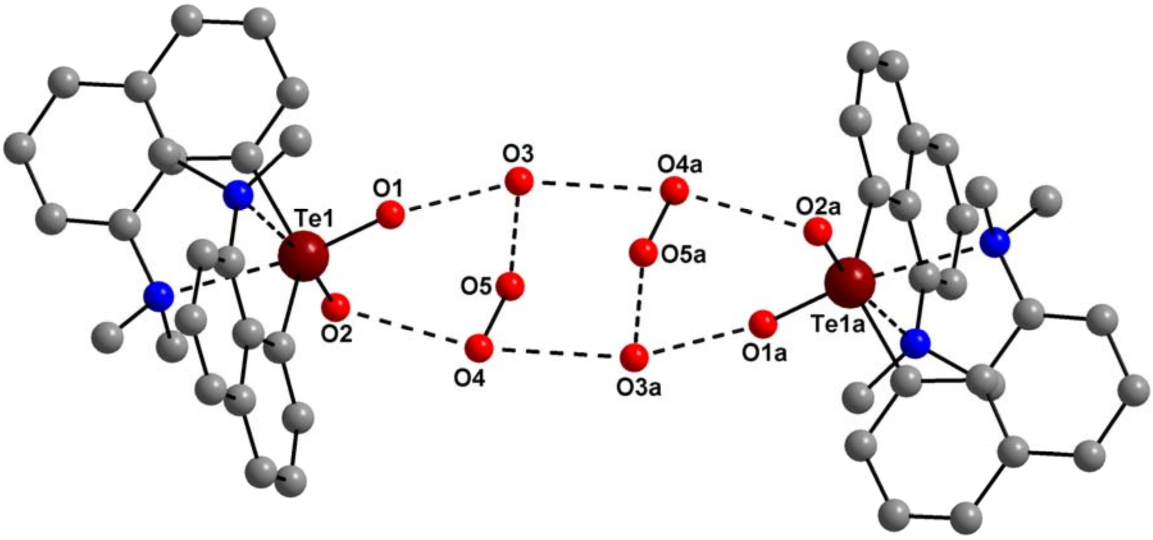


Figure S2. Supramolecular association of **3** · H_2O · H_2O_2. Selected bond parameters [Å]:

O1···O3 2.675(8), O2···O4 2.616(9), O3···O4a 2.97(1), O3···O5 2.70(1), O4-O5 1.449(8).

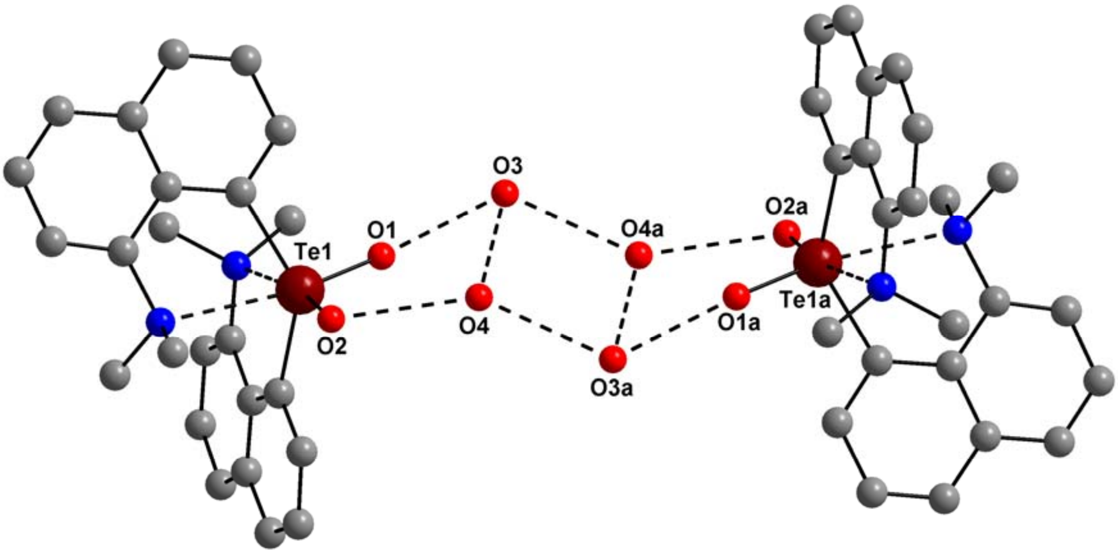


Figure S3. Supramolecular association of **3** · 2 H_2O. Selected bond parameters [Å]:

O1···O3 2.726(6), O2···O4 2.773(7), O3···O4 2.839(9), O3···O4a 2.891(8).

Computational results:

All energies are given in Hartree/Particle

$(8\text{-}Me_2NC_{10}H_6)_2Te$ (**1**):

```
Te,0,-0.0005367157,-0.0000000004,-0.0002580707
N,0,0.0000475824,-0.0004317124,2.8458704677
N,0,2.2228862279,0.0004317113,-1.7770074655
C,0,-0.6233455555,-0.4004740553,-2.0161296017
C,0,-1.9639965212,0.4004740547,0.7720465794
C,0,-1.3699568025,-0.2759962457,3.1182175713
C,0,1.5801407393,0.2759962449,-3.0171539069
C,0,0.2019924402,-0.0689646781,-3.1330587365
C,0,-2.3210439563,0.0689646775,2.1141459157
C,0,-0.3693787881,-0.0860713962,-4.4435972901
C,0,-3.7014621386,0.0860713958,2.4861970177
C,0,0.965713539,-0.9392532586,3.3821596084
H,0,1.9379979558,-0.7483249954,2.9201372186
H,0,1.0952012819,-0.8575863689,4.4725347372
H,0,0.6644070707,-1.9581880983,3.137326849
C,0,0.3571115829,1.3834406517,3.1432603894
H,0,0.3743067433,1.578344373,4.2272975789
H,0,1.3463925081,1.5995089195,2.7323838524
H,0,-0.3613093743,2.0603992178,2.6805091612
C,0,3.2447617312,0.9392532573,-1.3576183403
H,0,4.1772894022,0.8575863675,-1.9373399459
H,0,2.8653828563,1.9581880971,-1.4400824961
H,0,3.4910074166,0.7483249939,-0.3096847841
C,0,2.6781331568,-1.3834406529,-1.683810365
H,0,3.5355916131,-1.5783443743,-2.3472840248
H,0,2.9749410331,-1.5995089208,-0.6545381163
H,0,1.8680837481,-2.0603992188,-1.9560002378
C,0,-1.7870177974,-0.7740415525,4.3301979538
H,0,-1.0547720502,-1.0482814477,5.0807925884
C,0,-3.1551090793,-0.876107456,4.6358728185
H,0,-3.4601144375,-1.2734845929,5.5978962799
C,0,-4.0884259356,-0.4139216598,3.7509242875
H,0,-5.1435863284,-0.4243486921,4.0046151429
C,0,-4.6578617934,0.6003320604,1.5835077857
H,0,-5.7002361206,0.6288553327,1.8837507845
C,0,-4.2646577415,1.0713840657,0.3615916775
H,0,-4.9895542381,1.5060868569,-0.3187283761
C,0,-2.9251091003,0.9506351271,-0.0470448129
H,0,-2.6630105406,1.2612560534,-1.0513678643
C,0,-1.8632693781,-0.9506351274,-2.2553721833
H,0,-2.4840654478,-1.2612560536,-1.4235232268
C,0,-2.3805443047,-1.0713840658,-3.556833283
H,0,-3.364576194,-1.5060868567,-3.6982247506
C,0,-1.6716564416,-0.6003320605,-4.6269577615
H,0,-2.0880311888,-0.6288553327,-5.6286174673
C,0,0.3768446749,0.4139216594,-5.535580161
H,0,-0.0838750789,0.4243486919,-6.5181583071
C,0,1.6508518231,0.8761074553,-5.3591714225
H,0,2.2118162114,1.2734845922,-6.1981209824
C,0,2.2663710198,0.7740415516,-4.0997084428
H,0,3.3098821646,1.0482814466,-3.996458113

Full point group                 C2

Zero-point correction=                   0.418257
Thermal correction to Energy=            0.443247
Thermal correction to Enthalpy=          0.444191
Thermal correction to Gibbs Free Energy= 0.362730
Sum of electronic and
zero-point Energies=          -1046.080006
Sum of electronic and
thermal Energies=             -1046.055015
Sum of electronic and
thermal Enthalpies=           -1046.054071
Sum of electronic and
thermal Free Energies=        -1046.135532
```

$(8\text{-}Me_2NC_{10}H_6)_2TeO$ (**2**):

```
Te,0,0.,0.,0.
C,0,0.,0.,2.16076566
C,0,1.2368941965,0.,2.8649376873
C,0,-1.1746124872,-0.1847947212,2.8457449686
C,0,-1.177771046,-0.4176050118,4.2348799141
C,0,0.0033232906,-0.5396397749,4.912000005
C,0,1.2375211797,-0.3522414903,4.2493676421
C,0,2.485574207,0.3262261245,2.2569479444
C,0,3.6600550752,0.129480261,2.9434914963
C,0,3.6521902306,-0.3168785129,4.2767765297
C,0,2.4666069143,-0.5137004914,4.9283723036
N,0,2.4432951887,0.9138626887,0.961588431
C,0,2.2414885459,2.3658631181,1.0220998564
C,0,3.5243448729,0.5608694129,0.058645724
H,0,-2.1193588673,-0.1787341808,2.3149165131
H,0,-2.1229240203,-0.5422761028,4.7523154764
H,0,0.0119309096,-0.7794692931,5.9705981009
H,0,4.6062560175,0.3634467278,2.4695403436
H,0,4.5932371429,-0.4577654621,4.7972077254
H,0,2.451097867,-0.8005944804,5.9748196206
H,0,1.9755642624,2.7318763668,0.0309991189
H,0,1.4073795155,2.5950269572,1.6832497175
H,0,3.1463797957,2.8704281053,1.3921977036
H,0,3.2619211249,0.8972365417,-0.9471381143
H,0,3.6570338294,-0.5221372801,0.0406203968
H,0,4.482775384,1.029506788,0.3265096677
C,0,-2.0673842787,-0.6331661455,-0.156978472
C,0,-2.5823562875,-1.9243216643,0.1430197572
C,0,-2.9062724629,0.3707962302,-0.5695142806
C,0,-4.2922975261,0.1544879931,-0.6911570422
C,0,-4.8247792386,-1.059104051,-0.3563225474
C,0,-3.9977918048,-2.1194315667,0.0812598572
C,0,-1.7733517135,-3.0268430873,0.5429099096
C,0,-2.3575626587,-4.2039800722,0.9458961247
C,0,-3.753190486,-4.3677995882,0.9286298091
C,0,-4.5545687855,-3.354988263,0.4811035578
N,0,-0.3529343812,-2.882121813,0.4650069905
C,0,0.4004004178,-3.4865971049,1.551898958
C,0,0.1577570256,-3.2959542011,-0.8384756433
H,0,-2.4677821166,1.3456072251,-0.7759170107
H,0,-4.9342915288,0.9619615287,-1.0270410786
H,0,-5.895679622,-1.2279947597,-0.4131571933
H,0,-1.7333082621,-5.03211382,1.2614741438
H,0,-4.1852558929,-5.3092395475,1.249960841
H,0,-5.6317426961,-3.4802667584,0.437426971
H,0,1.4323501206,-3.1298005523,1.5099467302
H,0,-0.0270116432,-3.1852896297,2.5081825733
H,0,0.4277684374,-4.5862612475,1.5048385845
H,0,1.2120854934,-3.0209338562,-0.9230940888
H,0,-0.3943520918,-2.7916850655,-1.6335289405
H,0,0.0646392058,-4.3821612648,-0.9903760274
O,0,-0.299921471,1.733848439,-0.4785156533

Full point group                 C1      NOp   1

Zero-point correction=                 0.422065
Thermal correction to Energy=          0.447949
Thermal correction to Enthalpy=        0.448893
Thermal correction to Gibbs Free Energy=0.366257
Sum of electronic and
zero-point Energies=           -1121.266980
Sum of electronic and
thermal Energies=              -1121.241096
Sum of electronic and
thermal Enthalpies=            -1121.240152
Sum of electronic and
thermal Free Energies=         -1121.322788
```

$(8\text{-}Me_2NC_{10}H_6)_2TeO_2$ (**3**):

```
Te,0,0.058169759,-0.0099101855,0.032379402
O,0,0.0685707071,-0.1072660352,1.8294864909
O,0,1.7131608555,0.0839708107,-0.6684887014
C,0,-0.7661620619,-1.9128787656,-0.4730233595
C,0,-1.3043844279,-2.327425939,-1.7143894384
C,0,-0.7362446427,-2.7402626635,0.6199689101
C,0,-1.246386573,-4.0485766565,0.5297375824
C,0,-1.8309179959,-4.4709948371,-0.6308006839
C,0,-1.8952469019,-3.6298224705,-1.7649559024
C,0,-1.3268465415,-1.5273012525,-2.8915216304
C,0,-1.9948251071,-1.9751697731,-4.0068709601
C,0,-2.6176349641,-3.2339492755,-4.0325359455
C,0,-2.5471040585,-4.0556202587,-2.9430868023
N,0,-0.6053055609,-0.2965894158,-2.8835786901
C,0,0.7561048913,-0.4902106467,-3.4013470831
C,0,-1.2661131448,0.7950287616,-3.5882058536
H,0,-0.3392365264,-2.3627968527,1.5581525807
H,0,-1.1958508144,-4.7017071496,1.3937214893
H,0,-2.263591099,-5.4638962646,-0.7000701305
H,0,-2.0199845959,-1.3594336962,-4.8980771215
H,0,-3.1295470929,-3.558038072,-4.9319509607
H,0,-2.9946099873,-5.0437867997,-2.9637025902
H,0,1.3298549479,0.4239179701,-3.254634763
H,0,0.7330524413,-0.7492291224,-4.470753941
H,0,1.2609458066,-1.2776095715,-2.8455648721
H,0,-0.7326764354,1.7225176508,-3.3757845642
H,0,-1.272898983,0.6576813064,-4.6798055811
H,0,-2.2944544429,0.8989575781,-3.2415494493
C,0,-0.7249997382,1.8974228197,-0.5213866997
C,0,-2.0767703376,2.315680909,-0.5298537701
C,0,0.2945518996,2.7219097429,-0.922390975
C,0,0.0150524384,4.0307165044,-1.3570515652
C,0,-1.2807450695,4.4557567645,-1.4423095538
C,0,-2.3515486798,3.6173080115,-1.0569317993
C,0,-3.1703342976,1.5190143411,-0.0871793057
C,0,-4.4573498737,1.9681542301,-0.2688647856
C,0,-4.7217807945,3.2255306806,-0.8366821072
C,0,-3.6899760314,4.0448809492,-1.198614501
N,0,-2.8816617344,0.2914262409,0.5787455937
C,0,-2.8086490186,0.4938950505,2.0325135526
C,0,-3.7975583225,-0.7978397752,0.2642202915
H,0,1.3121211428,2.341319023,-0.9259783967
H,0,0.831411451,4.6817536048,-1.6491483464
H,0,-1.5116931832,5.4483948596,-1.8154468321
H,0,-5.2889446462,1.3552239773,0.0579169059
H,0,-5.7492032936,3.5505914123,-0.9582653758
H,0,-3.8822031687,5.0322857501,-1.6050645886
H,0,-2.4438575026,-0.4175517454,2.5041115517
H,0,-3.7973997844,0.7559454387,2.4386402073
H,0,-2.0966710068,1.2823745852,2.2672956171
H,0,-3.3913604943,-1.7251114263,0.6705372243
H,0,-4.7980855353,-0.6544225326,0.6989965727
H,0,-3.8972052161,-0.9064046982,-0.8159703221

Full point group                 C1

Zero-point correction=                   0.426352
Thermal correction to Energy=            0.452942
Thermal correction to Enthalpy=          0.453886
Thermal correction to Gibbs Free Energy= 0.369981
Sum of electronic and
zero-point Energies=          -1196.418152
Sum of electronic and
thermal Energies=             -1196.391562
Sum of electronic and
thermal Enthalpies=           -1196.390618
Sum of electronic and
thermal Free Energies=        -1196.474523
```

$[(8\text{-}Me_2NC_{10}H_6)_2Te(OH)]^+$ (**4a**):

```
Te,0,0.0001897213,-0.003929487,0.0025532395
O,0,0.002424229,-0.0120334361,1.9749211161
C,0,2.1204848574,0.0016425441,-0.030255662
C,0,2.7912080824,0.080035726,-1.2782423401
C,0,2.8256000396,-0.0959265921,1.1435471308
C,0,4.2330197209,-0.1133854566,1.1271677587
C,0,4.9098055027,-0.0152139125,-0.0572164372
C,0,4.2179242047,0.0916107652,-1.2850303373
C,0,2.1099353639,0.1749060057,-2.5149317271
C,0,2.8068246673,0.3100117439,-3.6886728667
C,0,4.2119408987,0.3399899976,-3.6877858191
C,0,4.902397382,0.222285155,-2.5127293092
N,0,0.6651281565,0.0648986799,-2.4920855055
C,0,-0.0162873643,1.1144814438,-3.263079546
C,0,0.2403232799,-1.2725470711,-2.9448298439
H,0,-0.4065574744,-0.8152985664,2.3155976489
H,0,2.2965139103,-0.1437002726,2.0874175517
H,0,4.7738395748,-0.1934394307,2.0629564056
H,0,5.9945477483,-0.0127246907,-0.0702040164
H,0,2.2801821222,0.3814346795,-4.633544166
H,0,4.7421093642,0.4463028387,-4.6268004858
H,0,5.98690599,0.2326242643,-2.5084276516
H,0,0.3385343944,2.0932266263,-2.946165773
H,0,0.1508970864,1.0017026985,-4.3391939384
H,0,-1.0909266458,1.0540038268,-3.0826656195
H,0,0.7340734794,-2.0398871494,-2.3465427763
H,0,0.4976073461,-1.4349005835,-3.9964262534
H,0,-0.8408606966,-1.3715246834,-2.8277532781
C,0,-0.2818923985,2.085487768,-0.0528716967
C,0,-1.5841000055,2.6478528867,0.0637695183
C,0,0.8283672549,2.881257501,-0.191823891
C,0,0.7086166485,4.2807465308,-0.2365943006
C,0,-0.5258766005,4.8586372714,-0.1475393339
C,0,-1.6909564266,4.0744407834,0.0050954114
C,0,-2.7775063869,1.901864414,0.2535717414
C,0,-3.9879201422,2.5417096384,0.357117546
C,0,-4.0861876568,3.9395028417,0.2829662009
C,0,-2.9567354554,4.689620685,0.1131983396
N,0,-2.6874644442,0.4684066588,0.3445526045
C,0,-3.3407823537,-0.2127954571,-0.7739461924
C,0,-3.1606001727,-0.0517896194,1.6295013427
H,0,1.8156923163,2.440688173,-0.2578886897
H,0,1.5993198487,4.8894605369,-0.3381275936
H,0,-0.6305228843,5.937802381,-0.1837290413
H,0,-4.8895501067,1.9575612532,0.5053860121
H,0,-5.0561367098,4.4150500849,0.3682281481
H,0,-3.0141858965,5.771499321,0.064465611
H,0,-2.9864471382,0.2007915479,-1.7196699627
H,0,-3.0993811494,-1.2785581245,-0.741843799
H,0,-4.4328333717,-0.1103429093,-0.7488992205
H,0,-2.648102646,0.4598470964,2.4431079081
H,0,-2.9452245933,-1.1225288286,1.6844854361
H,0,-4.2430907118,0.0734173286,1.7573842793

Full point group                 C1

Zero-point correction=                   0.435095
Thermal correction to Energy=            0.461218
Thermal correction to Enthalpy=          0.462162
Thermal correction to Gibbs Free Energy= 0.379321
Sum of electronic and
zero-point Energies=          -1121.687437
Sum of electronic and
thermal Energies=             -1121.661314
Sum of electronic and
thermal Enthalpies=           -1121.660370
Sum of electronic and
thermal Free Energies=        -1121.743210
```

(8-$Me_2NC_{10}H_6)_2Te(OH)_2$ (**5**):

```
Te,0,0.0357565488,-0.0000000001,0.0169278542
N,0,-0.0292326071,-0.0857561132,2.941832219
N,0,2.2569255931,0.0857561123,-1.8871985099
C,0,-0.5693885561,-0.5599052262,-1.9654102523
C,0,-1.8810981008,0.559905227,0.8053016348
C,0,-1.4248467268,-0.242132773,3.1506955687
C,0,1.5339115812,0.2421327728,-3.0990621194
C,0,0.1717279267,-0.191466189,-3.1227826847
C,0,-2.3065713234,0.1914661896,2.1121057996
C,0,-0.4755144953,-0.2738380008,-4.3939116644
C,0,-3.7000006959,0.2738380022,2.4171405837
C,0,0.8441143915,-0.9995145487,3.6519558928
H,0,1.8450961426,-0.9376022753,3.2177615142
H,0,0.9321627047,-0.7700312686,4.7254327148
H,0,0.4871124501,-2.0252412684,3.5471981632
C,0,0.4179654545,1.2989965295,3.0907011288
H,0,0.3791476701,1.6237944951,4.1412352291
H,0,1.4479494079,1.3857829146,2.7364276969
H,0,-0.2042031596,1.9661033906,2.4942159396
C,0,3.3597368158,0.999514547,-1.6617699836
H,0,4.2458582772,0.7700312666,-2.2740556591
H,0,3.0524341891,2.025241267,-1.8715071125
H,0,3.6583360846,0.9376022731,-0.6123283697
C,0,2.6555153834,-1.2989965308,-1.6356548023
H,0,3.4434809895,-1.6237944967,-2.3315275779
H,0,3.0343141837,-1.3857829163,-0.6144358848
H,0,1.7998029649,-1.9661033913,-1.738827584
C,0,-1.9370259755,-0.7468424418,4.3235979298
H,0,-1.2651875349,-1.0914152374,5.1007036815
C,0,-3.3225025818,-0.7710517227,4.5609298922
H,0,-3.6961116303,-1.1753216264,5.4953032998
C,0,-4.1815887493,-0.2310329633,3.6468070591
H,0,-5.2471150955,-0.1853287429,3.8466813305
C,0,-4.5816520984,0.8566438709,1.4796908634
H,0,-5.6346209781,0.9294744754,1.7328203436
C,0,-4.116044406,1.3294505394,0.2852372355
H,0,-4.7900424682,1.804452357,-0.4194660131
C,0,-2.7643433328,1.1530792287,-0.061749556
H,0,-2.4168163372,1.4762530194,-1.0347581132
C,0,-1.7998540444,-1.1530792271,-2.0990313221
H,0,-2.3321894497,-1.4762530178,-1.2135147038
C,0,-2.388199184,-1.3294505371,-3.3644741781
H,0,-3.3604667667,-1.8044523541,-3.4391454902
C,0,-1.7594217683,-0.8566438686,-4.4816800471
H,0,-2.2310218482,-0.9294744726,-5.456570482
C,0,0.17037077,0.2310329646,-5.5457966057
H,0,-0.3503804005,0.1853287449,-6.4966458772
C,0,1.4219328567,0.7710517233,-5.4606970098
H,0,1.9078533889,1.1753216269,-6.3418999504
C,0,2.1165015708,0.7468424416,-4.2386306499
H,0,3.1434023656,1.0914152366,-4.2115198101
O,0,-0.4972285629,-1.9715463186,0.3768431663
H,0,-0.5511538817,-2.1316037372,1.3235470931
O,0,-0.0236713092,1.9715463187,-0.6234474186
H,0,0.6744081105,2.131603737,-1.2651961147

Full point group                C2

Zero-point correction=                  0.446266
Thermal correction to Energy=           0.474735
Thermal correction to Enthalpy=         0.475679
Thermal correction to Gibbs Free Energy= 0.389236
Sum of electronic and
zero-point Energies=         -1197.680768
Sum of electronic and
thermal Energies=            -1197.652299
Sum of electronic and
thermal Enthalpies=          -1197.651354
Sum of electronic and
thermal Free Energies=       -1197.737797
```

Ph_2Te (**6**):

```
Te,0,0.7252595126,0.7684946418,-0.9244993704
C,0,0.7388242144,0.7624972347,1.1877181593
C,0,1.9611310558,0.8368416391,1.8514938261
C,0,-0.443436863,0.738326433,1.92475648
C,0,1.9988326313,0.8971940904,3.2390860916
H,0,2.8884296632,0.8364999209,1.2886038005
C,0,-0.3977846104,0.7747169268,3.3112147683
H,0,-1.4009405485,0.6908460728,1.4184100451
C,0,0.8214390065,0.8607841566,3.9721123144
H,0,2.955662798,0.9584791232,3.746596124
H,0,-1.3229109634,0.7479694989,3.8773111969
H,0,0.8521853719,0.8977341401,5.0554324466
C,0,-0.7213463732,-0.7439325237,-1.2100595372
C,0,-0.6818781328,-1.9361501532,-0.4898567213
C,0,-1.7040151764,-0.5589823173,-2.1797491655
C,0,-1.6257572244,-2.9243308312,-0.7312001309
H,0,0.0847744586,-2.095170462,0.2600870457
C,0,-2.6314326604,-1.5620568422,-2.4332444456
H,0,-1.756075167,0.3728150514,-2.7326959749
C,0,-2.5984126851,-2.7436834045,-1.7069227407
H,0,-1.5921035071,-3.8464242305,-0.1605459641
H,0,-3.3906994412,-1.4098074932,-3.1929647569
H,0,-3.3287964104,-3.522009445,-1.8983600927

Full point group                 C1      NOp   1

Zero-point correction=                   0.180020
Thermal correction to Energy=            0.191570
Thermal correction to Enthalpy=          0.192515
Thermal correction to Gibbs Free Energy= 0.137901
Sum of electronic and
zero-point Energies=           -471.170811
Sum of electronic and
thermal Energies=              -471.159261
Sum of electronic and
thermal Enthalpies=            -471.158317
Sum of electronic and
thermal Free Energies=         -471.212930
```

Ph_2TeO (**7**):

```
Te,0,0.0041351043,-0.0046969246,0.004754927
O,0,0.0031323436,-0.0035579228,1.8199489183
C,0,2.107258212,-0.0033218655,-0.3624471325
C,0,2.64128834,0.083977107,-1.6415916184
C,0,2.9277695619,-0.0571091346,0.7541885396
C,0,4.0207990103,0.0981702118,-1.8035762119
H,0,1.9979759194,0.1421008854,-2.5148529273
C,0,4.3064790735,-0.0393645805,0.584405377
H,0,2.4743972067,-0.1068368217,1.7408193406
C,0,4.8510558778,0.0353826805,-0.6913471209
H,0,4.4473156731,0.1628191222,-2.7987960655
H,0,4.9568852262,-0.0821162013,1.4515032904
H,0,5.9278163988,0.0505713692,-0.8204179981
C,0,-0.2637169585,-2.0906940409,-0.3624471325
C,0,-0.4179795793,-2.6093580285,-1.6415916184
C,0,-0.3143307527,-2.9114072609,0.7541885396
C,0,-0.6068569716,-3.9759510419,-1.8035762119
H,0,-0.3941203317,-1.9638659833,-2.5148529273
C,0,-0.5066294532,-4.2767555668,0.584405377
H,0,-0.2075567807,-2.4679902402,1.7408193406
C,0,-0.649777909,-4.8074716569,-0.6913471209
H,0,-0.7250289955,-4.3908381567,-2.7987960655
H,0,-0.5466358059,-4.9273363506,1.4515032904
H,0,-0.8012811936,-5.8736286203,-0.8204179981

Full point group                 CS

Zero-point correction=                   0.182861
Thermal correction to Energy=            0.195574
Thermal correction to Enthalpy=          0.196518
Thermal correction to Gibbs Free Energy= 0.140764
Sum of electronic and
zero-point Energies=           -546.347432
Sum of electronic and
thermal Energies=              -546.334719
Sum of electronic and
thermal Enthalpies=            -546.333775
Sum of electronic and
thermal Free Energies=         -546.389530
```

Ph_2TeO_2 (**8**):

```
Te,0,0.0005099515,0.0066404092,0.0003303755
C,0,-0.0379672451,-0.0893919564,2.103963397
C,0,1.1483668307,0.0306713,2.8151027572
C,0,-1.2556526814,-0.3006108537,2.7358860524
C,0,1.1053977899,-0.0460776715,4.2004207432
H,0,2.0913844755,0.1601992854,2.2950486591
C,0,-1.2831897646,-0.3761648525,4.1220849536
H,0,-2.1603972259,-0.4249551716,2.1503194801
C,0,-0.1070439586,-0.2449818321,4.8494993906
H,0,2.0218935577,0.0420064015,4.7730780946
H,0,-2.2243544736,-0.5451817129,4.6332594516
H,0,-0.1338102134,-0.3067881828,5.9318641506
C,0,-0.0970687574,2.0523222115,-0.4912209351
C,0,1.0878045085,2.7330781882,-0.7348482331
C,0,-1.3351618624,2.6727183188,-0.5901398211
C,0,1.0265466526,4.0790107331,-1.0705708496
H,0,2.0376882783,2.2115641829,-0.683254678
C,0,-1.3809170791,4.018849191,-0.9258385774
H,0,-2.2478705838,2.1092456924,-0.4289778686
C,0,-0.2034579327,4.7182277304,-1.1610177666
H,0,1.9412575959,4.6264204184,-1.2688096227
H,0,-2.3386181646,4.5200247688,-1.0112563118
H,0,-0.2457823927,5.7690665728,-1.425586781
O,0,1.6306005796,-0.5417940514,-0.5146260454
O,0,-1.5396678505,-0.7335729593,-0.5501977342

Full point group                 C1      NOp   1

Zero-point correction=                   0.186188
Thermal correction to Energy=            0.200193
Thermal correction to Enthalpy=          0.201137
Thermal correction to Gibbs Free Energy= 0.141780
Sum of electronic and
zero-point Energies=           -621.506219
Sum of electronic and
thermal Energies=              -621.492215
Sum of electronic and
thermal Enthalpies=            -621.491271
Sum of electronic and
thermal Free Energies=         -621.550628
```

$[Ph_2Te(OH)]^+$ (**9**):

```
Te,0,-0.0344925094,0.0002083759,-0.0237152442
C,0,0.003130072,-0.0001507043,2.0671828804
C,0,2.0031721136,-0.0027084355,-0.4341017506
C,0,0.0748216276,-1.2313903222,2.712134901
C,0,-0.0740344787,1.1982754885,2.7655432975
C,0,2.3802644206,-0.4060409325,-1.7157663523
C,0,2.9429903207,0.3801287981,0.519951787
C,0,0.0852512998,-1.2544618678,4.0990358737
C,0,-0.066235451,1.1525078896,4.1537405703
C,0,3.7261345917,-0.4078352835,-2.0472516231
C,0,4.2835513517,0.3727588513,0.1703284373
C,0,0.0147356308,-0.0659281969,4.8150624144
C,0,4.6714518946,-0.0185897588,-1.1066858335
H,0,-0.1448417004,2.1461625373,2.2454728325
H,0,2.6405129166,0.6772946532,1.5173747859
H,0,-0.126378515,2.0764354797,4.7171002475
H,0,5.0289444756,0.6707234837,0.8983352802
H,0,0.016992035,-0.0907505741,5.8986392791
H,0,5.7231436054,-0.0246401864,-1.3692725239
H,0,0.1414545036,-2.2038692229,4.6183805375
H,0,0.1209298529,-2.1653176041,2.1603802046
H,0,1.644704932,-0.714691233,-2.4519134175
H,0,4.0354970623,-0.7162949192,-3.0388218594
O,0,-0.3249503806,1.8970580284,-0.1945315645
H,0,-1.0901134354,2.0982121208,-0.7502309928

Full point group                 C1

Zero-point correction=                   0.194578
Thermal correction to Energy=            0.208001
Thermal correction to Enthalpy=          0.208945
Thermal correction to Gibbs Free Energy= 0.151524
Sum of electronic and
zero-point Energies=           -546.727551
Sum of electronic and
thermal Energies=              -546.714127
Sum of electronic and
thermal Enthalpies=            -546.713183
Sum of electronic and
thermal Free Energies=         -546.770604
```

$Ph_2Te(OH)_2$ (**10**):

```
Te,0,-0.0261506624,0.0000000002,-0.0224230223
C,0,-0.0326350163,-0.1335565075,2.102960826
C,0,2.0733561622,0.133556507,-0.3531338375
C,0,-0.1748790699,1.0193344227,2.8652867699
C,0,2.8050511421,-1.0193344234,-0.6100320105
C,0,-0.1843591163,0.920152888,4.2510178776
C,0,4.1731092388,-0.9201528892,-0.8308432837
C,0,4.8019018918,0.3167160388,-0.7976193918
H,0,5.8701851088,0.3881729234,-0.9720127996
C,0,4.0602681286,1.462188201,-0.5432126208
H,0,4.5461055671,2.4317025983,-0.5162099155
C,0,2.691463208,1.3775839404,-0.3227041252
H,0,2.1003143864,2.2637014207,-0.1263835701
C,0,0.0917524389,-1.3775839411,2.7091868958
H,0,0.195573502,-2.2637014212,2.0950046128
C,0,0.0826855789,-1.4621882023,4.0956098829
H,0,0.183503755,-2.4317025998,4.571638094
C,0,-0.0555797338,-0.3167160404,4.8673780785
H,0,-0.0649267023,-0.3881729254,5.9497618952
H,0,2.3041155239,-1.9790568859,-0.6284002457
H,0,4.7476155154,-1.8186057453,-1.0297024793
H,0,-0.2694676437,1.9790568854,2.3730196809
H,0,-0.2932285016,1.8186057439,4.8491398542
O,0,0.1998338127,-2.0559885972,-0.0804008082
H,0,-0.5143795605,-2.4117740356,-0.6172135868
O,0,-0.0489676297,2.0559885976,0.2097618028
H,0,-0.6884729734,2.4117740365,-0.4141785924

Full point group                 C2

Zero-point correction=                           0.207805
Thermal correction to Energy=                    0.222910
Thermal correction to Enthalpy=                  0.223854
Thermal correction to Gibbs Free Energy=         0.164203
Sum of electronic and
zero-point Energies=                 -622.777305
Sum of electronic and
thermal Energies=                    -622.762200
Sum of electronic and
thermal Enthalpies=                  -622.761256
Sum of electronic and
thermal Free Energies=               -622.820906
```

H_2O:

```
O,0,-0.0157750784,0.,-0.0111487231
H,0,0.0200177246,0.,0.9484105462
H,0,0.9006931849,0.,-0.2977164089

Full point group                 C2V

Zero-point correction=                           0.021437
Thermal correction to Energy=                    0.024273
Thermal correction to Enthalpy=                  0.025217
Thermal correction to Gibbs Free Energy=         0.003801
Sum of electronic and
zero-point Energies=                 -76.408607
Sum of electronic and
thermal Energies=                    -76.405771
Sum of electronic and
thermal Enthalpies=                  -76.404827
Sum of electronic and
thermal Free Energies=               -76.426243
```

H_2O_2:

```
O,0,0.0066386869,-0.0091721379,0.0083148458
H,0,-0.0185159475,0.0194221323,0.9733849106
O,0,1.4213169986,-0.0119968883,-0.2258987378
H,0,1.5384110815,-0.8834531272,-0.6254780381

Full point group                 C2

Zero-point correction=                           0.026822
Thermal correction to Energy=                    0.030021
Thermal correction to Enthalpy=                  0.030965
Thermal correction to Gibbs Free Energy=         0.005220
Sum of electronic and
zero-point Energies=                -151.521250
Sum of electronic and
thermal Energies=                   -151.518052
Sum of electronic and
thermal Enthalpies=                 -151.517108
Sum of electronic and
thermal Free Energies=              -151.542853
```

$(OH)^-$:

```
O,0,0.,0.,-0.1071277345
H,0,0.,0.,0.857021876

Full point group                 C*V     NOp   4

Zero-point correction=                            0.008638
Thermal correction to Energy=                     0.010998
Thermal correction to Enthalpy=                   0.011942
Thermal correction to Gibbs Free Energy=         -0.007614
Sum of electronic and
zero-point Energies=                 -75.784089
Sum of electronic and
thermal Energies=                    -75.781729
Sum of electronic and
thermal Enthalpies=                  -75.780784
Sum of electronic and
thermal Free Energies=               -75.800340
```

MANUSCRIPT IV

6 Diarylhalotelluronium(IV) Cations [(8-$Me_2NC_{10}H_6$)$_2$TeX]$^+$ (X = Cl, Br, I) Stabilized by Intramolecularly Coordinating N-Donor Substituents

Jens Beckmann, Jens Bolsinger, Pamela Finke and Andrew Duthie to be published

6.1 SYNOPSIS

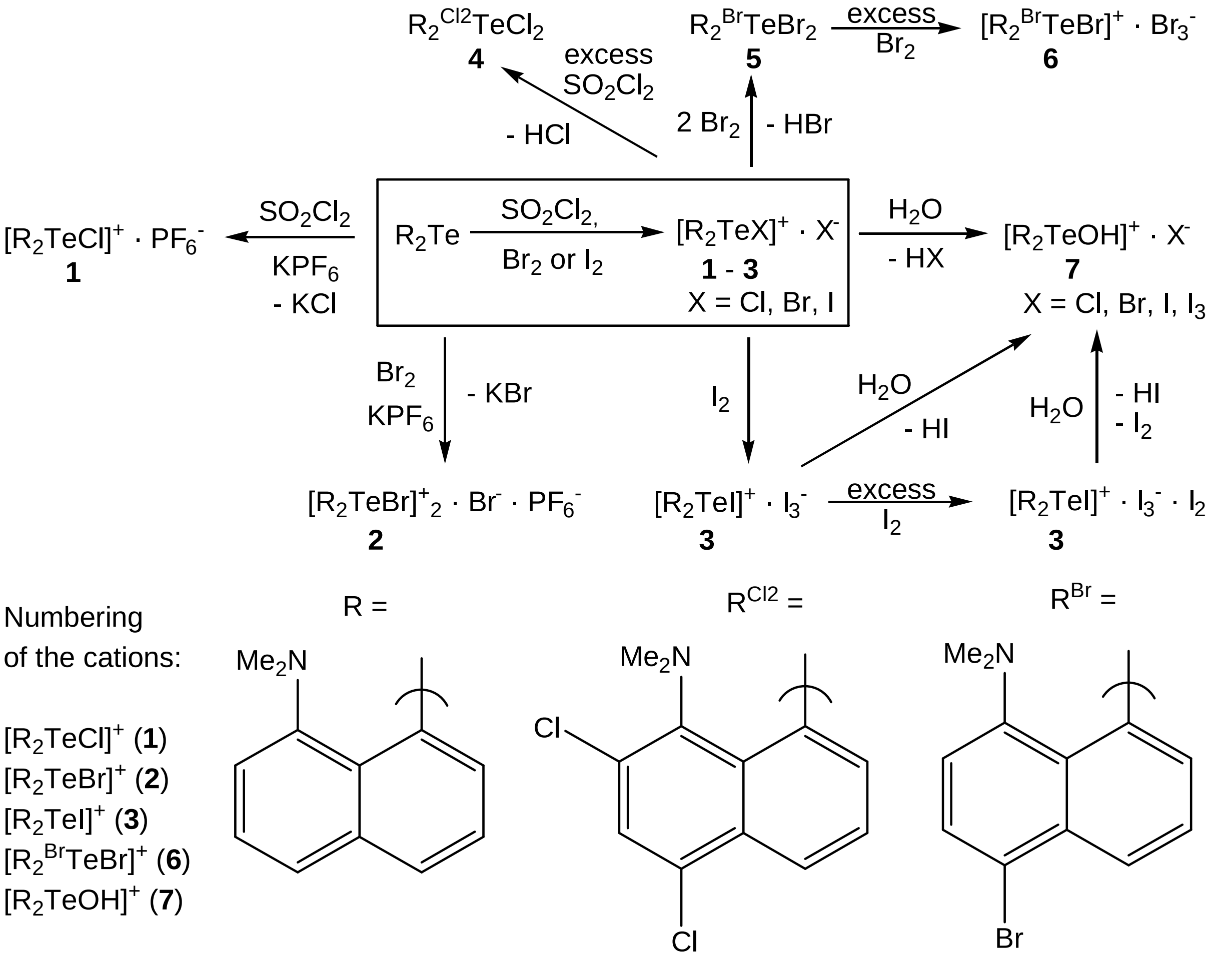
The previous results showed that organotellurium compounds are stabilized by secondary interactions and give rise to a diversity of structures. Therefore, the possibility of stabilizing an organotellurium halide in the cationic state R_2TeX^+ Y^- by intermolecular coordination was examined, comparable to the previously described diarylhydroxytellurium cation $[R_2TeOH]^+$.

Very few organotellurium halides stabilized by intermolecular coordination are known. Only two members of these compound class, namely $[(2\text{-}Me_2NCH_2C_6H_4)PhTeX]^+X^-$ (X = Br, I), were isolated and characterized by X-ray crystallography[38]. During the course of this work, another diarylhalotelluronium cation, namely $[(2\text{-}PhNNC_6H_4)_2TeI]^+I_3^-$ containing two intramolecularly coordinating rather flexible 2-phenylazophenyl groups was reported[26].

A new series of diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = OH, Cl, Br, I), which are stabilized by intramolecularly coordinating stiff 8-dimethylaminonaphthyl groups could be established (Scheme 8)[72].

The reaction of bis(8-dimethylaminonaphthyl) telluride, $(8\text{-}Me_2NC_{10}H_6)_2Te$,[73] with one equivalent of SO_2Cl_2, Br_2 and I_2 afforded the diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl; Br; I), which were isolated as $[(8\text{-}Me_2NC_{10}H_6)_2TeCl]^+\cdot Cl^-\cdot H_2O\cdot 1/2THF$, $[(8\text{-}Me_2NC_{10}H_6)_2TeBr]^+\cdot Br^-$, $[(8\text{-}Me_2NC_{10}H_6)_2TeBr]^+\cdot Br^-\cdot H_2O$ and $[(8\text{-}Me_2NC_{10}H_6)_2TeI]^+\cdot I^-$, respectively. In the presence of KPF_6 the chlorination and bromination yielded $[(8\text{-}Me_2NC_{10}H_6)_2TeCl]^+\cdot PF_6^-$ and $[(8\text{-}Me_2NC_{10}H_6)_2TeBr]^+{}_2\cdot Br^-\cdot PF_6^-$.

Using an excess of SO_2Cl_2 a double electrophilic substitution at the 8-dimethylaminonaphthyl residues (in *ortho*- and *para*-positions) took place, which provided the diaryltellurium dichloride $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$. However, the bromination with three equivalents proceeded with a single electrophilic substitution in *para*-position and gave rise to the formation of the diaryltellurium dibromide $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$, whereas an excess of Br_2 gave the diarylbromotelluronium cation, which was isolated as $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+\cdot Br_3^-$. Two or three equivalents of iodine provided $[(8\text{-}Me_2NC_{10}H_6)_2TeI]^+\cdot I_3^-$ and $[(8\text{-}Me_2NC_{10}H_6)_2TeI]^+\cdot I_3^-\cdot I_2$, respectively.



Scheme 8: Synthesis of intramolecularly coordinated diarylhalotelluronium cations, diaryltellurium dihalides and diarylhydroxytelluronium cation.

A hydrolysis of the above mentioned diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl; Br; I) yielded the diarylhydroxytelluronium cation $(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$, which was isolated as $[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+\ Y^-$ (Y= Cl^-; $Br^-\cdot H_2O\cdot THF$; I^-; $I_3^-\cdot H_2O$), respectively. The same cation $[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+\cdot O_3SCF_3^-$, isolated by the protonation of the diaryltellurium oxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$ with triflic acid was already discussed in the previous paper[73].

The structural analysis shows that the Te···N bond lengths in axial coordination of all the diarylhalotellurium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl; Br; I), respectively $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+$ are significantly shorter than the Te···N bond lengths of the equatorial coordination. A similar observation was made for the diarylhydroxytelluronium cation $[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+ \cdot O_3SCF_3^-$[73]. Furthermore, the Te-X bond lengths are significantly shorter than those of the related diaryltellurium dihalides Ph_2TeX_2 (X = Cl; Br; I)[74-76] and $(4\text{-}Me_2NC_6H_4)_2TeX_2$ (X = Cl; Br; I), respectively[77].

These short bond lengths could be due to the compensation of the formal positive charge situated at the Te atoms by strong attractive interactions. In the solid state the Te atoms of the cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl; Br; I) are weakly associated with the halogen atoms of the anions (weak ion pairing) via secondary Te···Y interactions (Y = Cl, Br, I).

However, within the diaryltellurium dihalides $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$ and $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ the tellurium-halogen bond lengths compare well with those of the related diaryltellurium dihalides Ph_2TeX_2 (X = Cl; Br)[74,75] and $(4\text{-}Me_2NC_6H_4)_2TeX_2$ (X = Cl, Br), respectively[77]. Additionally, the Te···N bond lengths compare well with the weaker equatorial N coordination found in the above mentioned diaryltellurium cations or the average Te···N bond length of $(8\text{-}Me_2NC_{10}H_6)_2Te$[73], indication only a weak interaction with the intramolecularly coordinating ligand.

The molecular structure of the isolated diarylhydroxytelluronium cations $[8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$ X^- ($X=Cl^-$, $Br^-\cdot H_2O\cdot THF$,I^-,$I_3^-\cdot H_2O$) comprise very similar structural parameters as the previously isolated compound $[8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$ featuring the triflat counteranion[73]. However, unlike the diarylhydroxytelluronium triflat these compounds reveal significant Te···Y interactions (Y = Cl, Br, I) between the cations and halide anions.

The behavior of the synthesized compound in solution is interesting. The diarylhalotellurium cations reveal in the ^1H and ^{13}C NMR spectra (CD_3CN, –35°C) two sets of signals for the two magnetically inequivalent 8-dimethylaminonaphthyl substituents and four signals for the magnetically inequivalent methyl groups, which suggests that the cationic structures are retained in solution. The ^{125}Te NMR spectra (CD_3CN, –35℃) exhibit signals for the diarylhalotelluronium cations respectively, regardless of the counter ions.

In contrast, the ^1H and ^{13}C NMR spectra ($CDCl_3$) of the diaryltellurium dichloride $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$ show one set of signals for the 8-dimethylaminonaphthyl substituents. All four methyl groups are magnetically equivalent. The ^{125}Te NMR ($CDCl_3$) reveals a signal that is shifted significantly to highfield compared to the diarylhalotelluronium cations.

However, the structure of the diaryltellurium dibromide $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ in solution depends on the solvent. In acetonitrile, electrolytic dissociation of $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ into $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+$ Br^- takes place, while in chloroform, the solid state structure of $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ is retained. This observation is consistent with the fact that the solvatisation energy for ions is higher in polar solvents than in non-polar solvents.

Thus, the ^1H and ^{125}Te NMR spectra (CD_3CN, –35℃) of $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ are identical with those of $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+$ Br_3^-, whereby the ^1H NMR and ^{125}Te NMR spectra ($CDCl_3$) of $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ resembles that of $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$.

These results show that the intramolecular coordination by the 8-dimethylaminonaphthyl ligand has a stabilizing effect on the organotellurium cations. Furthermore, small changes on the ligand system have a significant influence on the formation of the organotellurium cations. The effect of the intramolecular coordination of the $8\text{-}Me_2NC_{10}H_6$ ligand system was further studied with the respective monoorganotellurium compounds.

6.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote this manuscript together with Prof. Dr. Jens Beckmann.

X-Ray Crystallography: Prof. Dr. Jens Beckmann
^{125}Te MAS-NMR spectra and analysis thereof: Dr. Andrew Duthie

All the experimental contributions are finished, however, the DFT-calculations – carried out by my colleague Pamela Finke – are unfinished at the moment. Upon conclusion of this calculation the manuscript will be completed and send to organometallics.

.

Organometallics – Full Paper

Diarylhalotelluronium(IV) Cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl, Br, I) Stabilized by Intramolecularly Coordinating N-Donor Substituents

Jens Beckmann,[a,b] * Jens Bolsinger,[a] Andrew Duthie,[c] Pamela Finke[a,b]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstr. 34/36, 14195 Berlin, Germany*

[b] *Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Str. 28359 Bremen, Germany.*

[c] *School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia*

Abstract

The stoechiometrically controlled halogenation of the intramolecularly coordinated diaryltelluride $(8\text{-}Me_2NC_{10}H_6)_2Te$ using SO_2Cl_2, Br_2 and I_2 was studied. At an equimolar ratio, the diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (**1**, X = Cl; **2**, X = Br; **3**, X = I) formed that were isolated as $\mathbf{1}\cdot Cl^{-}\cdot H_2O\cdot 1/2THF$, $\mathbf{2}\cdot Br^{-}$, $\mathbf{2}\cdot Br^{-}\cdot H_2O$, and $\mathbf{3}\cdot I^{-}$, respectively. When the same reactions were carried out in the presence of KPF_6, $\mathbf{1}\cdot PF_6^{-}$ and $\mathbf{2}_2\cdot Br^{-}\cdot PF_6^{-}$ were obtained. The chlorination of $(8\text{-}Me_2NC_{10}H_6)_2Te$ with an excess of SO_2Cl_2 occurred with a double electrophilic substitution at the 8-dimethylaminonaphthyl residues (in the *ortho*- and *para*-positions) and afforded the diaryltellurium dichloride $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$ (**4**). The bromination of $(8\text{-}Me_2NC_{10}H_6)_2Te$ with three equivalents of Br_2 took place with a single electrophilic substitution at the 8-dimethylaminonaphthyl residues (in the para-positions) and provided the diaryltellurium dibromide $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ (**5**), while an excess of Br_2 produced the diarylbromotelluronium cation $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+$

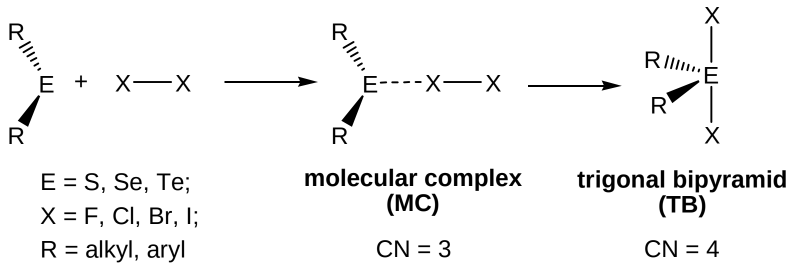
---

[*] Correspondence to Jens Beckmann: Fax ++49(0)421 218 9863160, E-mail: j.beckmann@uni-bremen.de

(**6**) that was isolated as **6**·Br_3^-. The reaction of $(8\text{-}Me_2NC_{10}H_6)_2Te$ with two or three equivalents of iodine provided **3**·I_3^- and **3**·I_3^-·I_2, respectively. In the presence of water, **1**·Cl^-·H_2O·1/2THF, **2**·Br^-, **3**·I^- and **3**·I_3^- hydrolyzed to give the previously known diarylhydroxytelluronium cation $(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$ (**7**) that was isolated as **7**·Cl^-, **7**·Br^-·H_2O·THF, **7**·I^-, **7**·I_3^-·H_2O, respectively. The molecular structures of **1** - **7** were investigated in the solid-state by ^{125}Te MAS NMR spectroscopy and X-ray crystallography and in solution by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{125}Te), electrospray mass spectrometry and conductivity measurements.

Introduction

The halogenation of diorganylchalkogenides R_2E can afford two principles products (Scheme 1).[1] Initially, always a molecular (charge transfer) complex (**MC**) $R_2E\cdots X\text{-}X$, is formed (E = S, Se, Te; X = F, Cl, Br, I; R = alkyl, aryl). This molecular complex (**MC**) is persistent when the electronegativity of the chalcogen is larger than that of the halogen. However, if the electronegativity of the halogen is larger, the molecular complex (**MC**) rearranges into trigonal bipyramidal product (**TB**) R_2EX_2 when taking into account the stereochemically active lone pair of the chalcogen.[1]

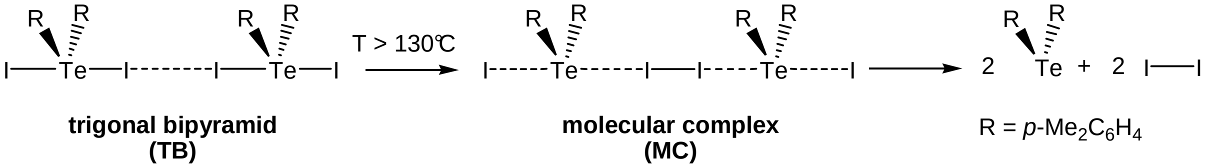


	F	Cl	Br	I
S	TB	TB MC	MC	MC
Se	TB	TB	TB MC	MC
Te	TB	TB	TB	TB MC

Scheme 1. Halogenation of diorganylchalogenides

If the electronegativity difference is reasonably small the outcome of the halogenation may be influenced by the choice of the organic groups. It is has been demonstrated that the bromination of diarylselenides affords either molecular complexes (**MC**) $R_2Se\cdots Br\text{-}Br$ or trigonal bipyramidal products (**TB**) R_2SeBr_2 depending on the electronic influence of the substituents (e.g. OMe, Cl, COOEt, CN, NO_2).[2] When the energy difference is small, both principle products may be even in equilibrium in solution.

The halogenation of diorganyltellurides usually proceeds *via* oxidative addition and almost exclusively provides diorganotellurium(IV) dihalides R_2TeX_2 (X = F, Cl, Br, I; R = alkyl, aryl). However, recently it has been shown that the iodination of bulky diaryltellurides R_2Te (R = Mes = 2,4,6-trimethylphenyl, Tmp = 2,3,5,6-tetramethylphenyl) gives rise to the formation of the first molecular complexes (**MC**) $R_2Te\cdots I\text{-}I$ (R = Mes, Tmp).[3] In these cases the sterically encumbered substituents prevent the increase of the coordination number at the tellurium atom from CN = 3 to 4 and the formation of trigonal bipyramidal (**TB**) products R2TeI$_2$ (Scheme 1). In the solid state, most diorganotellurium(IV) dihalides R_2TeX_2 are involved in intermolecular secondary $Te\cdots X$ interactions, which have been analyzed in detail.[4] A noticeable exception are bis(*p*-dimethylaminophenyl)tellurium(IV) dihalides, which are associated by intermolecular $X\cdots X$ interactions.[5] One of these compounds, namely, $(p\text{-}Me_2NC_6H_4)_2TeI_2$ is thermally unstable and decomposes in the solid state above 130°C into $(p\text{-}Me_2NC_6H_4)_2Te$ and iodine. The mechanism of the reductive elimination is presumably initiated by thermal vibration and formation of a molecular complex (**MC**).



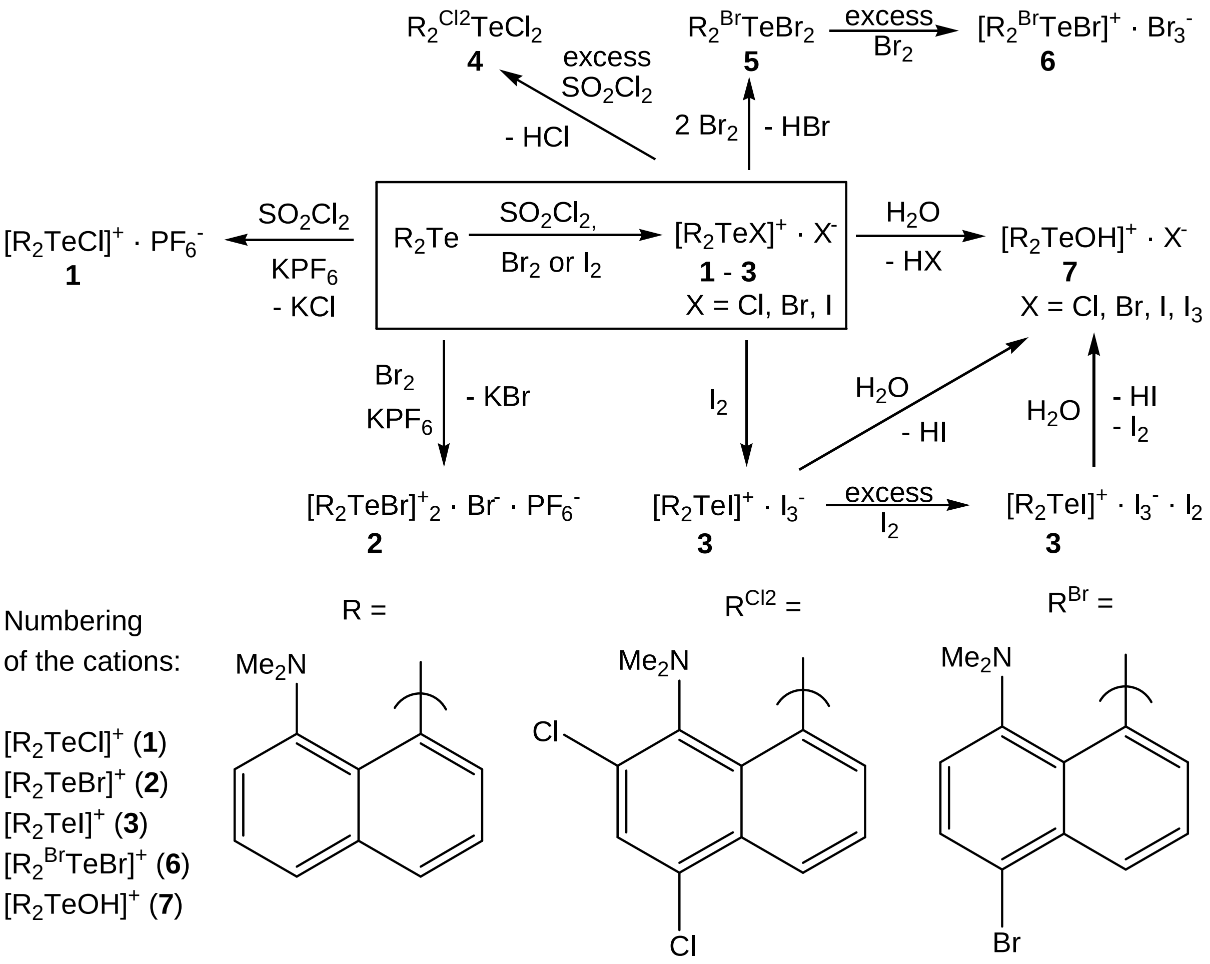
Scheme 2. Proposed mechanism for the reductive elimination of (p-$Me_2NC_6H_4)_2TeI_2$ in the solid state.

In solution, particularly in polar solvents, a different mechanism of the interconversion of molecular complexes (**MC**) and trigonal bipyramidal products (**TB**) might be operative, which has been suggested on the basis of stop-flow kinetic measurements and involves diarylhalotelluronium halides featuring cationic intermediates (**CI**) $[R_2EX]^+X^-$.[6] Two members of these compound class, namely $[(2\text{-}Me_2NCH_2C_6H_4)PhTeX]^+X^-$ (X = Br, I), were isolated and characterized by X-ray crystallography, however, their ^{1}H-NMR analysis was complicated, presumably due to the dynamic behaviour of the intramolecularly coordinating, albeit *flexible* 2-dimethylaminomethyphenyl groups. During the course of this work, another diarylhalotelluronium cation, namely $[(2\text{-}PhNNC_6H_4)_2TeI]^+I_3^-$ containing two intramolecularly coordinating rather *flexible* 2-phenylazophenyl groups was reported.[7] We now describe the synthesis, structure and reactivity of a new series of diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (**1**, X = Cl; **2**, X = Br; **3**, X = I) that are stabilized by two intramolecularly coordinating *stiff* 8-dimethylaminonaphthyl groups.[8]

Results and Discussion

Synthetic Aspects

The reaction of bis(8-dimethylaminonaphthyl) telluride $(8\text{-}Me_2NC_{10}H_6)_2Te$ with one equivalent of SO_2Cl_2, Br_2 and I_2 afforded the diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (**1**, X = Cl; **2**, X = Br; **3**, X = I) that were isolated as **1**$\cdot Cl^-\cdot H_2O\cdot$1/2THF (green plates), **2**$\cdot Br^-$ (brown plates), **2**$\cdot Br^-\cdot H_2O$ (slightly green prisms) and **3**$\cdot I^-$ (red solid), respectively (Scheme 3). When the chlorination and bromination were carried out in the presence of KPF_6, **1**$\cdot PF_6^-$ (yellow plates) and **2**$_2\cdot Br^-\cdot PF_6^-$ (orange plates) were obtained (Scheme 3).



Scheme 3. Synthesis of intramolecurlary coordinated diarylhalotelluronium cations **1** - **3**, **5** and **6**, the diaryltellurium dihalides **4** and **5** and the diarylhydroxotelluronium cation **7**.

The chlorination of $(8\text{-}Me_2NC_{10}H_6)_2Te$ using an excess of SO_2Cl_2 took place with a double electrophilic substitution at the 8-dimethylaminonaphthyl residues (in *ortho*- and *para*-positions) and provided the diaryltellurium dichloride $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$ (**4**) as colorless crystals (Scheme 3). The bromination of $(8\text{-}Me_2NC_{10}H_6)_2Te$ with three equivalents of Br_2 proceeded with a single electrophilic substitution at the 8-dimethylaminonaphthyl residues (in *para*-positions) and gave rise to the formation of the diaryltellurium dibromide $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ (**5**) that was obtained as yellow crystals, while an excess of Br_2 gave the diarylbromotelluronium cation $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+$ (**6**) that was isolated as **6**$\cdot Br_3^-$ (red crystals). The reaction of $(8\text{-}Me_2NC_{10}H_6)_2Te$ with two or three equivalents of iodine provided **3**·I_3^- (violet red crystals) and **3**·I_3^-·I_2 (dark red crystals) respectively (Scheme 3). When reacted with water, **1**·Cl^-·H_2O·1/2THF, **2**·Br^-, **3**·I^- and **3**·I_3^- hydrolyzed to give the diarylhydroxytelluronium cation $(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$ (**7**) that was isolated as **7**·Cl^- (yellow plates), **7**·Br^-·H_2O·THF (green plates), **7**·I^- (orange prisms) **7**·I_3^-·H_2O (black red prisms), respectively (Scheme 3). In preceding work, we already reported the synthesis of the same cation $[8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$ (**7**) by the protonation of the diaryltellurium oxide $[8\text{-}Me_2NC_{10}H_6)_2TeO$ with triflic acid, which was isolated as colorless **7**·$O_3SCF_3^-$.[9]

Molecular structures in the solid-state

The molecular structures of the diarylhalotelluronium cations **1**·Cl^-·H_2O·1/2 THF, **1**·PF_6^-, **2**·Br^- and **3**·I_3^- are shown in Figures 1 - 4, those of **2**$_2$·Br^-·PF_6^-, **3**·I_3^-·I_2 and **6**·Br_3^- are shown in Figures S1, S2 and S4 of the Supporting Information. The molecular structure of the diaryltellurium dihalide **4** is shown in Figure 5, that of **5** is shown in Figure S3 of the Supporting Information. The molecular structure of the diarylhydroxytelluronium cations 7, as present in **7**·Cl^-, **7**·Br^-·H_2O·THF, **7**·I^-, **7**·I_3^-·H_2O, are shown in Figures S5 - S8 of the Supporting Information. Within the diarylhalotelluronium cations **1** - **3** and **6**, the spatial arrangement of the Te atoms is distorted trigonal bipyramidal and defined by a C_2N_2X donor set (X = Cl, Br, I). In this arrangement the equatorial positions are occupied by C10, C20 and N2, whereas N1 and the halogen atom X1 are situated in the axial positions. The Te1-X1 bond lengths of the diarylchlorotelluronium cations **1**·Cl^-·H_2O·½THF (Te1-Cl1 2.444(1) Å) and **1**·PF_6^- (Te1-Cl1 2.427(1) Å), of the diarylbromotelluronium cations **2**·Br^- (Te1-Br1 2.591(2) Å), **2**$_2$·Br^-·PF_6^- (Te1-Br1 2.582(2) Å) and **6**·Br_3^- (Te1-Br1 2.5808(8) Å) and of the diaryliodotelluronium cations **3**·I_3^- (Te1-I1 2.780(2) Å) and **3**·I_3^-·I_2 (Te1-I1 2.7827(8) Å) are significantly shorter than those of the related diaryltellurium dihalides Ph_2TeX_2 (X = Cl: av. 2.506(2) Å;[10] X = Br: 2.6818(6) Å;[11] X = I: 2.928(1) Å)[12] and $(4\text{-}Me_2NC_6H_4)_2TeX_2$ (X = Cl: av. 2.519(1) Å; X = Br: av. 2.681(1) Å; X = I: av. 2.935(3) Å), respectively.[5] The

Te1···N1 bond lengths (varying between 2.426(4) and2.532(7) Å, av. 2.485(7) Å) of the axial coordination are significantly shorter than the Te1···N2 bond lengths of the equatorial coordination (varying between 2.701(3) and 2.800(3) Å, av. 2.748(7) Å). Both the short Te1-X1 bond lengths and the short Te1···N1 bond lengths may be attributed to strong attractive interactions that may be related to the compensation of the formal positive charge situated at the Te atoms. In the solid-state the Te atoms of the cations are weakly associated with halogen atoms of the anions (weak ion pairing) via secondary Te···Y interactions (Y = F, Cl, Br, I). The Te···Y bond lengths are larger than 3 Å, but significantly shorter than the sum of van der Waals radii (given in brackets): Te1···F1 3.053(4)Å for **1**·PF_6^- (3.53 Å), Te1···Cl2 3.173(1) for **1**·Cl^-·H_2O·½THF (3.81 Å), Te1···Br2 3.411(4) Å for **2**·Br^-, Te1···Br2 3.272(4) Å for **2**$_2$·Br^-·PF_6^-, Te1···Br2 3.720(1) Å for **6**·Br_3^- (3.91 Å), Te1···I2 4.037(2) for **3**·I_3^- and Te1···I2 3.8606(8) for **3**·I_3^-·I_2 (4.04 Å). Within the diaryltellurium dihalides **4** and **5**, the spatial arrangement of the Te atoms is distorted octahedral and defined by a $C_2N_2X_2$ donor set (X = Cl, Br). In this arrangement C and N atoms are situated in mutual *cis*-position, whereas the halogen atoms X1 and X2 adopt a *trans*-position. The Te-Cl bond lengths of **4** (2.521(1), Te1-Cl2 2.516(1) Å) and the Te-Br bond lengths of **5** (2.662(1), Te1-Br2 2.712(2) Å) compare well with those of the related diaryltellurium dihalides Ph_2TeX_2 (X = Cl: av. 2.506(2) Å;[10] X = Br: 2.6818(6) Å)[11] and $(4\text{-}Me_2NC_6H_4)_2TeX_2$ (X = Cl: av. 2.519(1) Å; X = Br: av. 2.681(1) Å), respectively.[5] The Te1···N bond lengths of **4** and **5** (varying between 2.726(5) and 2.7477(5) Å, av. 2.736(5) Å) compare well with the Te1···N2 bond lengths of the diarylhalotelluronium cations **1** - **3** and **6** (see above) being associated with the weaker equatorial N-coordination and the av. Te···N bond length of $(8\text{-}Me_2NC_{10}H_6)_2Te$ (2.763 Å).[9] The molecular structure of the diarylhydroxytelluronium cation **7**, isolated as **7**·$O_3SCF_3^-$, was already discussed in detail in our preceding paper [9] The same cation $[8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$ (**7**) with very similar structural parameters is present in the crystals of **7**·Cl^-, **7**·Br^-·H_2O·THF, **7**·I^-, **7**·I_3^-·H_2O. However, unlike **7**·O_3SCF_3, the latter compounds reveal significant Te···Y interactions (Y = Cl, Br, I) between the cations and halide anions. The Te···Y bond lengths are larger than 3 Å, but significantly shorter than the sum of van der Waals radii (given in brackets): Te1···Cl1 3.2535(7) Å for **1**·Cl^-·(3.81 Å), Te1···Br1 3.4777(9) Å for **7**·Br^-·H_2O·THF (3.91 Å), Te1···I1 3.595(2) Å for **7**·I^- and Te1···I1 3.9635(5) Å for **7**·I_3^-·H_2O (4.04 Å).

Molecular structures in solution

The diarylhalotelluronium salts **1**·Cl^-, **1**·PF_6^-, **2**·Br^-, **2**$_2$·Br^-·PF_6^-, **3**·I^-, **3**·I_3^- and **6**·Br_3^- are reasonably soluble in rather strongly polar solvents, such as MeCN, but only poorly soluble in less polar solvents. At room temperature these solutions appear to be of limited stability, however, it was possible to effectively suppress the decomposition by cooling to lower temperatures. The ^{1}H and ^{13}C NMR spectra (CD_3CN, –35°C) show two sets of signals for the two inequivalent 8-dimethylaminonaphthyl substituents and four signals for the magnetically inequivalent methyl groups (see experimental section), which suggests that the cationic structures are retained in solution. The ^{125}Te NMR spectra (CD_3CN, –35°C) exhibit signals for the diarylhalotelluronium cations at δ = 1197.5 (**1**), 1196.6 (**2**), 1184.4 (**3**) and 1196.1 (**6**), respectively, regardless of the counter ions. ESI MS spectra (MeCN, positive mode) of **1**·Cl^-, **2**·Br^- and **3**·I^- show only one prominent mass cluster for the $[8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ cations at 505.07 (X = Cl), 549.02 (X = Br), 597.00 (X = I), respectively. Molar conductivity measurements (MeCN, c = $5\cdot10^{-7}$ mol l^{-1}) of **1**·Cl^- (Λ = 92 Ω^{-1} cm^2 mol^{-1}), **1**·PF_6^- (Λ = 123 Ω^{-1} cm^2 mol^{-1}), **2**·Br^- (Λ = 162 Ω^{-1} cm^2 mol^{-1}), **2**$_2$·Br^-·PF_6^- (Λ = 292 Ω^{-1} cm^2 mol^{-1}), **3**·I^- (Λ = 171 Ω^{-1} cm^2 mol^{-1}), **3**·I_3^- (Λ = 173 Ω^{-1} cm^2 mol^{-1}), **3**·I_3^-·I_2 (Λ = 176 Ω^{-1} cm^2 mol^{-1}) and **6**·Br_3^- (Λ = 92 Ω^{-1} cm^2 mol^{-1}) reveal a significant concentration of electrolytes in solution. The diaryltellurium dichloride **4** is soluble best in less polar solvents, such as $CHCl_3$. No signs of decomposition were found. The ^{1}H and ^{13}C NMR spectra ($CDCl_3$) show one set of signals for the 8-dimethylaminonaphthyl substituents. All four methyl groups of **4** are magnetically equivalent (see experimental section). The ^{125}Te NMR ($CDCl_3$) of **4** shows a signal at δ = 1031.3 that is shifted more than 150 ppm highfield compared to the diarylhalotelluronium cations **1**, **2**, **3** and **6**. The molar conductivity (MeCN, c = $5\cdot10^{-7}$ mol l^{-1}) of **4** was below the detection limit. The structure of the diaryltellurium dibromide **5** in solution depends on the solvent. In acetonitrile, electrolytic dissociation of **5** into **6**$\cdot$Br$^-$ takes place, while in chloroform, the solid state structure of **5** is retained. This observation is consistent with the fact that the solvatisation energy for ions is higher in polar solvents. Thus, the ^{1}H and ^{125}Te NMR spectra (CD_3CN, –35°C) of **5** are identical with those of **6**. The molar conductivity (MeCN, c = $5\cdot10^{-7}$ mol l^{-1}) of **5** is $\Lambda = 170\ \Omega^{-1}$ cm^2 mol^{-1}. The ^{1}H NMR spectrum ($CDCl_3$) of **5** resembles that of **4** and shows one set of signals for the two 8-dimethylaminonaphthyl substituents. The ^{125}Te NMR spectrum ($CDCl_3$) of **5** shows a signal at δ = 1000.5, which compares also well with that of **4** (1031.3). Compounds **7**$\cdot$Cl$^-$, **7**$\cdot$Br$^-$, **7**$\cdot$I$^-$ and **7**$\cdot$$I_3^-$ containing the diarlhydroxytelluronium cation **7** are soluble in at least moderately polar solvents. The ^{1}H, ^{13}C and ^{125}Te NMR spectra ($CDCl_3$ or CD_3CN) compare well with those of **7**$\cdot$$O_3SCF_3^-$,[9] and are consistent with an ionic structure in solution. However, in $CDCl_3$, the chemical shifts for **7**$\cdot$Cl$^-$ and **7**$\cdot$Br$^-$ slightly different, which apparently suggests some degree of association between the diarlhydroxytelluronium cation **7** and counterions. The molar conductivity measurements (MeCN, c = $5\cdot10^{-7}$ mol l^{-1}) of **7**$\cdot$Cl$^-$ ($\Lambda = 129\ \Omega^{-1}$ cm^2 mol^{-1}), **7**$\cdot$Br$^-$ ($\Lambda = 128\ \Omega^{-1}$ cm^2 mol^{-1}), **7**$\cdot$I$^-$ ($\Lambda = 121\ \Omega^{-1}$ cm^2 mol^{-1}) and **3**$\cdot$$I_3^-$ ($\Lambda = 121\ \Omega^{-1}$ cm^2 mol^{-1}) confirm the presence of significant concentration of electrolytes in solution.

Experimental

General. The (8-$Me_2C_{10}H_6)_2$Te was prepared according to literature procedures. The ^{1}H, ^{13}C and ^{125}Te NMR spectra were recorded using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^1H, ^{13}C) and Me_2Te (^{125}Te). The ^{125}Te CP MAS NMR spectra were obtained at 126.26 MHz using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 8 and 10 kHz. A 30 s recycle delay was used and typically 5000 to 10000 transitions were accumulated to obtain adequate signal-to-noise ratios. The isotropic chemical shifts δ_{iso} were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced against Me_2Te using solid $Te(OH)_6$ as the secondary reference (δ_{iso} 692.2 / 685.5). The conductivity measurements were obtained using a SevenEasy^{TM} Conductivity Meter from Mettler Toledo. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of bis(8-dimethylaminonaphthyl)halotelluronium halides $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ X^-.

To a solution of $(8\text{-}Me_2C_{10}H_6)_2Te$ (470 mg, 1 mmol) in THF (10 mL for **1**·Cl^-, **2**·Br^- and **3**·I^-, 50 mL for **3**·I_3^-·I_2) or a suspension in acetonitrile (5mL for **3**·I_3^-) the appropriate halogenation reagent (SO_2Cl_2: 65 mg, Br_2: 160 mg, I_2: 254 mg for **3**·I^-, 508 mg for **3**·I_3^-, 1,0 g for **3**·I_3^-·I_2) was slowly added. In case of **1**·Cl^- the solution was stirred for 15 min. Slow evaporation yielded to yellow green plates (280 mg) of **1**·Cl^-. In case of **2**·Br^- the solution was stirred for 15 min before acetonitrile (10 mL) and hexane (30 mL) were added. Crystallization afforded brown plates (307 mg) of **2**·Br^-. Whereas slow evaporaton of the THF solution afforded slightly green prisms (160 mg) of **2**·Br^-·H_2O**.** In case of **3**·I^- the solution was stirred for one day. A red solid (680 mg; **3**·I^-**)** was separated through filtration. No Crystals could be obtained of **3**·I^-. In case of **3**·I_3^- a few minutes after the addition of the halogenation agent, the suspension becomes a clear solution and was stirred for one day. The solvent was removed under reduced pressure to obtain **3**·I_3^- (815 mg). Recrystallization in Acetonitrile and storage under –20°C afforded violett-red plates of **3**·I_3^-. In case of **3**·I_3^-·I_2 the solution and was stirred for one day. The solvent was removed under reduced pressure to obtain **3**$\cdot I_3^-\cdot I_2$ (1150 mg). Recrystallization in CH_2Cl_2/hexane (1:3) afforded black needles of **3**$\cdot I_3^-\cdot I_2$.

1$\cdot Cl^-$: Yield 280 mg, 0.53 mmol, 53%; Mp. 212-214°C. ^{1}H-NMR (CD_3CN, –35°C): δ = 8.75 (dd, 1H; Ar), 8.44 (dd, 1H; Ar), 8.17 (m, 2H; Ar), 8.04 (t, 1H; Ar), 7.98-7.93 (m, 2H; Ar), 7.85-7.72 (m, 3H; Ar), 7.26 (t, 1H; Ar), 7.01 (d, 1H; Ar), 3.29 (s, 3H; Me), 3.06 (s, 3H; Me), 2.99 (s, 3H; Me), 2.38 (s, 3H; Me). ^{13}C-NMR ($CDCN_3$, –35°C): δ = 148.9, 147.8, 136.4, 136.3, 136.3, 135.3, 134.6, 133.7, 133.3, 130.2, 130.0, 129.0, 128.9, 128.9, 128.6, 128.0, 128.0, 126.7, 123.8, 122.3 (Ar), 52.8, 48.6, 47.7, 47.6 (Me). ^{125}Te-NMR (CD_3CN, –35°C): δ = 1197.5. ^{125}Te CP MAS NMR: δ_{iso} = 1175. ESI MS (MeCN, postive mode): m/z = 505.07 $[C_{24}H_{24}TeCl]^+$. Mol. conductivity (MeCN, c = $5\cdot 10^{-7}$ mol l^{-1}): $\Lambda = 92\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd. for $C_{24}H_{24}N_2Cl_2Te$ (538.97): C, 53.48; H, 4.49; N, 5.20. Found C, 52.92; H, 4.27.; N, 5.19.

2$\cdot Br^-$: Yield 307 mg, 0.56 mmol, 56 %; Mp. 215-218°C. ^{1}H-NMR (CD_3CN, –35°C): δ = 8.89 (dd, 1H; Ar), 8.44 (dd, 1H; Ar), 8.16 (m, 2H; Ar), 8.02 (t, 1H; Ar), 7.96 (m, 2H; Ar), 7.87-7.72 (m, 3H; Ar), 7.25 (t, 1H; Ar), 7.03 (d, 1H; Ar), 3.31 (s, 3H; Me); 3.12 (s, 3H; Me); 3.02 (s, 3H; Me); 2.39 (s, 3H; Me). ^{125}Te-NMR (CD_3CN, –35°C): δ = 1196.6. ^{125}Te CP MAS NMR: δ_{iso} = 1198. ESI MS (MeCN, positive mode): m/z = 549.02 $[C_{24}H_{24}TeBr]^+$. Mol. conductivity (MeCN, c = $5\cdot 10^{-7}$ mol l^{-1}): $\Lambda = 162\ \Omega^{-1}\ cm^2\ mol^{-1}$. Anal. Calcd. for $C_{24}H_{24}N_2Br_2Te$ (627.87): C, 45.91; H, 3.85; N, 4.46. Found C, 45.41; H, 2.78; N, 4.33.

3$\cdot I^-$: Yield 680 mg, 0.94 mmol, 94%; Mp. 222-225°C. ^{1}H-NMR (CD_3CN, –35°C): δ = 8.98 (dd, 1H, Ar), 8.50 (dd, 1H; Ar), 8.17 (d, 1H; Ar), 8.11 (d, 1H; Ar), 7.96 (m, 3H; Ar), 7.87-7.74 (m, 3H; Ar), 7.22 (t, 1H; Ar), 7.02 (d, 1H; Ar), 3.23 (s, 3H; Me); 3.19 (s, 3H; Me), 3.06 (s, 3H; Me), 2.38 (s, 3H; Me). ^{125}Te-NMR (CD_3CN, –35°C): δ = 1184.4. ESI MS (MeCN, positive mode): m/z = 597.00 $[C_{24}H_{24}TeI]^+$. Mol. conductivity (MeCN, c = $5 \cdot 10^{-7}$ mol l^{-1}): Λ = 171 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd. for $C_{24}H_{24}N_2TeI_2$ (721.87): C, 39.93; H, 3.35; N, 3.88. Found: C, 39.96; H, 2.93; N, 3.73.

3$\cdot I_3^-$: Yield 815 mg, 0.84 mmol, 84%; Mp. 199-202°C (dec.). ^{1}H-NMR (CD_3CN, –35°C): see **3**$\cdot I^-$. ^{125}Te-NMR (CD_3CN, –35°C): see **3**$\cdot I^-$. Mol. conductivity (MeCN, c = $5 \cdot 10^{-7}$ mol l^{-1}): Λ = 173 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd. for $C_{24}H_{24}N_2TeI_4$ (975.68): C, 29.54; H, 2.48; N, 2.87. Found: C, 29.80; H, 2.99; N, 2.79.

3$\cdot I_3^- \cdot I_2$: Yield 1.15 g, 0.93 mmol, 91%; Mp. 154-158°C. ^{1}H-NMR (CD_3CN, –35°C): see **3**$\cdot I^-$. ^{125}Te-NMR (CD_3CN, –35°C): see **3**$\cdot I^-$. Mol. conductivity (MeCN, c = $5 \cdot 10^{-7}$ mol l^{-1}): Λ = 177 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd. for $C_{24}H_{24}N_2TeI_6$ (1229.44): C, 23.45; H, 1.97; N, 2.28. Found: C, 23.54; H, 1.42; N, 2.35.

Synthesis of bis(8-dimethylaminonaphthyl)chlorotelluronium hexafluorophosphate $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ PF_6^- and bis(8-dimethylaminonaphthyl)bromotelluronium bromide hexafluorophosphate $[(8\text{-}Me_2NC_{10}H_6)_2TeBr]^+_2$ Br^- PF_6^-.

To a suspension of $(8\text{-}Me_2C_{10}H_6)_2Te$ (235 mg, 0.50 mmol) in dry acetonitrile (10 ml) the appropriate halogenation reagent (SO_2Cl_2: 65 mg, Br_2: 80 mg; 0.50 mmol) was slowly added and stirred for 15 minutes. To the now clear reactionmixture a solution of potassium hexafluorophosphate (91.3 mg, 0.50 mmol) in acetonitrile (10 mL) was added and stirred for 1 d. The precipitated potassium halide was filtered off. Slow evaporation of the solvent produced yellow plates of **1**$\cdot PF_6^-$, orange plates of $\mathbf{2}_2 \cdot Br^- \cdot PF_6^-$ respectively.

1$\cdot PF_6^-$: Yield 129.7 mg, 0.20 mmol, 40%; Mp. 223-225°C (dec.). ^{1}H-NMR (CD_3CN, –35 °C): see **1·Cl**$^-$.^{19}F-NMR (CD_3CN, –35°C): δ = –73.2 ($^1J(^{19}F\text{-}^{31}P)$ = 688 Hz). ^{31}P-NMR

(CD_3CN, –35°C): δ = –147.0. ^{125}Te-NMR (CD_3CN, –35°C): see **$1\cdot Cl^-$**. Mol. conductivity (MeCN, c = $5\cdot 10^{-7}$ mol l^{-1}): Λ = 123 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd. for $C_{24}H_{24}N_2ClPF_6Te$ (648.48): C, 44.45; H, 3.73; N, 4.32. Found: C, 44.30; H, 3.45; N, 4.27.

2_2 $\cdot Br^-\cdot PF_6^-$: Yield 102 mg, 0.15 mmol, 30%; Mp. 221-224°C (dec.). ^{1}H-NMR (CD_3CN, –35°C): see **2**$\cdot Br^-$. ^{19}F-NMR (CD_3CN, –35°C): δ = –73.2 ($^1J(^{19}F-^{31}P)$ = 688 Hz). ^{31}P-NMR (CD_3CN, –35°C): δ = –147.1. ^{125}Te-NMR (CD_3CN, –35°C): see **2**$\cdot Br^-$. Mol. conductivity (MeCN, c = $5\cdot 10^{-7}$ mol l^{-1}): Λ = 292 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd. for $C_{48}H_{48}N_4Br_3PF_6Te_2$ (1320.81): C, 43.65; H, 3.66; N, 4.24. Found: C, 43.19; H, 3.21; N, 4.01.

Synthesis of bis(5,7-dichloro-8-dimethylaminonaphthyl)tellurium dichloride $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_6)_2TeCl_2$ (4).

To a suspension of $(8\text{-}Me_2C_{10}H_6)_2Te$ (520 mg, 1.11 mmol) in dry acetonitrile (20 ml) sulfuryl chloride (1.5 g, 10 mmol) was added and stirred for 15 min. During this time the suspension turned into a clear orange solution. A few minutes after the end of the addition a white precipitate of **4** was filtered off.

4: Yield: 475 mg, 0.7 mmol, 68%; Mp. 238-243°C. ^{1}H-NMR ($CDCl_3$): δ = 8.38 (d, 1H; Ar), 8.02 (d, 1H; Ar) 7.62 (s, 1H; Ar), 7.61 (t, 1H; Ar), 3.16 (s, 6H; Me). ^{13}C-NMR ($CDCl_3$): δ = 142.4, 139.2, 138.7, 134.0, 131.5, 131.2, 131.1, 129.1, 127.9, 126.6 (Ar), 44.5 (Me). ^{125}Te-NMR ($CDCl_3$): δ = 1031.3. Anal. Calcd. for $C_{24}H_{20}N_2TeCl_6$ (676.75): C, 42.59; H, 2.98; N, 4.14. Found: C, 41.98; H, 2.29; N, 3.85.

Synthesis of bis(5-bromo-8-dimethylaminonaphthyl)tellurium dibromide $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_6)_2TeBr_2$ (5) and bis(5-bromo-8-dimethylaminonaphthyl)bromotelluronium tribromide $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_6)_2TeBr]^+\ Br_3^-$ ($6\cdot Br_3^-$).

To a solution of $(8\text{-}Me_2C_{10}H_6)_2Te$ (960 mg, 2.05 mmol) in THF (50 ml) bromine (0.64 g, 4.00

mmol for **5**; 1.28 g, 8.00 mmol for **6**·Br_3^-) was added and stirred for 15 minutes. Slow evaporation of the solvent yielded to yellow crystals of **5** and red crystals of **6**·Br_3^-.

5: Yield: 958 mg, 1.22 mmol, 60%; Mp. 247-251°C (dec.). ^{1}H-NMR ($CDCl_3$): δ = 8.35 (d, 1H; Ar); 7.95 (s, 1H; Ar), 7.82 (s, 1H; Ar), 7.54 (s, 1H; Ar), 7.32 (s, 1H; Ar), 3.01 (s, 6 H; Me). ^{1}H-NMR (CD_3CN, –35°C): see **6**·Br_3^-. ^{125}Te-NMR ($CDCl_3$): δ = 1000.5. ^{125}Te-NMR (CD_3CN, –35°C): see **6**·Br_3^-. Mol. conductivity (MeCN, $c = 5\cdot10^{-7}$ mol l^{-1}): $\Lambda = 123\ \Omega^{-1}$ cm^2 mol^{-1}. Anal. Calcd. for $C_{24}H_{22}N_2TeBr_4$ (785.66): C, 36.69; H, 2.82; N, 3.57. Found: C, 36.30; H, 0.91; N, 3.515.

6·Br_3^-: Yield: 884 mg, 0.93 mmol, 46%; Mp. 195-200°C (dec.). ^{1}H-NMR (CD_3CN): δ = 9.01 (d, 1H; Ar), 8.76 (d, 1H; Ar), 8.49 (d, 1H; Ar), 8.16 (t, 1H; Ar), 8.12 (d, 2H; Ar), 7.84 (d, 1H, Ar), 7.70 (d, 1H; Ar), 7.40 (t, 1H; Ar), 7.09 (d, 1H; Ar), 3.22 (s, 3H; Me), 3.13 (s, 3H; Me), 3.04 (s, 3H; Me), 2.39 (s, 3H; Me). ^{125}Te-NMR (CD_3CN): δ = 1196.1. Mol. conductivity (MeCN, $c = 5\cdot10^{-7}$ mol l^{-1}): $\Lambda = 170\ \Omega^{-1}$ cm^2 mol^{-1}. Anal. Calcd. for $C_{24}H_{22}N_2TeBr_6$ (945.47): C, 30.49, H, 2.35; N, 2.96. Found: C, 30.50; H, 2.49; N, 2.89.

Synthesis of bis(8-dimethylaminonaphthyl)hydroxytelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+ X^-$ (7·X^-).

To a solution of $(8\text{-}Me_2C_{10}H_6)_2Te$ (462 mg, 1 mmol) in THF (60 ml) the appropriate halogenation reagent (SO_2Cl_2: 135 mg, Br_2: 160 mg, I_2: 260 mg; 1 mmol for **7**·I^- , 520 mg; 2 mmol for **7**·I_3^-) was slowly added and stirred for 15 minutes. The reaction mixture was quenched with 5 ml of water. Slow evaporation yielded to yellow plates of **7**·Cl^-**,** green plates of **7**·Br^-, orange prisms of **7**·I^- and black-red prism of **7**·I_3^-.

A more direkt synthesis of **7**$\cdot I_3^-$ yielded to a much better result (Method B). To a solution of **7**$\cdot I^-$ (145 mg; 0.24 mmol) in DCM (20 mL) was added iodine (65 mg; 0.25 mmol) and stirred for 15 min. Slow evaporation of the solvent afforded black-red prism of **7**$\cdot I_3^-$.

7$\cdot Cl^-$: Yield: 68 mg, 0.13 mmol, 13 %; Mp. 225-237°C (dec.). ^{1}H-NMR ($CDCl_3$): δ = 8.65 (d, 1H; Ar), 8.08 (d, 1H; Ar), 7.86 (m, 2H; Ar), 7.79 (t, 1H; Ar), 7.73 (d, 1H; Ar), 7.66 (d, 1H; Ar), 7.57-7.48 (m, 2H; Ar), 7.38 (d, 1H; Ar), 7.04 (t, 1H; Ar), 6.73 (d, 1H; Ar), 3.06 (s, 3H; Me), 3.00 (s, 3H; Me), 2.82 (s, 3H; Me), 1.89 (s, 3H; Me). ^{13}C-NMR ($CDCl_3$): δ = 149.0, 147.9, 135.0, 134.9, 134.2, 133.0, 132.5, 132.3, 131.3, 130.9, 129.5, 128.2, 128.1, 127.2, 127.1, 127.0, 126.7, 126.5, 121.6, 120.5 (Ar), 50.5, 47.3, 46.4, 45.0 (Me). ^{125}Te-NMR ($CDCl_3$): δ = 1187.6. Mol. conductivity (MeCN, $c = 5\cdot10^{-7}$ mol l^{-1}): $\Lambda = 129\ \Omega^{-1}\ cm^2\ mol^{-1}$. IR: $\tilde{\nu}$(OH) = 3393 cm^{-1}. Anal. Calcd. for $C_{24}H_{25}ClN_2OTe$ (520.52): C, 55.38; H, 4.84; N, 5.38. Found: C, 54.65; H, 4.63; N, 4.89.

7$\cdot Br^-$: Yield 265 mg, 0.40 mmol, 40 %; Mp. 224-226°C (dec.). ^{1}H-NMR ($CDCl_3$): δ = 8.73 (dd, 1H; Ar), 8.13 (dd, 1H; Ar), 7.94-7.86 (m, 3H; Ar), 7.78 (dd, 1H; Ar), 7.73 (dd, 1H; Ar), 7.62 (t, 1H; Ar), 7.57 (t, 1H; Ar), 7.44 (dd, 1H; Ar), 7.09 (t, 1H; Ar), 6.76 (dd, 1H; Ar), 5.82 (s, 1H; OH), 3.15 (s, 3H; Me), 3.06 (s, 3H; Me); 2.92 (s, 3H; Me); 1.99(s, 3H; Me). ^{1}H-NMR (CD_3CN): δ = 8.49 (dd, 1H, Ar), 8.30 (dd, 1H; Ar), 8.07 (m, 2H; Ar), 7.96-7.88 (m, 3H; Ar), 7.75-7.67 (m, 3H; Ar), 7.18 (t, 1H; Ar), 6.82 (d, 1H; Ar), 5.82 (s, 1H; OH), 3.04 (s, 3H, Me), 2.96 (s, 3H; Me), 2.86 (s, 3H; Me); 2.06 (s, 3H; Me). ^{13}C-NMR ($CDCl_3$): δ = 148.2, 147.9, 135.1, 135.0, 134.8, 133.3, 132.6, 132.4, 131.4, 130.8, 129.6, 128.3, 128.2, 127.3, 127.2, 126.7, 126.6, 126.5, 121.7, 120.0 (Ar), 50.6, 47.7, 46.5, 45.7 (Me). ^{125}Te-NMR ($CDCl_3$): δ = 1176.4. ^{125}Te-NMR (CD_3CN): δ = 1166.2. Mol. conductivity (MeCN, $c = 5\cdot10^{-7}$ mol l^{-1}): Λ = 128 Ω^{-1} cm^2 mol^{-1}. IR: $\tilde{\nu}$(OH) = 3400 cm^{-1}. Anal. Calcd. for $C_{28}H_{35}BrN_2O_3Te$ (655.09): C, 50.45; H, 5.05; N, 4.53. Found: C, 50.65; H, 4.13; N, 4.23.

7·I$^-$: Yield: 440 mg, 0.72 mmol, 72%; Mp. 227-233°C. ^{1}H-NMR ($CDCl_3$): δ = see **7**·Br$^-$. ^{1}H-NMR (CD_3CN): δ = see **7**·Br$^-$. ^{13}C-NMR ($CDCl_3$): see **7**·Br$^-$. ^{125}Te-NMR ($CDCl_3$): see **7**·Br$^-$. ^{125}Te-NMR (CD_3CN): see **7**·Br$^-$. Mol. conductivity (MeCN, c = $5\cdot10^{-7}$ mol l^{-1}): $\Lambda = 121\ \Omega^{-1}$ cm^2 mol^{-1}. IR: $\tilde{\nu}$(OH) = 3376 cm^{-1}. Anal. Calcd. for $C_{24}H_{25}N_2OTeI$ (611.97): C, 47.10; H, 4.12; N, 4.58. Found: C, 46.88; H, 4.08; N, 4.51 %.

7·I_3^-. Yield: 237 mg, 0.27 mmol, 27%; 195 mg, 0.23 mmol, 94%; Mp. 192-199°C (dec. ^{1}H-NMR ($CDCl_3$): δ = see **7**·Br$^-$. ^{1}H-NMR (CD_3CN): δ = see **7**·Br$^-$. ^{13}C-NMR ($CDCl_3$): see **7**·Br$^-$. ^{125}Te-NMR ($CDCl_3$): see **7**·Br$^-$. ^{125}Te-NMR (CD_3CN): see **7**·Br$^-$. Mol. conductivity (MeCN, c = $5\cdot10^{-7}$ mol l^{-1}): $\Lambda = 121\ \Omega^{-1}$ cm^2 mol^{-1}. IR: $\tilde{\nu}$(OH) = 3307 cm^{-1}. Anal. Calcd. for $C_{24}H_{25}N_2OTeI_3$ (865.78): C, 33.29; H, 2.91; N, 3.24. Found: C, 33.23; H, 2.86; N, 3.31.

X-ray crystallography. Intensity data were collected on a Bruker SMART 1000 CCD (**3**·I_3^-·I_2, **7**·Cl$^-$) at 173 K and a STOE IPDS 2T diffractometer (**1**·Cl$^-$·H_2O·1/2THF, **1**·PF_6^-, **2**·Br$^-$, **2**$_2$·Br$^-$·PF_6^-, **3**·I_3^-, **4**, **5**, **6**·Br_3^-, **7**·Br$^-$·H_2O·THF, **7**·I$^-$·,**7**·I_3^-·H_2O) at 150 K with graphite-monochromated Mo-Kα (0.7107 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 and SHELXL-97 implemented in the program WinGX 2002. Full-matrix least-squares refinements on F^2, using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Crystal and refinement data are collected in Table 1. The absolute structure of **5**, **7**·Cl$^-$ and **7**·I$^-$ was determined by refinement of the Flack parameter (0.00(1), 0.39(4) and 0.00(1)). Figures were created using DIAMOND. Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

References

[1] P. D. Boyle, S. M. Godfrey *Coord. Chem. Rev*. **2001**, *223*, 265-299.

[2] (a) W. Nakanishi, S. Hayashi, H. Tukada, H. Iwamura *J. Phys. Org. Chem*. **1990**, *3*, 369-368. (b) W. Nakanishi, Y. Yamamoto, S. Hayashi, H. Tukada, H. Iwamura *J. Phys. Org. Chem.* **1990**, *3*, 369-374. (c) W. Nakanishi, S. Hayashi, H. Kihara *J. Org. Chem*. **1999**, *64*, 2630-2637. (d) W. Nakanishi, S. Hayashi *Heteratom Chem*. **2001**, *12*, 369-379. (e) W. Nakanishi, S. Hayashi, Y. Kusuyama *J. Chem. Soc. Perkin Trans. 2*, **2002**, 262-270.

[3] (a) P. H. Laur, S. M. Saberi-Niaki, M. Scheiter, C. Hu, U. Englert, Y. Wang, J. Fleischhauer *Phosphorous, Sulfur, Silicon* **2005**, *180*, 1035-1044. (b) E. Faoro, G. Manzoni den Oliveira, E. Schulz Lang, C. B. Pereira *J. Organomet. Chem*. **2010**, *695*, 1480-1486.

[4] J. Zukerman-Schpector, I. Haiduc, *Phosphorous, Sulfur, Silicon* **2001**, *171*, 73

[5] J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, M. Schürmann *Aust. J. Chem.* **2005**, *58*, 119.

[6] (a) M. R. Detty, A. E. Friedman, M. McMillian, *Organometallics* **1994**, *13*, 3338-3345. (b) M. R. Detty, A. J. Williams, J. M. Hewitt, M. McMillan *Organometallics* **1995**, *14*, 5258-5262.

[7] Srivastava, K.; Shah, R.; Singh, H. B.; Butcher, R. J. *Organometallics* **2011**, *30*, 534-546.

[8] This work was presented in part at the Tenth International Conference on the Chemistry of Selenium and Tellurium (ICCST-10), Lodz, Poland, 22-27 June **2007**, Book of Abstracts and Program, Poster P4.

[9] J. Beckmann, J. Bolsinger, A. Duthie, P. Finke, *Organometallics* **2011** submitted.

[10] N. W. Alcock, W. D. Harrison, *J. Chem. Soc., Dalton Trans.* **1982**, 251.

[11] (a) G. D. Christofferson, J. D. McCullough, *Acta Crystallogr*. **1959**, *11*, 249. (b) For redetermination of the X-ray structure of Ph_2TeBr_2 see: J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, *Acta Crystallogr*. **2004**, *E60*, o2511.

[12] N. W. Alcock, W. D. Harrison, *J. Chem. Soc., Dalton Trans.* **1984**, 869.

[13] J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, M. Schürmann *Aust. J. Chem.* **2005**, *58*, 119-127.

Table 1. Crystal data and structure refinement of **1 - 7**.

	1·Cl$^-$·H$_2$O·½THF	**1**·PF$_6^-$	**2**·Br$^-$
Formula	$C_{52}H_{56}Cl_4N_4O_3Te_2$	$C_{24}H_{24}ClF_6N_2PTe$	$C_{26}H_{27}Br_2N_3Te$
Formula weight, g mol^{-1}	1182.01	648.47	668.93
Crystal system	Monoclinic	Triclinic	Triclinic
Crystal size, mm	0.41 × 0.35 × 0.15	0.27 × 0.21 × 0.07	0.36 × 0.28 × 0.17
Space group	$P2_1/c$	P-1	P-1
a, Å	33.779(2)	9.2967(10)	8.785(8)
b, Å	8.8592(8)	10.2462(11)	11.671(13)
c, Å	17.7936(12)	13.4833(16)	14.197(12)
α, °	90.00	92.378(9)	105.03(9)
β, °	109.754(5)	98.203(9)	98.59(7)
γ, °	90.00	97.233(9)	109.95(8)
V, Å^3	5011.5(6)	1258.8(2)	1275(2)
Z	2	2	2
ρ_{calcd}, Mg m^{-3}	1.567	1.711	1.742
μ (Mo $K\alpha$), mm^{-1}	1.424	1.412	4.318
F(000)	1184	640	652
θ range, deg	2.39 to 29.32	2.01 to 29.18	2.05 to 29.23
Index ranges	$-45 \leq h \leq 46$	$-11 \leq h \leq 12$	$-12 \leq h \leq 11$
	$-11 \leq k \leq 12$	$-14 \leq k \leq 14$	$-16 \leq k \leq 16$
	$-11 \leq l \leq 24$	$-18 \leq l \leq 16$	$-19 \leq l \leq 19$
No. of reflns collected	10858	14301	13649
Completeness to θ_{max}	97.4%	98.6%	98.1%
No. indep. Reflns	5704	6712	6791
No. obsd reflns with ($I>2\sigma(I)$)	4370	4804	5311
No. refined params	286	316	289
GooF (F^2)	0.980	0.913	1.041
R_1 (F) ($I > 2\sigma(I)$)	0.0361	0.0411	0.0486
wR_2 (F^2) (all data)	0.0909	0.0953	0.1246
Largest diff peak/hole, e Å^{-3}	0.655 / –1.030	0.876 / –0.694	1.705 / –1.195

Table 1. cont.

$\mathbf{2}_2\cdot\mathrm{Br}^-\cdot\mathrm{PF}_6^-$	$\mathbf{3}\cdot\mathrm{I}_3^-$	$\mathbf{3}\cdot\mathrm{I}_3^-\cdot\mathrm{I}_2$	**4**
$C_{48}H_{48}Br_3F_6N_4PTe_2$	$C_{24}H_{24}I_4N_2Te$	$C_{24}H_{24}I_6N_2Te$	$C_{24}H_{20}Cl_6N_2Te$
1320.80	975.65	1229.45	676.72
Monoclinic	Monoclinic	Monoclinic	Tetragonal
0.31 × 0.25 × 0.18	0.18 × 0.15 × 0.06	0.49×0.17×0.04	0.50 × 0.20 × 0.12
$P2_1/c$	$P2_1/c$	$C2/c$	I-4
15.915(18)	7.837(3)	31.471(5)	22.4140(11)
9.941(7)	17.587(9)	12.1929(17)	22.4140(11)
16.361(13)	19.891(11)	21.729(3)	10.7778(5)
90	90	90	90
110.84(8)	97.28(4)	132.577(2)	90
90	90	90	90
2419(4)	2719(2)	6139.8(15)	5414.6(5)
2	4	8	8
1.813	2.383	2.660	1.660
3.778	5.650	7.019	1.707
1284	1784	4416	2656
2.05 to 29.25	2.06 to 29.21	1.76 to 30.54	2.78 to 29.17
$-18 \leq h \leq 21$	$-10 \leq h \leq 10$	$-44 \leq h \leq 32$	$-30 \leq h \leq 30$
$-13 \leq k \leq 13$	$-24 \leq k \leq 24$	$-0 \leq k \leq 17$	$-30 \leq k \leq 30$
$-22 \leq l \leq 22$	$-27 \leq l \leq 22$	$-0 \leq l \leq 30$	$-14 \leq l \leq 14$
18185	21035	9367	25830
98.7%	98.8%	99.6%	99.5%
6501	7292	9367	7259
2951	3531	7256	6514
290	280	298	298
0.846	0.802	1.067	1.013
0.0628	0.0434	0.0509	0.0318
0.1330	0.1129	0.1640	0.0852
1.584 / –0.969	0.853 / –1.709	2.422 / –4.745	0.897 / –0.638

Table 1. cont.

5	**6**·Br_3^-	**7**·Cl^-	**7**·Br^-·H_2O·THF
$C_{24}H_{22}Br_4N_2Te$	$C_{24}H_{22}Br_6N_2Te$	$C_{24}H_{25}ClN_2OTe$	$C_{28}H_{35}BrN_2O_3Te$
785.68	945.50	520.51	655.09
Orthorhombic	Triclinic	Orthorhombic	Monoclinic
0.10 × 0.10 × 0.05	0.39 × 0.14 × 0.12	0.42 × 0.39 × 0.13	0.50 × 0.11 × 0.06
*P*bca	*P*-1	*P*ca2_1	*P*2_1/c
14.315(6)	9.2192(12)	12.8089(18)	13.2151(13)
23.765(6)	12.0020(16)	10.4279(14)	9.0546(5)
14.779(12)	14.3375(18)	16.766(2)	23.424(2)
90	89.947(10)	90	90
90	108.386(10)	90	103.826(8)
90	110.917(10)	90	90
5028(5)	1395.0(3)	2239.4(5)	2721.7(4)
8	2	4	4
2.076	2.251	1.544	1.599
7.556	9.676	1.465	2.593
2976	884	1040	1312
2.16 to 29.27	1.83 to 29.20	1.95 to 30.50	1.79 to 29.24
0 ≤ h ≤ 19	–12 ≤ h ≤ 12	– 15 ≤ h ≤ 18	–18 ≤ h ≤ 17
0 ≤ k ≤ 32	–16 ≤ k ≤ 16	–14 ≤ k ≤ 14	–10 ≤ k ≤ 12
0 ≤ l ≤ 20	–19 ≤ l ≤ 19	–20 ≤ l ≤ 23	–32 ≤ l ≤ 32
6764	14896	17741	19661
98.6%	98.0%	99.9%	98.7%
6764	7426	5910	7309
4008	4811	5180	4080
280	298	266	328
0.928	0.964	1.069	0.866
0.0492	0.0514	0.0219	0.0430
0.0807	0.1048	0.0489	0.1086
0.721 / –1.040	0.885 / –0.954	0.681 / –0.479	0.642 / –0. 839

Table 1. cont.

7·I^-	**7**·I_3^-·H_2O
$C_{24}H_{25}IN_2OTe$	$C_{24}H_{25}I_3N_2OTe$
611.96	865.76
Orthorhombic	Monoclinic
0.21 × 0.17 × 0.12	0.33 × 0.210 × 0.08
$Pca2_1$	$P2_1/n$
11.496(5)	11.2981(10)
21.960(11)	12.4425(7)
18.202(9)	19.647(2)
90	90
90	94.176(8)
90	90
4595(4)	2754.6(4)
8	4
1.769	2.088
2.656	4.460
2368	1608
1.85 to 29.22	2.70 to 29.21
$0 \leq h \leq 15$	$-15 \leq h \leq 15$
$0 \leq k \leq 29$	$-14 \leq k \leq 17$
$-24 \leq l \leq 23$	$-19 \leq l \leq 26$
9791	19462
98.0%	97.8%
9791	7311
4926	5035
524	280
0.859	0.849
0.0580	0.0354
0.1386	0.0864
0.847 / –0.977	1.522 / –1.244

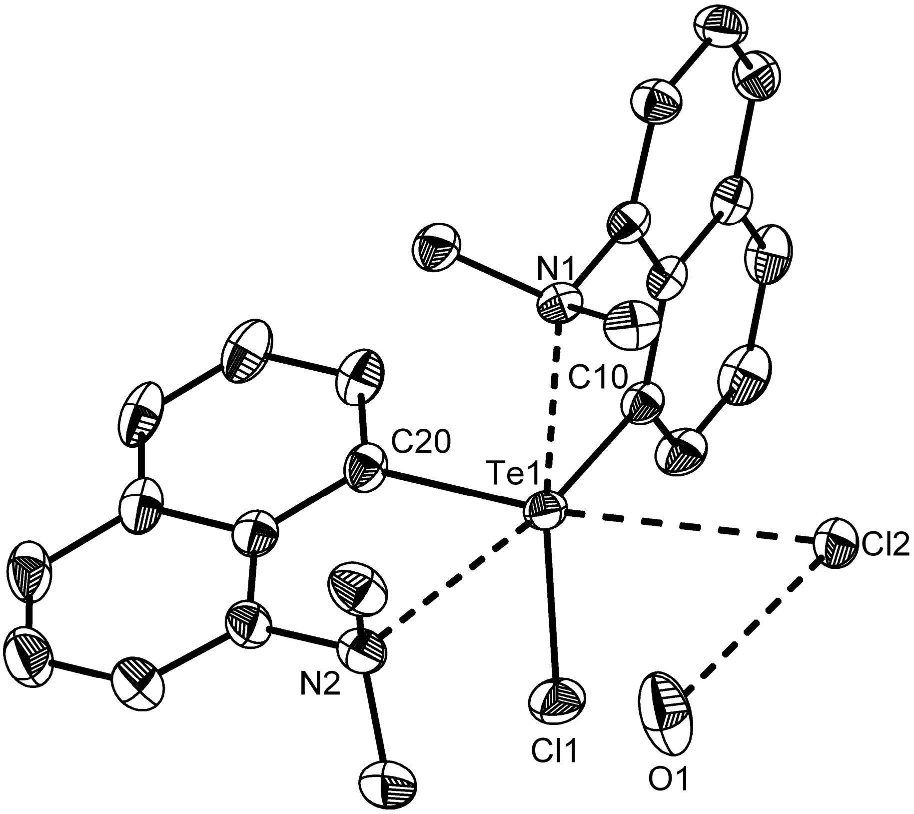


Figure 1. Molecular structure of **1**·Cl^-·H_2O·½THF showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Cl1 2.444(1), Te1-C10 2.141(3), Te1-C20 2.145(3), Te1···N1 2.445(3), Te1···N2 2.800(3), C10-Te1-C20 92.8(1), Cl1-Te1-C10 92.63(9), Cl1-Te1-C20 90.4(1), Ion contact: Te1···Cl2 3.173(1).

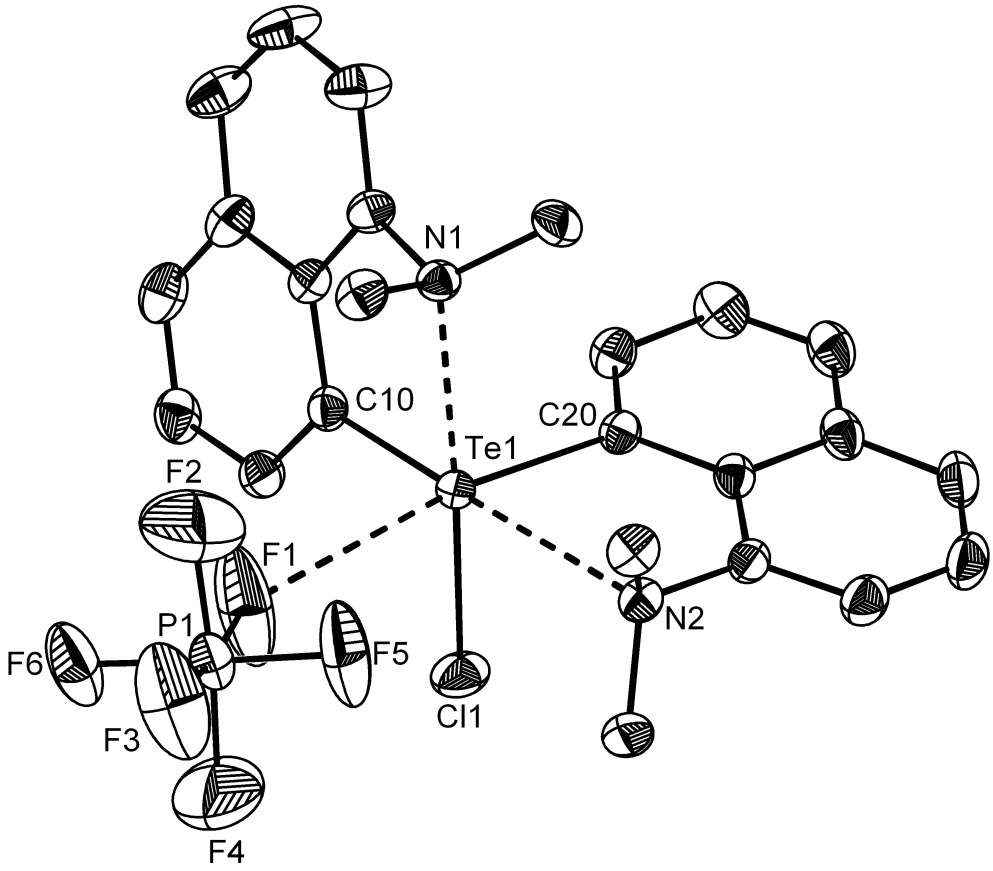


Figure 2. Molecular structure of **1**·PF_6^- showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Cl1 2.427(1), Te1-C10 2.134(4), Te1-C20 2.122(4), Te1···N1 2.426(4),Te1···N2 2.701(3), C10-Te1-C20 99.1(1), Cl1-Te1-C10 90.7(1), Cl1-Te1-C20 89.3(1), Ion contact: Te1···F1 3.053(4).

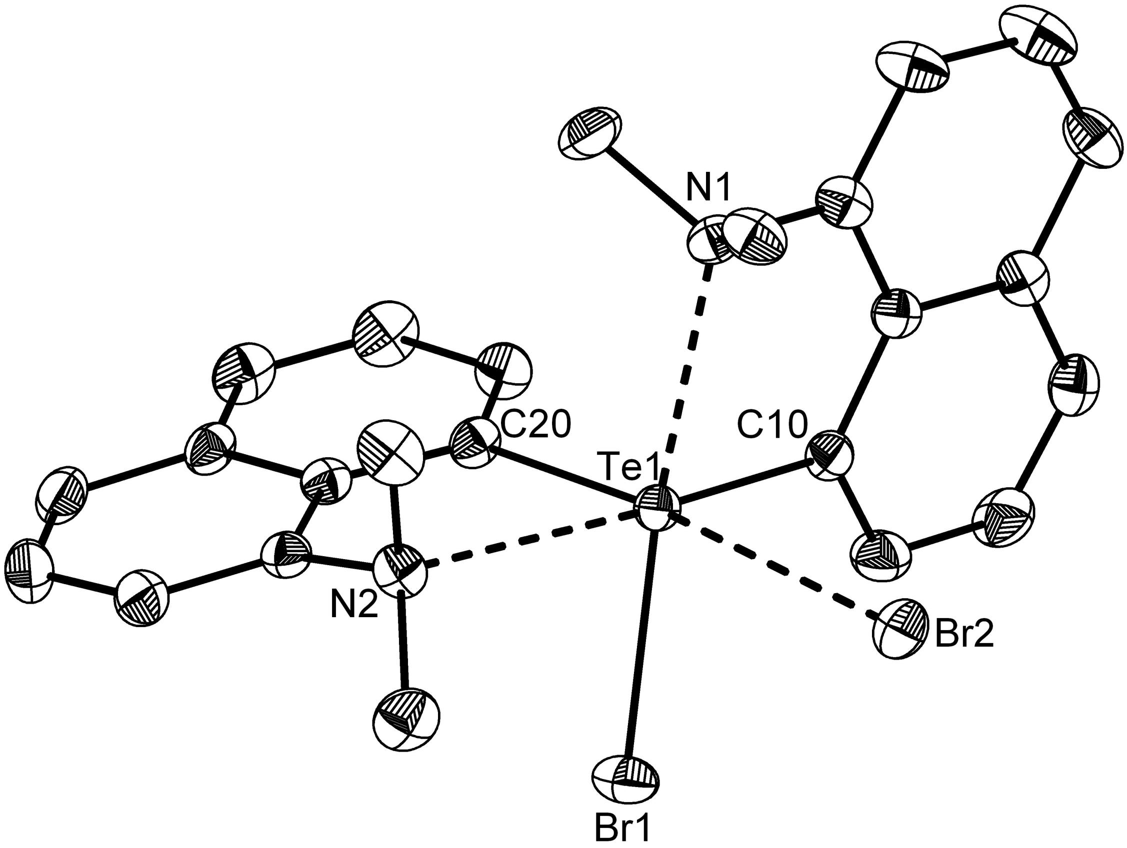


Figure 3. Molecular structure of **2**·Br$^-$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Br1 2.591(2), Te1···N1 2.490(6), Te1···N2 2.722(6), Te1-C10 2.140(6), Te1-C20 2.125(6), Br1-Te1-C10 93.5(2), Br1-Te1-C20 88.8(2), C10-Te1-C20 96.1(2), Ion contact: Te1···Br2 3.411(4).

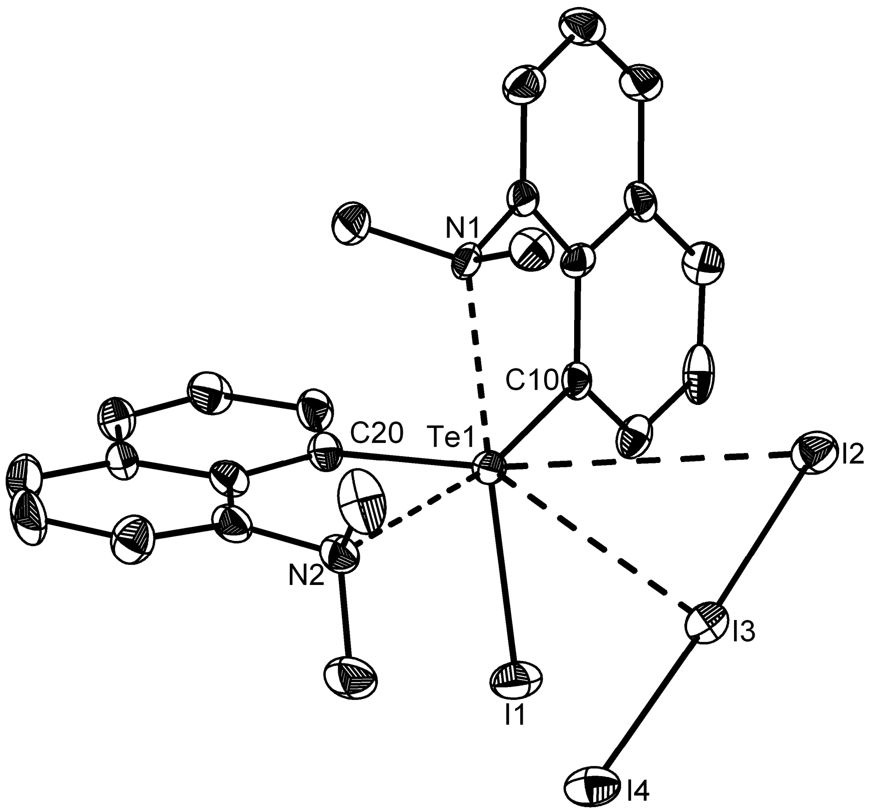


Figure 4. Molecular structure of **3**$\cdot$I$_3^-$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]:

Te1-I1 2.780(2), Te1-C10 2.165(8), Te1-C20 2.136(8), Te1···N1 2.532(7), Te2···N2 2.743(7), I2-I3 2.921(2), I3-I4 2.918(1), I1-Te1-C10 95.2(2), I1-Te1-C20 91.8(3), C10-Te1-C20 96.7(3), Ion contacts: Te1···I2 4.037(2), Te1··I3 4.219(2).

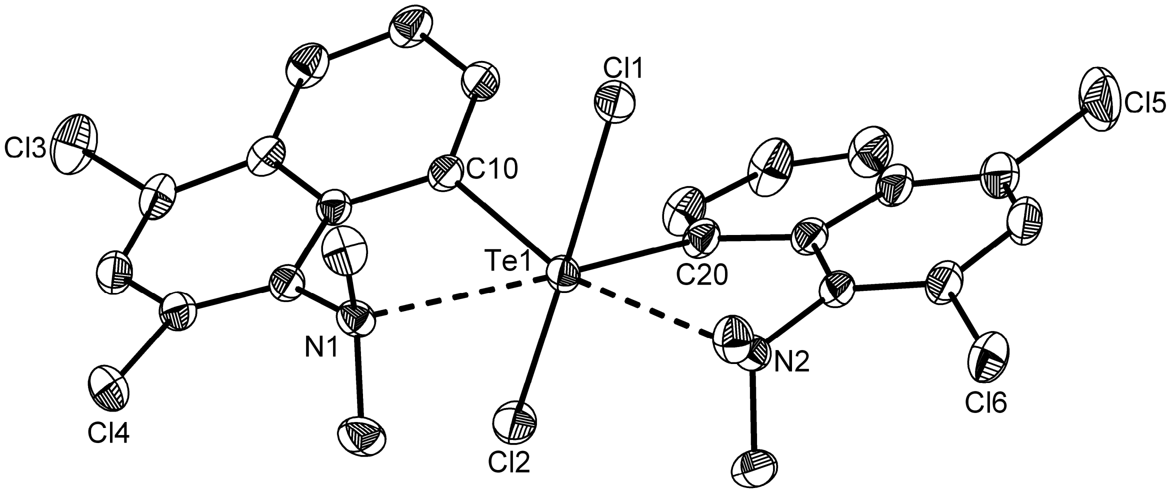


Figure 5. Molecular structure of **4** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Cl1 2.521(1), Te1-Cl2 2.516(1), Te1-C10 2.152(4), Te1-C20 2.154(4), Te1···N1 2.730(3), Te1···N2 2.740(3), Cl1-Te1-Cl2 169.30(4), Cl1-Te1-C10 86.8(1), C1-Te1-C20 86.7(1), Cl2-Te1-C10 86.0(1), Cl2-Te1-C20 86.4(1), C10-Te1-C20 96.9(2).

Caption of Figures

Figure 1. Molecular structure of $\mathbf{1}\cdot Cl^{-}\cdot H_2O\cdot \frac{1}{2}THF$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Cl1 2.444(1), Te1-C10 2.141(3), Te1-C20 2.145(3), Te1···N1 2.445(3), Te1···N2 2.800(3), C10-Te1-C20 92.8(1), Cl1-Te1-C10 92.63(9), Cl1-Te1-C20 90.4(1), Ion contact: Te1···Cl2 3.173(1).

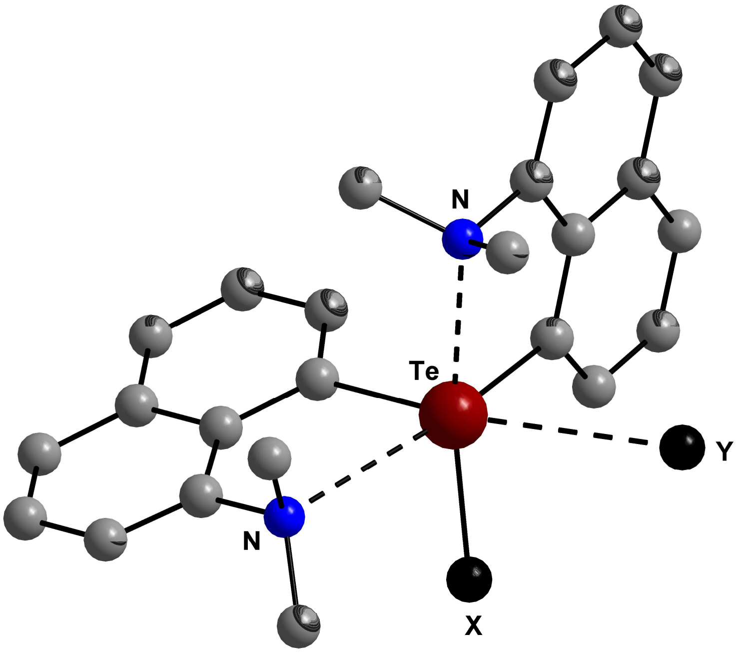
Figure 2. Molecular structure of $\mathbf{1}\cdot PF_6^{-}$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Cl1 2.427(1), Te1-C10 2.134(4), Te1-C20 2.122(4), Te1···N1 2.426(4),Te1···N2 2.701(3), C10-Te1-C20 99.1(1), Cl1-Te1-C10 90.7(1), Cl1-Te1-C20 89.3(1), Ion contact: Te1···F1 3.053(4).

Figure 3. Molecular structure of $\mathbf{2}\cdot Br^{-}$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Br1 2.591(2), Te1···N1 2.490(6), Te1···N2 2.722(6), Te1-C10 2.140(6), Te1-C20 2.125(6), Br1-Te1-C10 93.5(2), Br1-Te1-C20 88.8(2), C10-Te1-C20 96.1(2), Ion contact: Te1···Br2 3.411(4).

Figure 4. Molecular structure of $\mathbf{3}\cdot I_3^{-}$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-I1 2.780(2), Te1-C10 2.165(8), Te1-C20 2.136(8), Te1···N1 2.532(7),Te2···N2 2.743(7), I2-I3 2.921(2), I3-I4 2.918(1), I1-Te1-C10 95.2(2), I1-Te1-C20 91.8(3), C10-Te1-C20 96.7(3), Ion contacts: Te1···I2 4.037(2), Te1···I3 4.219(2).

Figure 5. Molecular structure of **4** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Cl1 2.521(1), Te1-Cl2 2.516(1), Te1-C10 2.152(4), Te1-C20 2.154(4), Te1···N1 2.730(3), Te1···N2 2.740(3), Cl1-Te1-Cl2 169.30(4), Cl1-Te1-C10 86.8(1), C1-Te1-C20 86.7(1), Cl2-Te1-C10 86.0(1), Cl2-Te1-C20 86.4(1), C10-Te1-C20 96.9(2).

For table of contents use only.



The novel diaryltellurium(IV) cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]Y$ (X = Cl, Br, I, OH; Y = Cl, Br, I, I_3, PF_6) are stabilized by intramolecularly coordinating N-donor ligands.

Organometallics – Full Paper

Diarylhalotelluronium(IV) Cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl, Br, I) Stabilized by Intramolecularly Coordinating N-Donor Substituents

Jens Beckmann,[a,b] * Jens Bolsinger,[a] Andrew Duthie,[c] Pamela Finke[a,b]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstr. 34/36, 14195 Berlin, Germany*

[b] *Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Str. 28359 Bremen, Germany.*

[c] *School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia*

Supporting Information

---

* Correspondence to Jens Beckmann: Fax ++49(0)421 218 9863160, E-mail: j.beckmann@uni-bremen.de

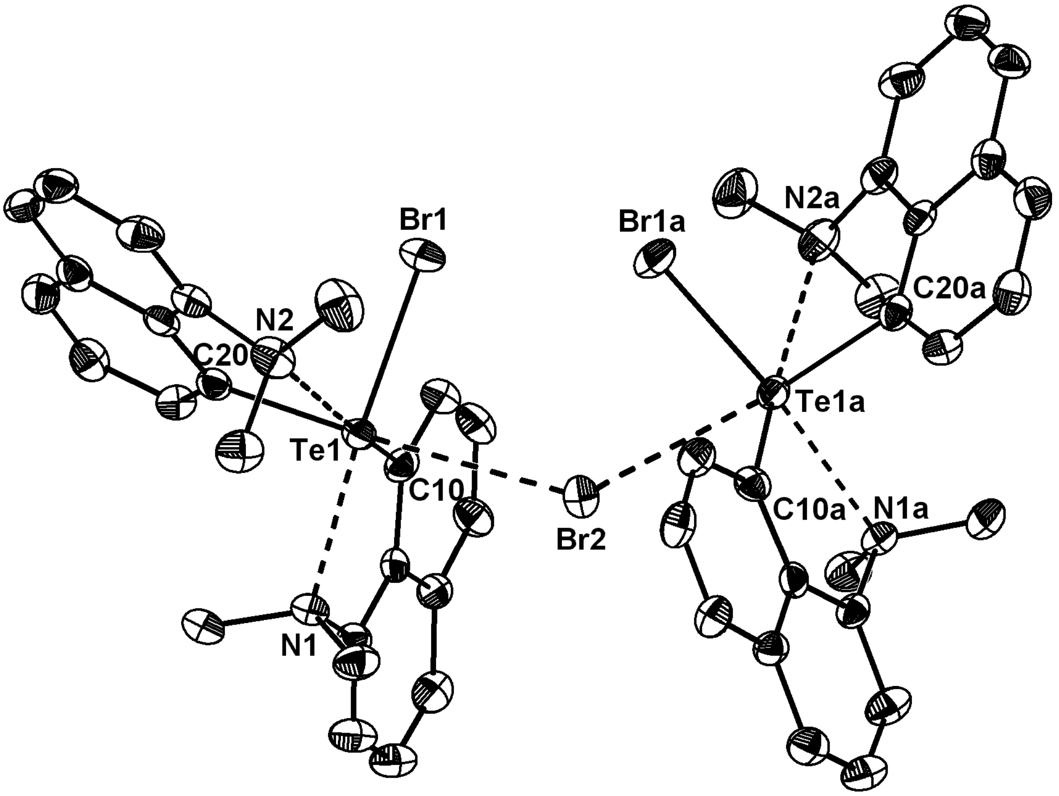


Figure S1. Molecular structure of $\mathbf{2}_2\cdot\mathrm{Br}^-\cdot\mathrm{PF}_6^-$ showing 30% probability ellipsoids and the crystallographic numbering scheme (Symmetry code used to generate equivalent atoms: a = 1 – x, y, 0.5 – z). Selected bond parameters [Å, °]: Te1-Br1 2.582(2), Te1-C10 2.132(7), Te1-C20 2.137(8), Te1···N1 2.502(6), Te1···N2 2.732(8), Br1-Te1-C10 93.2(2), Br1-Te1-C20 89.7(2), C10-Te1-C20 95.5(3), Ion contact: Te1···Br2 3.272(4)

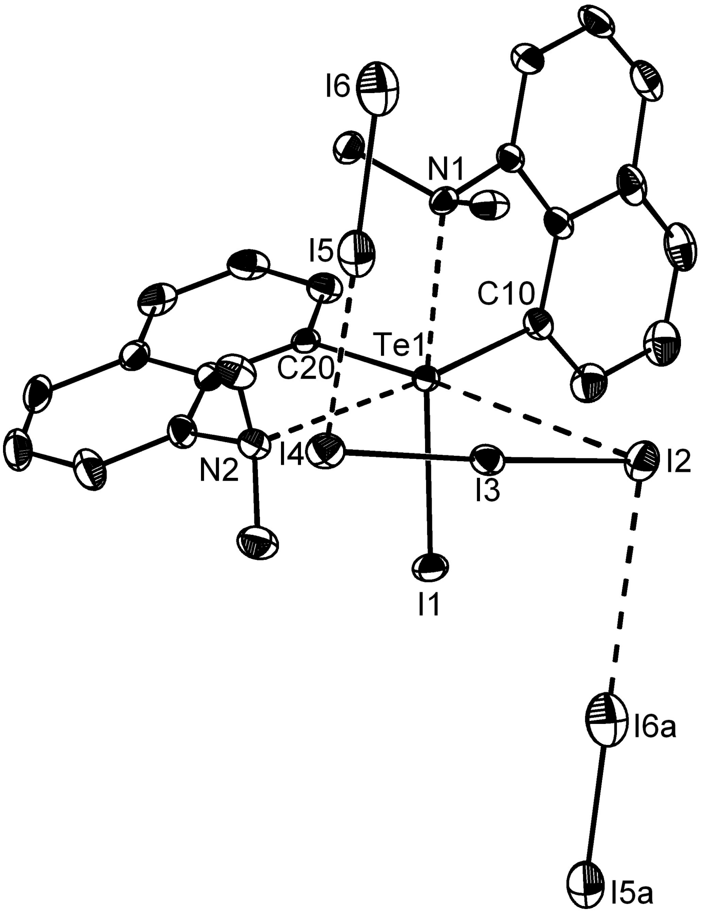


Figure S2. Molecular structure of **3**$\cdot I_3^- \cdot I_2$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-I1 2.7827(8), Te1-C10 2.16(1), Te1-C20 2.138(6), Te1···N1 2.515(7), Te1···N2 2.80(1), I1-Te1-C10 94.9(2), I1-Te1-C20 91.6(2), C10-Te1-C20 96.2(3), Ion contact: Te1···I2 3.8606(8).

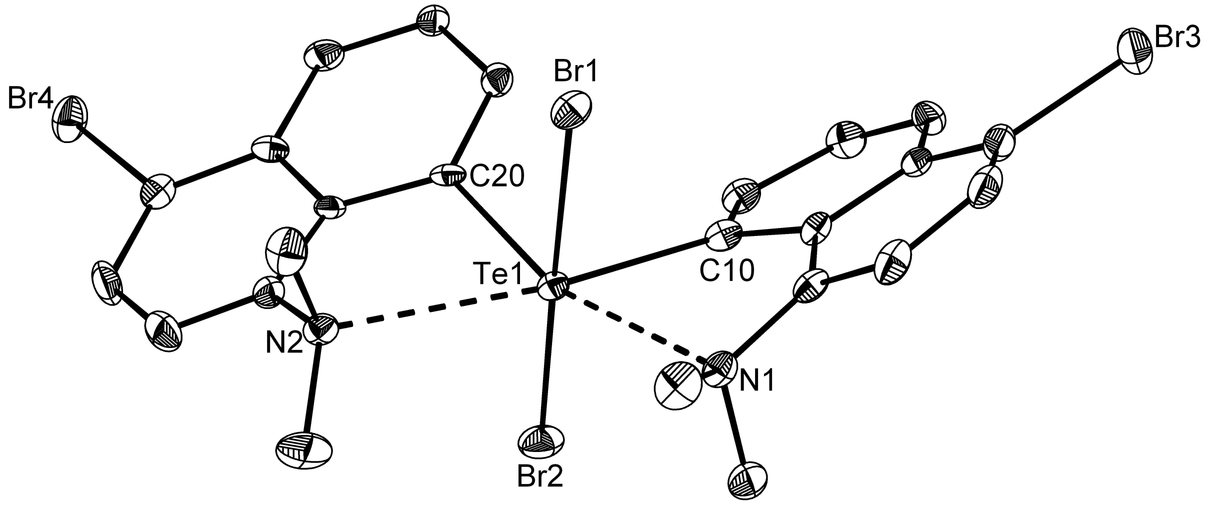


Figure S3. Molecular structure of **5** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, º]: Te1-Br1 2.662(1), Te1-Br2 2.712(2), Te1-C10 2.162(6), Te1-C20 2.170(5), Te1···N1 2.726(5), Te1···N2 2.7477(5), Br1-Te1-Br2 171.48(2), Br1-Te1-C10 86.2(2), Br1-Te1-C20 88.4(1), Br2-Te1-C10 88.9(2), Br2-Te1-C20 85.5(1), C10-Te1-C20 98.9(2).

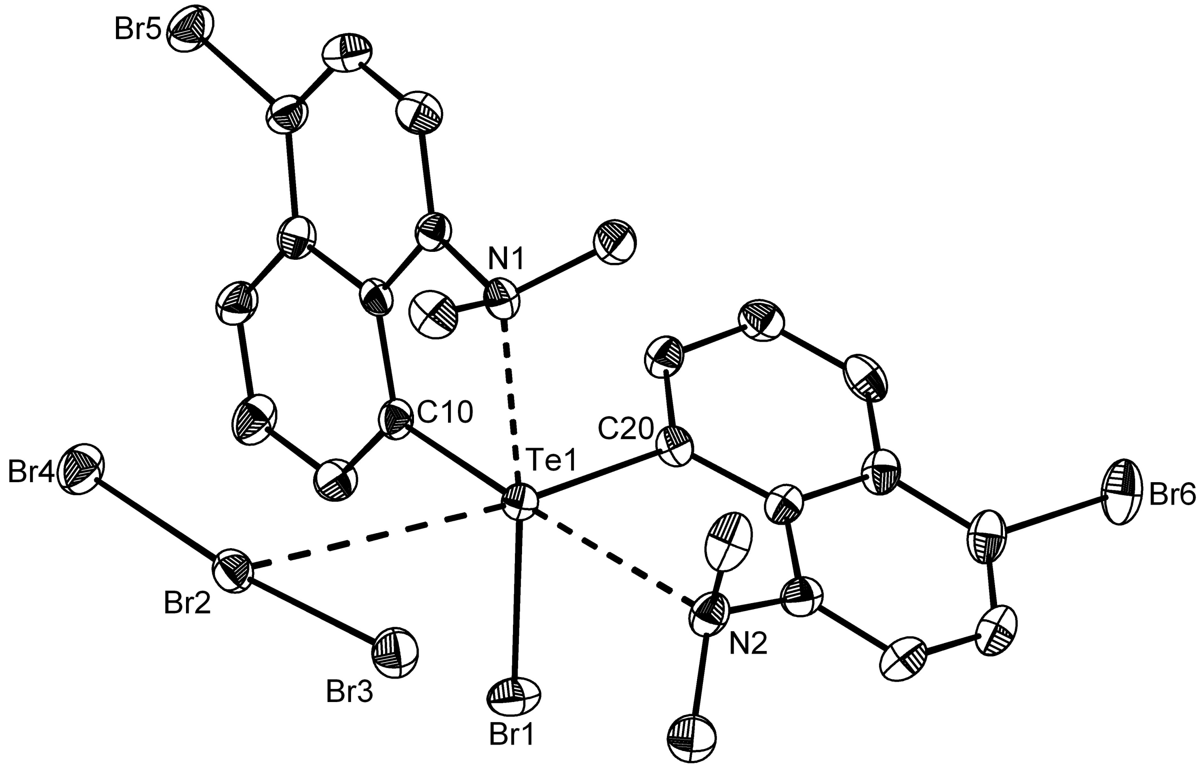


Figure S4. Molecular structure of **6**·Br$_3^-$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-Br1 2.5808(8), Te1-C10 2.135(6), Te1-C20 2.133(5), Te1···N1 2.486(5), Te1···N2 2.735(5), Br1-Te1-C10 93.0(2), Br1-Te1-C20 91.9(2), C10-Te1-C20 97.1(2), Ion contact: Te1···Br2 3.720(1)

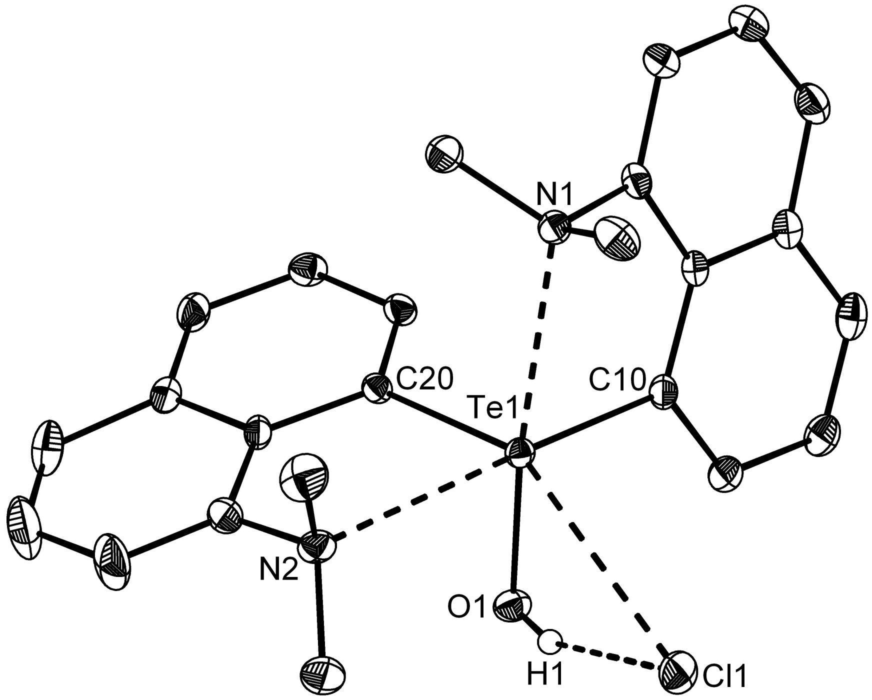


Figure S5. Molecular structure of **7**·Cl$^-$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-O1 1.951(2), Te1-C10 2.134(2), Te1-C20 2.123(2), Te1···N1 2.596(2),Te1···N2 2.682(2), O1-H1 0.70(3), O1···Cl1 2.960(2), Cl1···H1 2.32(3), O1-Te1-C10 91.25(9), O1-Te1-C20 89.00(8), C10-Te1-C20 96.81(9). Ion contact: Te1···Cl1 3.2535(7).

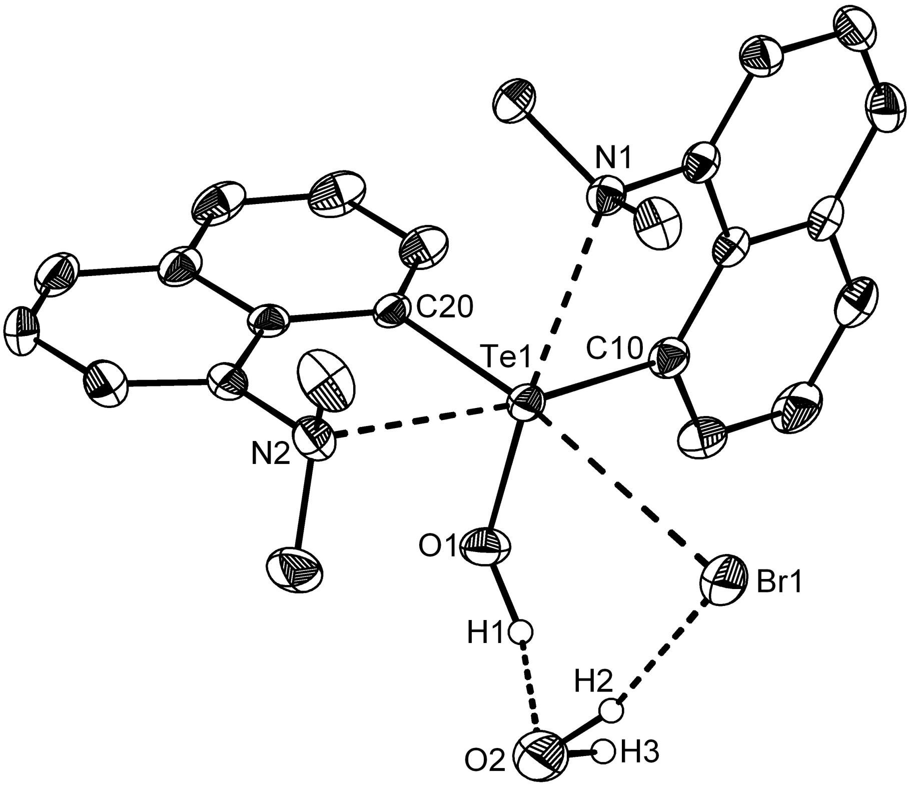


Figure S6. Molecular structure of **7**$\cdot$Br$^-$$\cdot$H$_2O\cdot$THF showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-O1 1.957(3), Te1-C10 2.130(5), Te1-C20 2.127(5), Te1···N1 2.586(3), Te1···N2 2.709(4), O1-H1 1.07(9), O2···H1 1.71(9), O1···O2 2.729(8), O2-H2 1.05(6), O2-H3 1.02(4), Br1···H2 2.20(6), O2···Br1 3.232(5), O1-Te1-C10 92.2(2), O1-Te1-C20 87.6(2), C10-Te1-C20 94.9(2), Ion contact: Te1···Br1 3.4777(9).

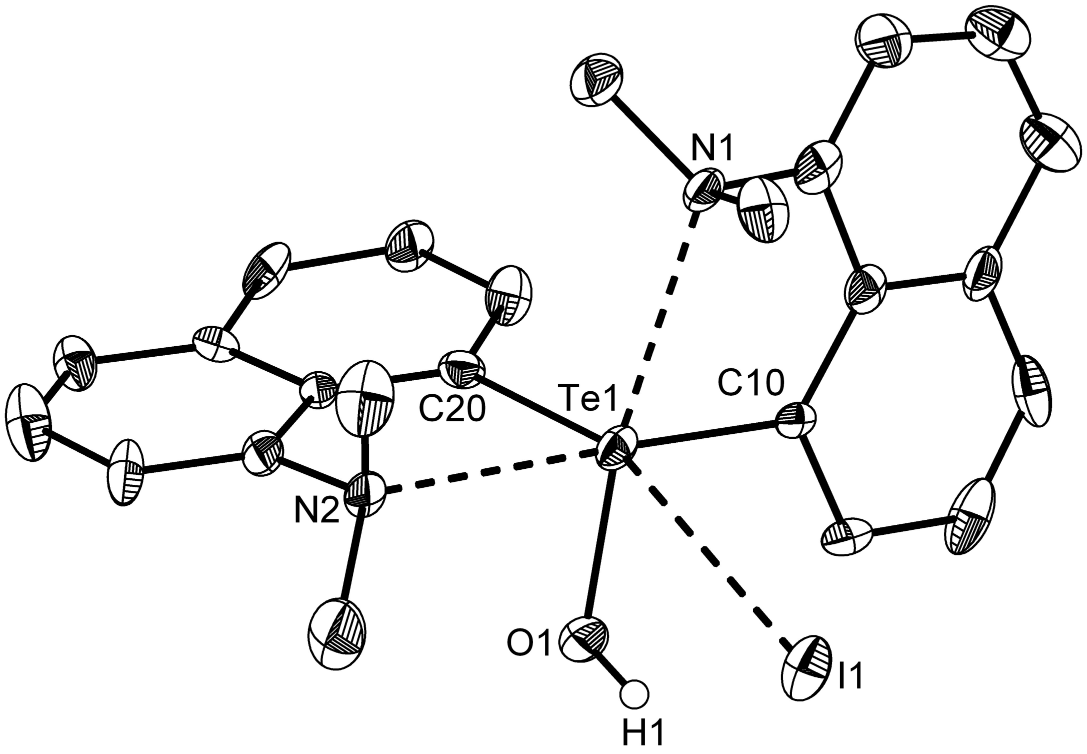


Figure S7. Molecular structure of **7**·I^- showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Conformer 1 (shown): Te1-O1 1.969(9), Te1-C10 2.15(1), Te1-C20 2.13(1), Te1···N1 2.61(1), Te1···N2 2.67(1), O1-Te1-C10 91.9(4), O1-Te1-C20 89.9(4), C10-Te1-C20 97.4(5). Ion contact: Te1···I1 3.595(2). Conformer 2 (not shown): Te2-O2 1.933(9), Te2-C30 2.15(1), Te2-C40 2.14(1), Te2-N3 2.595(9), Te2-N4 2.70(1), O2-Te2-C30 94.3(6), O2-Te2-C40 90.7(4), Ion contact: Te2···I2 3.591(2).

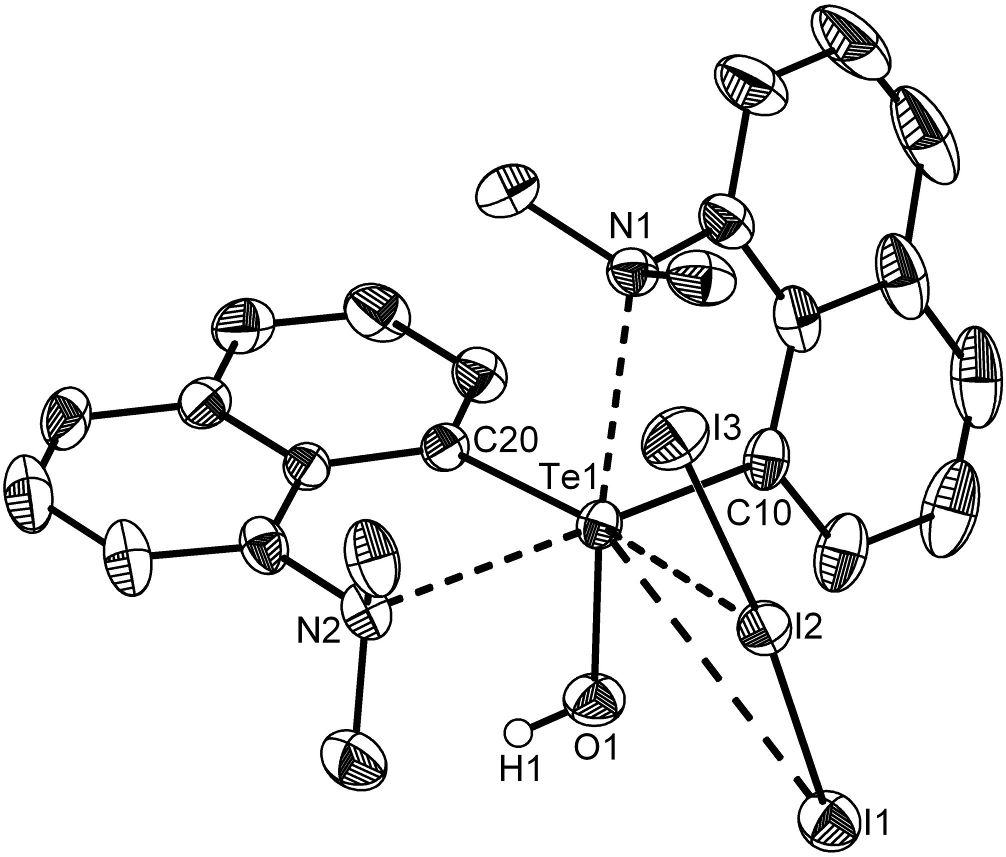


Figure S8. Molecular structure of **7**$\cdot I_3^{-} \cdot H_2O$ showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-O1 1.967(3), Te1-C10 2.118(5), Te1-C20 2.108(4), Te1···N1 2.566(4),Te1···N2 2.656(4), O1-H1 0.821(4), O1-Te1-C10 91.2(2), O1-Te1-C20 90.7(2). Ion contacts: Te1···I1 3.9635(5), Te1···I2 4.0977(5).

7 Reversible Oxygen Transfer From an Intramolecular Coordinated Diaryltellurium(IV) Oxide to Acetonitrile. Synthesis and Structure of a Novel Diaryltellurium(IV) Acetimidate.

7.1 INTRODUCTION

Diaryltellurium(IV) oxides, R_2TeO (e. g. R = Ph, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, Mes), have attracted considerable attention as mild oxidizing agent of alcohols[78], thiocarbonyls[79], arylhydrazines[79[,[80], and transition metal carbonyls[81]. They are used as a catalyst for the aldol condensation[82] and the aerobic oxidation of phosphate esters[83] and silanes[84]. Furthermore, they play an important role in the catalytic activation of hydrogen peroxide[85].

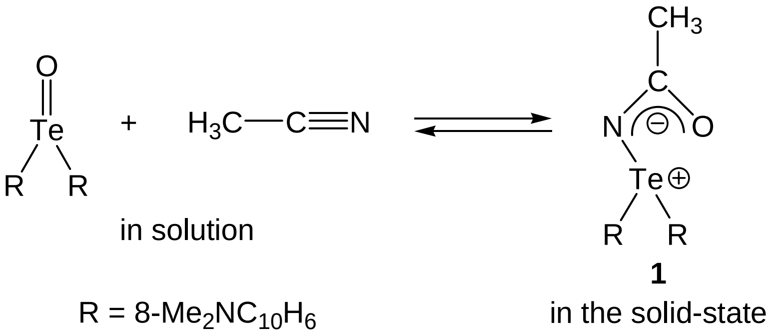
As already discussed diaryltellurium(IV) oxides are usually aggregated in the solid state. For example the Ph_2TeO gives rise to asymmetric dimers, which are further linked by long secondary Te···O interactions[17], however, (4-$MeOC_6H_4)_2TeO$ comprises a polymer structure and lacks any secondary interactions[19].

Since intramolecularly coordinated diaryltellurium(IV) oxides are very rare, the effect of intramolecularly coordinating ligands on the structure and reactivity of organotellurium compounds was studied. The first fully characterized example, namely (2-$Me_2NCH_2C_6H_4)_2TeO$, comprises a monomer structure in the solid state – due to the intramolecular N coordination – and lacks any secondary Te···O bonds[25]. The synthesis of (8-$Me_2NC_{10}H_6)_2TeO$ and its protonation with triflic acid to form the diarylhydroxytelluronium triflate [(8-$Me_2NC_{10}H_6)_2TeOH](O_3SCF_3)$ was discussed in detail further above[73].

However, in absence of the triflic acid an unusual reaction of (8-$Me_2NC_{10}H_6)_2TeO$ with acetonitrile takes place. The reaction proceeds with reversible oxygen transfer providing the diaryltellurium(IV) acetimidate (8-$Me_2NC_{10}H_8)_2TeNC(O)CH_3$ in the solid state. While the catalyzed hydrolysis of acetonitrile to acetamide in the coordination sphere of transitions metals, such as platinum and rhodium[86], is well documented such a facile formation of the acetimidate moiety is unprecedented.

7.2 DISCUSSION

The reaction of the freshly prepared diaryltellurium(IV) oxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO$[73], with acetonitrile proceeds with reversible oxygen transfer to give rise to the formation of the diaryltellurium(IV) acetimidate, $(8\text{-}Me_2NC_{10}H_8)_2TeNC(O)CH_3$ (**1**), which was obtained as colorless very fine needles in 57% yield (Scheme 9).



(1)

Scheme 9: Solution and solid state of the diaryltellurium(IV) acetimidate

The acetimidate **1** is sparingly soluble in reasonably polar solvents, such as $CHCl_3$ and THF. Surprisingly, all spectroscopic data of **1** measured in solution were identical with those of the starting materials, which originally lead to the conclusion that an acetonitrile solvate was isolated.

The ^{1}H-NMR spectrum ($CDCl_3$) of **1** closely resembles the spectra of the two starting materials and the ^{125}Te NMR spectrum ($CDCl_3$) shows a broad signal at $\delta=1282$, which is reminiscent of the value reported for $(8\text{-}Me_2NC_{10}H_6)_2TeO$ ($\delta = 1272$)[73].

The ^{125}Te CP MAS NMR reveals a substantially different signal at $\delta_{iso} = 1027$. The huge chemical shift of 245 ppm is a strong indication that the solution and solid-state structures are entirely different. This could be confirmed by X-ray crystallography.

Since the dimensions of the fine needles were too small (largest dimension: 60 µm) for conventional diffractometers, the data set was obtained from the APS synchrotron facility (Argonne, USA; beamline 1S-ID-B). The large primary intensity allowed the collection of about 90000 reflections in an exposure time less than 30 min.

The molecular structure of **1** is shown in Figure 1 and the crystal data and structure refinement in Table 1. Selected bond parameters are collected in the caption of the Figure 1. The primary and secondary coordination sphere of the Te atom is defined by a C_2N+N_2O donor set. The Te-C bonds lengths of **1** (2.133(2) and 2.152(1) Å) are only marginally longer than those of $(8\text{-}Me_2NC_{10}H_6)_2Te$ (2.173(3) and 2.155(2) Å)[73]. The Te-N bond length of **1** (2.006(1) Å) associated with the coordination of the acetimidate moiety resembles those of other Te-N compounds.

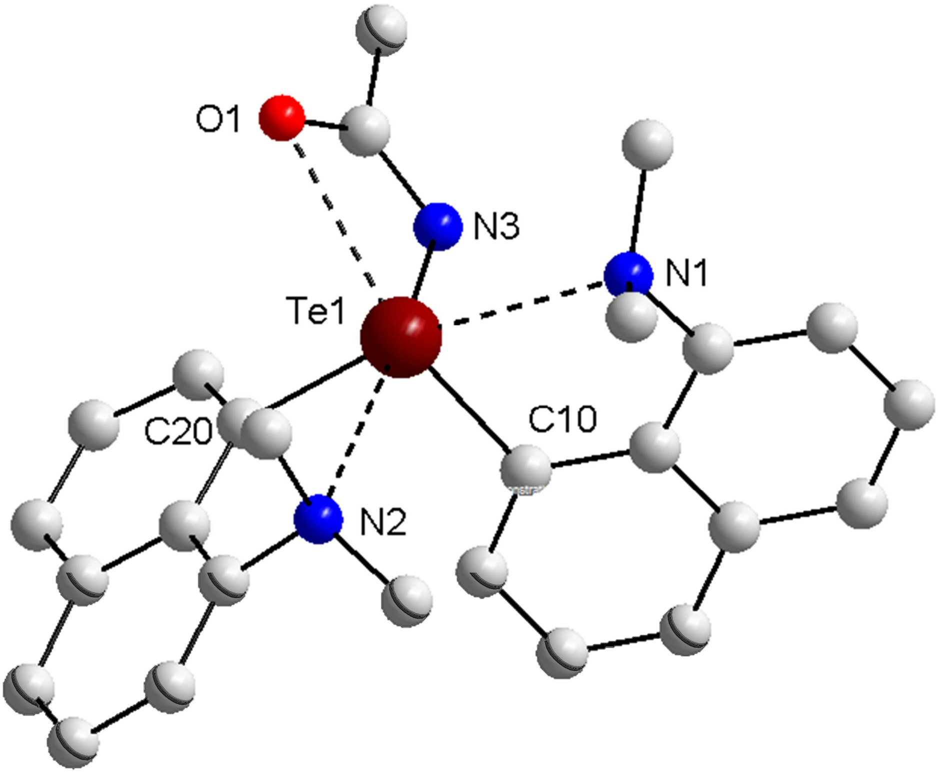


Figure 1: Molecular structure of $(8\text{-}Me_2NC_{10}H_8)_2TeNC(O)CH_3$. Selected bond parameters [Å, º]: Te1-N3 2.006(1), Te1-C10 2.133(2), Te1-C20 2.152(1), Te1···N1 2.704(2), Te1···N2 2.767(1), Te1-O1 2.785(2), C10-Te1-C20 94.43(4), N3-Te1-C10 90.65(4), N3-Te1-C20 96.63(3).

The Te···N distances of **1** (2.704(2), 2.767(1) Å) related to the N-donor substituents are similar to the average values of the diaryltelluride $(8\text{-}Me_2NC_{10}H_6)_2Te$ (2.699(4) and 2.827(4) Å)[73].

However, the shortest Te···N distances of **1** (2.704(2)) is significantly longer than the shortest Te···N distances of the protonated diaryltellurium oxide $[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$ (2.591(5))[73] or the previously describe, respective diaryltellurium halides $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X=Cl, Br, I) - varying between 2.426(4) and 2.532(7) Å -, which all comprise a strong attractive interaction to the Te atom. This points to a weak interaction of the intramolecularly coordinating 8-dimethylaminonaphthyl substituents with the tellurium atom in solid state.

The Te···O distance of **1** (2.785(2) Å) is also significantly shorter than the sum of van der Waals radii (ca. 3.5 Å). Considering the primary and the secondary coordination sphere the spatial arrangement can be also said to be distorted octahedral.

According to a literature search, there is only one other compound containing an acetimidate moiety, namely bis(trimethylstannyl)acetimidate $MeC(O)N(SnMe_3)_2$[87], which was obtained by the double lithiation of acetamide using *n*-butyllithium prior to reaction with two equivalents with trimethyltin chloride. It is worth mentioning that the free and hitherto unknown acetimidate ion is isoelectronic to the acetate ion.

The question why the compound **1** will react reversibly with acetonitrile remains unclear. The reversible reaction could be tentatively explained by a kinetic lability due to the entropic effect and a small energy difference between the respective compounds. However, calculations concerning the energies of the respective educt and the product as well as calculations concerning the electron density (AIM and ELI-D) are conducted by our work group, in order to shed some light on this unexpected reaction.

7.3 EXPERIMANTAL SECTION

The diaryltellurium(IV) oxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO$,[73] was prepared according to literature procedures. The ^1H, ^{13}C and ^{125}Te NMR spectra were recorded using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^1H, ^{13}C) and Me_2Te (^{125}Te). The ^{125}Te CP MAS NMR spectra were obtained using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 8 and 10 kHz. A 30 s recycle delay was used and typically 5000 to 10000 transitions were accumulated to obtain adequate signal-to-noise ratios. The isotropic chemical shifts δ_{iso} were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced using solid $Te(OH)_6$ as the secondary reference (δ_{iso} 692.2 / 685.5 ppm). The structural data set was obtained from the APS synchrotron facility (Argonne, USA; beamline 1S-ID-B). Microanalyses were obtained from a Vario EL elemental analyzer. The reaction was carried out under the exclusion of air in dry solvents.

Synthesis of $(8\text{-}Me_2NC_{10}H_8)_2TeNC(O)CH_3$:

To a suspension of diaryltellurium(VI) dioxide, $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$ (250 mg, 0.5 mmol) in Acetonitrile (100 mL), solid diaryltelluride(II), $(8\text{-}Me_2NC_{10}H_6)_2Te$ (233 mg, 0.5 mmol) was added and refluxed for five hours. Undissolved solid was separated through hot filtration. The now clear orange brown solution was reduced in vacuum to 50 mL. After one day brown needles precipitated and were collected through filtration (302 mg, 0.57 mmol, 57 %; Mp. 198-206 (dec.)℃).

^1H-NMR ($CDCl_3$) δ = 7.94 (s, br. 1H) 7.78 (s, br. 2H), 7.55- 7.50 (m, 3H) (Ar), 2.83 (s, br. 6H, Ar-NCH_3), 2.25 (s, br. 3H, $NCCH_3$). ^{125}Te-NMR ($CDCl_3$): δ = 1281.96 (very broad). ^{125}Te CP MAS NMR: δ_{iso} = 1026.9. Anal. Calcd. for $C_{26}H_{27}N_3OTe$ (525.11): C 59.47, H 5.18, N 8.00 Found: C 58,92; H 5.04, N 7.79.

Table 1: Crystal data and structure refinement of $(8\text{-}Me_2NC_{10}H_8)_2TeNC(O)CH_3$

	1	
Formula	$C_{26}H_{27}N_3OTe$	
Formula weight, g mol^{-1}	525.11	
Crystal system, space group	Orthorhombic, P b c a	
Crystal size, mm	0.06 x 0.03 x 0.03 mm	
Unit cell dimensions	a =12.601(3) Å	α =90 deg.
	b =16.923(3) Å	β =90 deg.
	c =20.807(4) Å	γ = 90 deg.
	V = 4437.0(15) Å^3	
	Z = 8	
$\rho_{calcd.}$, Mg m^{-3}	1.572	
μ (Mo $K\alpha$), mm^{-1}	0.322	
$F(000)$	2112	
θ range, deg	1.30 to 30.28	
Index ranges	$-16 \leq h \leq 30$	
	$-33 \leq k \leq 41$	
	$-31 \leq l \leq 48$	
No. of reflns collected	114915	
Completeness to θ_{max}	99.3%	
No. indep. Reflns	30425	
No. refined params	492	
GooF (F^2)	1.092	
R_1 (F) ($I > 2\sigma(I)$)	0.034	
wR_2 (F^2) (all data)	0.072	
Largest diff peak/hole, e Å^{-3}	1.918 / –1.648	

MANUSCRIPT V

8 Reactivity of (p-$MeOC_6H_4$)$_2$TeO toward t-$Bu_2Si(OH)_2$. Synthesis of a 12-Membered Tellurasiloxane Ring, *cyclo*-[(p-$MeOC_6H_4$)$_2$TeOSit-Bu_2O]$_3$

Jens Beckmann and Jens Bolsinger; *Organometallics* **2007**, *26*, 3601–3603

8.1 SYNOPSIS

The aim of this project was to examine the reactivity of diorganotellurium oxides toward organosilanoles.

The condensation reaction of t-Bu$_2$Si(OH)$_2$[88] with 1.2 equivalents of (p-MeOC$_6$H$_4$)$_2$TeO provided a rare 12-membered tellurasiloxane ring *cyclo*-[(p-MeOC$_6$H$_4$)$_2$TeOSit-Bu$_2$O]$_3$. To the best of our knowledge, there is only one other 12-membered metallasiloxane ring derived from t-Bu$_2$Si(OH)$_2$, namely, *cyclo*-[(O)(Cl)VOSit-Bu$_2$O]$_3$[89], whereby six- and eight-membered ring systems are more common[90]

The conformation of the inorganic 12-membered Te$_3$Si$_3$O$_6$ ring deviates from planarity. It has to be noted that the axial O coordination could be considered as rather symmetric, the Te-O bond lengths differ only marginally and no secondary Te···O intermolecular contacts could be observed. Thus, the coordination sphere of this 12-membered ring is comparable with the educt (p-MeOC$_6$H$_4$)$_2$TeO, but differs substantially from the structures of related tetraorganoditelluroxanes[20]-[22],[64] and tellurastannoxanes[48],[49],[91], which reveal a rather asymmetric axial O coordination and a number of secondary Te···O intra- and intermolecular contacts.

Furthermore, the exchange of the organosilandiole Ph$_2$Si(OH)$_2$ yielded under comparable conditions not tellurasiloxanes, but only condensation products of the silanol compound that give a mixture of the known siloxane rings *cyclo*-(Ph$_2$SiO)$_3$ and *cyclo*-(Ph$_2$SiO)$_4$, which could be identified by their ^{29}Si NMR chemical shifts[92].

8.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann.

X-Ray Crystallography: Prof. Dr. Jens Beckmann

Reactivity of (p-MeOC$_6$H$_4$)$_2$TeO toward t-Bu$_2$Si(OH)$_2$. Synthesis of a 12-Membered Tellurasiloxane Ring, *cyclo*-[(p-MeOC$_6$H$_4$)$_2$TeOSit-Bu$_2$O]$_3$

Jens Beckmann* and Jens Bolsinger[†]

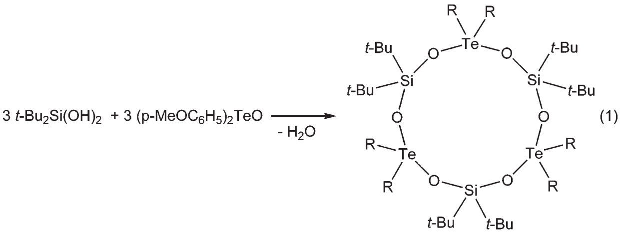
Institut für Chemie und Biochemie, Freie Universität Berlin, Germany

Received January 29, 2007

*Summary: Condensation of t-Bu$_2$Si(OH)$_2$ with (p-MeOC$_6$H$_4$)$_2$TeO in a Si/Te ratio of 1:1.2 exclusively produced the 12-membered tellurasiloxane ring cyclo-[(p-MeOC$_6$H$_4$)$_2$TeOSit-Bu$_2$O]$_3$ (**1**), whose molecular structure was determined by X-ray crystallography. At larger Si/Te ratios, the open-chain tellurasiloxanes HOt-Bu$_2$SiOR$_2$TeOSit-Bu$_2$OH (**2**, R = p-MeOC$_6$H$_4$) and HOt-Bu$_2$SiOR$_2$TeOSit-Bu$_2$OR$_2$TeOSit-Bu$_2$OH (**3**, R = p-MeOC$_6$H$_4$) were identified in solution by ^{29}Si and ^{125}Te NMR spectroscopy along with **1** and unreacted t-Bu$_2$Si(OH)$_2$. The analogous reaction of Ph$_2$Si(OH)$_2$ with (p-MeOC$_6$H$_4$)$_2$TeO did not provide tellurasiloxanes, but led to the formation of the known siloxanes rings cyclo-(Ph$_2$SiO)$_3$ and cyclo-(Ph$_2$SiO)$_4$.*

Although the first diorganotellurium oxides R$_2$TeO (R = alkyl, aryl) were prepared more than 90 years ago,[1] only recently has attention been paid to their structure and reactivity. While diorganotellurium oxides, such as R$_2$TeO, having polar Te−O double bonds (R = Ph, C$_6$F$_5$, p-MeC$_6$H$_4$, p-MeOC$_6$H$_4$), are monomers in chloroform,[2] the structures in the solid state are more diverse. For instance, Ph$_2$TeO[3] and (C$_6$F$_5$)$_2$TeO[4] are asymmetric dimers with elongated Te−O double bonds and secondary Te···O intermolecular contacts, whereas (p-MeOC$_6$H$_4$)$_2$TeO forms a 1D polymer with symmetric Te−O single bonds.[2] Diorganotellurium oxides have found applications as "oxygen" transfer reagents in organic[5] and organometallic synthesis.[6] Diorganotellurium oxides are Lewis bases and undergo condensation reactions to give tetraorganoditelluroxanes with proton acids, such as carboxylic acids,[7] HNO$_3$,[8] HO$_3$SCF$_3$, and HO$_2$PPh$_2$[9] Diorganotellurium oxides show potential for the preparation of tellurastannoxanes and related species featuring Te−O−Sn bonds, as well as for the fixation of carbon dioxide.[10]

Metallasiloxanes, compounds containing M−O−Si linkages (M includes metals as well as nonmetals), have attracted considerable attention in recent years owing to applications in material science and catalysis.[11] Although studies on metallasiloxanes have been extensive for most elements of the periodic table, there are very few reports on tellurasiloxanes.[12] As part of our interest in the chemistry of telluroxanes we have now investigated the reactivity of diorganotellurium oxides toward organosilanols. The condensation reaction of t-Bu$_2$Si(OH)$_2$ with 1.2 equiv of (p-MeOC$_6$H$_4$)$_2$TeO provided the 12-membered tellurasiloxane ring *cyclo*-[(p-MeOC$_6$H$_4$)$_2$TeOSit-Bu$_2$O]$_3$ (**1**) as colorless crystalline material in quantitative yield (eq 1).



1

R = p-MeOC$_6$H$_5$

The molecular structure of **1** has been established by X-ray crystallography and is shown in Figure 1. Selected bond parameters are collected in the caption of the figure. The geometry of the Te atoms of **1** can be described as distorted trigonal bipyramidal when taking into account the stereochemically active lone pair of Te.[2] The axial O coordination is rather symmetric, as the Te−O bond lengths (2.051(3)−2.064(3) Å) differ only marginally. No secondary Te···O intermolecular contacts are observed. Therefore, the coordination sphere of **1** resembles that of the parent (p-MeOC$_6$H$_5$)$_2$TeO, but differs substantially from those of related tetraorganoditelluroxanes[7−9] and tellurastannoxanes,[10] whose structures reveal a rather

---

* To whom correspondence should be addressed. E-mail: beckmann@chemie.fu-berlin.de. Fax: ++49-30838-52440.

[†] This work contains part of the intended Ph.D. Thesis of Jens Bolsinger.

(1) (a) Lederer, K. *Ann. Chem.* **1912**, *391*, 326. (b) Lederer, K. *Chem. Ber.* **1916**, *49*, 1076. For a review see: (c) Irgolic, K. I. *The Organic Chemistry of Tellurium*; Gordon and Breach: New York, 1974.

(2) Beckmann, J.; Dakternieks, D.; Duthie, A.; Ribot, F.; Schürmann M.; Lewcenko, N. A. *Organometallics* **2003**, *22*, 3257.

(3) Alcock, N. W.; Harrison, W. D. *J. Chem. Soc., Dalton Trans.* **1982**, 709.

(4) (a) Naumann, D.; Tyrra, W.; Hermann, R.; Pantenburg, I.; Wickleder, M. S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 833. (b) Klapötke, T. M.; Krumm, B.; Mayer P.; Piotrowski, H.; Ruscitti, O. P. *Z. Naturforsch.* **2002**, *B57*, 145.

(5) (a) Barton, D. H. R.; Ley, S. V.; Meerholz, C. A. *J. Chem. Soc., Chem. Commun.* **1979**, 755. (b) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron Lett.* **1980**, *21*, 1785. (c) Engman, L.; Cava, M. P. *Tetrahedron Lett.* **1981**, *22*, 5251. (d) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron, Suppl.* **1981**, 213.

(6) (a) Shen, J. K.; Gao, Y.; Shi, Q.; Rheingold, A. L.; Basolo, F. *Inorg. Chem.* **1991**, *30*, 1868. (b) Xue, M.; Gao, Y. C.; Shen, J. K.; Shi, Q. Z.; Basolo, F. *Inorg. Chim. Acta* **1993**, *207*, 207. (c) Liu, X.; Gao, Y. C.; Su, Z. X.; Wang, Y. Y.; Shi, Q. Z. *Trans. Met. Chem.* **1999**, *24*, 666. (d) Song, L. C.; Li, Q. S.; Hu, Q. M.; Dong, Y. B. *J. Organomet. Chem.* **2001**, *619*, 194.

(7) (a) Kobayashi, K.; Izawa, H.; Yamaguchi, K.; Horn, E.; Furukawa, N. *Chem. Commun.* **2001**, 1428. (b) Alcock, N. W.; Culver, J.; Roe, S. M. *J. Chem. Soc., Dalton Trans.* **1992**, 1477.

(8) Alcock, N. W.; Harrison, W. D. *J. Chem. Soc., Dalton Trans.* **1982**, 1421.

(9) Beckmann, J.; Dakternieks, D.; Duthie, A.; Lewcenko, N. A.; Mitchell, C.; Schürmann, M. *Z. Anorg. Allg. Chem.* **2005**, *631*, 1856.

(10) (a) Beckmann, J.; Dakternieks, D.; Duthie, A.; Lewcenko, N. A.; Mitchell, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6683. (b) Beckmann, J.; Dakternieks, D.; Duthie, A.; Mitchell, C. *Dalton Trans.* **2005**, 1563.

(11) (a) Schmidbaur, H. *Angew. Chem.* **1965**, *77*, 206. (b) Schindler, F.; Schmidbaur H. *Angew. Chem.* **1967**, *79*, 697. (c) Voronkov, M.G.; Lavrent'yev, V. I. *Top. Curr. Chem.* **1982**, *102*, 199. (d) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Rev.* **1996**, *96*, 2205.

(12) (a) Roesky, H. W.; Mazzah, A.; Hesse, D.; Noltemeyer, M. *Chem. Ber.* **1991**, *124*, 519. (b) Driess, M.; Von Hänisch, C.; Merz, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 493.

10.1021/om070084l CCC: $37.00

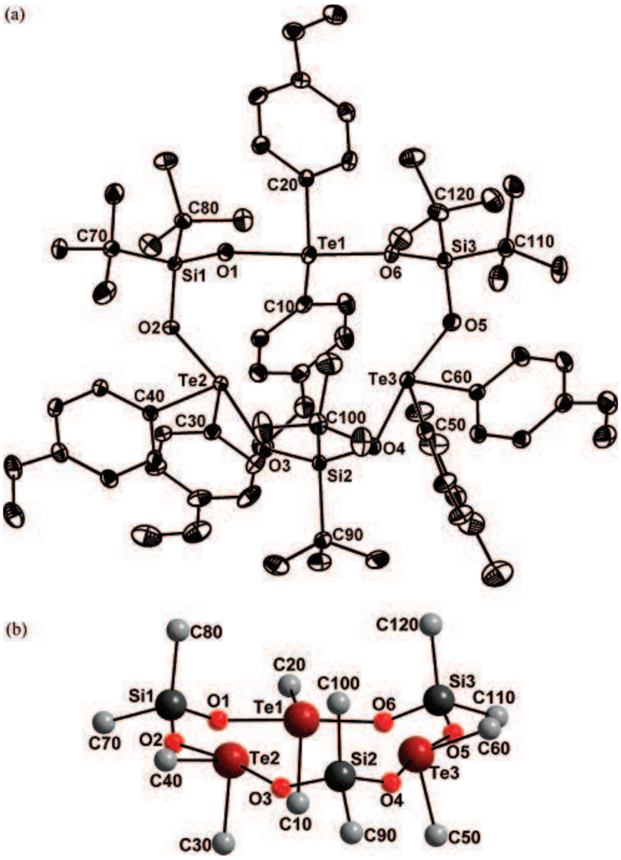


Figure 1. (a) Molecule of (*p*-MeOC$_6$H$_4$)$_2$TeOSi*t*-Bu$_2$O)$_3$ (**1**) showing 30% probability displacement ellipsoids and the atom numbering. Selected bond parameters [Å, deg]: Si−O 1.617(4)−1.630(2), Te−O 2.051(3)−2.064(3), Si−O−Te 134.80(12)−141.70-(13). (b) Ring conformation of **1** (only α-carbon atoms are shown for clarity) with the large deviation from the ideal Te$_3$Si$_3$O$_6$ plane being 0.46 Å for Si1. Selected torsion angles [deg]: Te1−O1−Si1−O2−64.35(24), O1−Si1−O2−Te2 57.77(22), Si1−O2−Te2−O3−159.67(51), O2−Te2−O3−Si2 170.02(50), Te2−O3−Si2−O4−60.71(24), O3−Si2−O4−Te3 53.82(25), Si2−O4−Te3−O5 177.20(45), O4−Te3−O5−Si3 174.29(45), Te3−O5−Si3−O6−54.56(24), O5−Si3−O6−Te1 69.63(21), Si3−O6−Te1−O1 166.05-(56), O6−Te1−O1−Si1−173.95(54).

asymmetric axial O coordination and a number of secondary Te•••O intra- and intermolecular contacts. The conformation of the inorganic 12-membered Te$_3$Si$_3$O$_6$ ring deviates from planarity, with the largest deviation of 0.46 Å being observed for Si1. Related torsion angles are collected in the caption of Figure 1. It is worth noting that the formation of 12-membered metallasiloxane rings is rare, while six- and eight-membered ring systems are more common.[11] We are aware of only one other 12-membered metallasiloxane ring derived from *t*-Bu$_2$Si(OH)$_2$, namely, *cyclo*-[(O)(Cl)VOSi*t*-Bu$_2$O]$_3$.[13] In CDCl$_3$ solution, the tellurasiloxane ring *cyclo*-[(*p*-MeOC$_6$H$_4$)$_2$TeOSi*t*-Bu$_2$O]$_3$ (**1**) is characterized by ^{29}Si and ^{125}Te NMR chemical shifts of δ −20.2 and 921.5, respectively.

In an effort to obtain insight into the formation of **1**, the reaction between *t*-Bu$_2$Si(OH)$_2$ and (*p*-MeOC$_6$H$_4$)$_2$TeO was monitored by ^{29}Si and ^{125}Te NMR spectroscopy. While the reaction was quantitative at a Si/Te ratio of 1:1.2, increasing amounts of *t*-Bu$_2$Si(OH)$_2$ give varying mixtures of *cyclo*-[(*p*-MeOC$_6$H$_4$)$_2$TeOSi*t*-Bu$_2$O]$_3$ (**1**) and the open-chain tellurasiloxanes HO*t*-Bu$_2$SiOR$_2$TeOSi*t*-Bu$_2$OH (**2**, δ(^{29}Si) −13.5, δ(^{125}Te) 957.2, R = *p*-MeOC$_6$H$_4$) and HO*t*-Bu$_2$SiOR$_2$TeOSi*t*-Bu$_2$OR$_2$-TeOSi*t*-Bu$_2$OH (**3**, δ(^{29}Si) −13.6, −18.4 (2:1), δ(^{125}Te) 940.0 R = *p*-MeOC$_6$H$_4$). At Si/Te ratios of 2:1 and 4:1, the molar distribution of **1**, **2**, **3**, and unreacted *t*-Bu$_2$Si(OH)$_2$ (δ(^{29}Si) −6.5) was 5, 66, 18, and 11% and 8, 47, 26, and 19%, respectively. The assignment of the NMR signals is based on the relative integral intensities at the varying Si/Te ratios and the fact that bridging TeO−Si−OTe units (δ(^{29}Si) −18.4, −20.2) and terminal TeO−Si−OH units (δ(^{29}Si) −13.5, −13.6) can be clearly distinguished. At a Si/Te ratio of 2:1, the ESI-MS spectrum (positive mode, cone voltage 30 V) of a diluted solution in MeCN (1:100) reveals four mass clusters with relative intensities greater than 10% based on the highest peak that were unambiguously assigned to the cations [R$_2$TeOH]$^+$ (361.01), [*t*-Bu$_2$SiOTeR$_2$OH]$^+$ (519.12), [R$_2$TeOR$_2$TeOH]$^+$ (717.01), and [*t*-Bu$_2$SiOR$_2$TeOR$_2$TeOH]$^+$ (875.12), respectively (R = *p*-MeOC$_6$H$_4$). While two of these cations confirm the presence of Si−O−Te linkages, no quantitative information can be obtained about neutral species in solution. Attempts to isolate **2** and **3** by fractional crystallization and column chromatography failed. The equimolar reaction of Ph$_2$Si(OH)$_2$ with (*p*-MeOC$_6$H$_4$)$_2$-TeO under similar conditions did not afford tellurasiloxanes, but proceeds with condensation of the silanol groups to give a mixture (ratio 46:54%) of the known siloxane rings *cyclo*-(Ph$_2$SiO)$_3$ (δ(^{29}Si) −33.4) and *cyclo*-(Ph$_2$SiO)$_4$ (δ(^{29}Si) −42.3), which have been unambiguously identified by their ^{29}Si NMR chemical shifts.[14]

Experimental Section

Synthesis of [(*p*-MeOC$_6$H$_4$)$_2$TeOSi*t*-Bu$_2$O]$_3$ (1). A solution of (*p*-MeOC$_6$H$_4$)$_2$TeO[2] (292 mg, 0.82 mmol) and (*t*-Bu)$_2$Si(OH)$_2$[15] (120 mg, 0.68 mmol) in toluene (30 mL) was heated at reflux for 12 h in a Dean-Stark apparatus. The solvent was removed in a vacuum, and the solid residue was dissolved in ether (10 mL) and filtered. Slow evaporation of the solvent afforded colorless crystals of **1** (341 mg, 0.22 mmol, 97%; mp 230−235 °C).

^{1}H NMR (CDCl$_3$): δ 8.03, (d, 12H; *p*-O$_m$MeC$_6$H$_4$), 6.78 (d, 12 H; *p*-O$_o$MeC$_6$H$_4$), 3.76 (s, 18 H; OCH$_3$), 0.93 (s, 54 H; CH$_3$). ^{13}C NMR (CDCl$_3$): δ 161.2 (*p*-O$_i$MeC$_6$H$_4$), 133.8 (*p*-O$_m$MeC$_6$H$_4$), 130.6 (*p*-O$_p$MeC$_6$H$_4$), 114.0 (*p*-O$_o$MeC$_6$H$_4$), 55.1 (OCH$_3$), 29.1 (CH$_3$), 21.6 (C$_q$CH$_3$). ^{29}Si NMR (CDCl$_3$): δ −20.2. ^{125}Te-NMR (CDCl$_3$): δ 921.5. Anal. Calcd for C$_{66}$H$_{96}$O$_{12}$Si$_3$Te$_3$ (1548.52): C, 51.19; H, 6.25. Found: C, 50.89; H, 5.86.

Crystallography. Single crystals were grown by slow evaporation of a ether/CH$_2$Cl$_2$ solution of [(*p*-MeOC$_6$H$_4$)$_2$TeOSi*t*-Bu$_2$O]$_3$ (**1**). Crystal data and structure solution: C$_{66}$H$_{96}$O$_{12}$Si$_3$Te$_3$, M_r = 1548.56, monoclinic, $P2_1/n$, a = 14.079(3) Å, b = 22.641(5) Å, c = 22.189(5) Å, β = 93.219(5)°, V = 7062(3) Å^3, Z = 4, D_x = 1.456 Mg/m^3, F(000) = 3144, μ = 1.338 mm^{-1}, T = 173 K. Intensity data were collected on a Bruker SMART 1000 CCD diffractometer fitted with Mo Kα radiation (graphite crystal monochromator, λ = 0.71073 Å) to a maximum of $\theta_{\max}$ = 30.540° via ω scans (completeness 99.4% to $\theta_{\max}$). Data were reduced and corrected for absorption using the programs SAINT and SADABS.[16] The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX

---

(13) Gosink, H.-J.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Freire-Erdbrügger, C.; Sheldrick, G. M. *Chem. Ber.* **1993**, *126*, 279.

(14) Foucher, D. A.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1996**, *108*, 1712.

(15) Weidenbruch, M.; Pesel, H.; Van Hieu, D. *Z. Naturforsch.* **1980**, *35b*, 31.

(16) *SMART*, *SAINT*, and *SADABS*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1999.

2002.[17] Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model (including free rotation about C−C) and were refined isotropically. $R_1 = 0.0409$ for 15 197 [$I > 2\sigma(I)$] and $wR_2 = 0.1102$ for 21 497 independent reflections. GooF = 1.047. The max. and min. residual electron densities were 1.742 and −0.762 e Å^{-3}. The figure was prepared using the DIAMOND program.[18]

Crystallographic data for **1** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-634720. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-(0)12 23-33 60 33; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgment. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support. Mrs. Irene Brüdgam (Freie Universität Berlin) is thanked for the X-ray data collection.

Supporting Information Available: A CIF file of the crystallographic data (excluding structure factors) of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM070084L

---

(17) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(18) *DIAMOND* V2.1d; Crystal Impact, K. Brandenburg & M. Berndt GbR: Bonn, Germany, 2002.

MANUSCRIPT VI

9 Molecular Stannatelluroxanes

Jens Beckmann, Jens Bolsinger and Malte Hesse; *Organometallics* **2009**, *28*, 4225–4228

9.1 SYNOPSIS

The aim of this project was to examine the formation of stannatelluroxanes and their ability to absorb CO_2.

Therefore, the reaction of di-*tert*-butyltin oxide with known aryltellurium trichlorides was examined. The reaction of $(t\text{-}Bu_2SnO)_3$ with 2,4,6-t-$Bu_3C_6H_2TeCl_3$, respectively 8-$Me_2NC_{10}H_6TeCl_3$, provided the dinuclear stannatelluroxanes 2,4,6-t-$Bu_3C_6H_2TeO_2Sn$-t-Bu_2Cl, respectively 8-$Me_2NC_{10}H_6TeO_2Sn$-t-Bu_2Cl. These compounds are rare examples of molecular oxides incorporating two heavy main group elements.

The primary Te-O bond lengths of these compounds are significantly shorter than the standard Te-O single bond of $[(4\text{-}MeOC_6H_4)_2TeO]_n$[19] pointing to a bond order of roughly 1.5. However, the axial Sn-Cl bond length of 2,4,6-t-$Bu_3C_6H_2TeO_2Snt$-Bu_2Cl and 8-$Me_2NC_{10}H_6TeO_2Sn$-t-Bu_2Cl are somewhat longer than those of t-Bu_2SnCl_2[93]. It has to be noted that the intramolecular Te···N contact of 8-$Me_2NC_{10}H_6TeO_2Sn$-t-Bu_2Cl is longer than that in 8-$Me_2NC_{10}H_6TeCl_3$[94], suggesting a reduced Lewis acidity of the Te atom. Besides the primary coordination sphere, the stannatelluroxane comprises two symmetry-related intermolecular secondary Te···O contacts, which link two molecules into a centrosymmetric dimer in the crystal lattice.

However, the reaction of $(t\text{-}Bu_2SnO)_3$ with 2,6-$Mes_2C_6H_3TeCl_3$ – depending on the stoichiometric ratio – produced the known dimeric aryltellurium oxo chloride $[2,6\text{-}Mes_2C_6H_3Te(O)Cl]_2$[51] or the new tetranuclear stannatelluroxane $(2,6\text{-}Mes_2C_6H_3Te)_2O_5(Snt\text{-}Bu_2)_2$, which shows two intramolecular Te···O contacts to the Sn-O-Sn linkage, whereby compound 2,4,6-t-$Bu_3C_6H_2TeO_2Sn$-t-Bu_2Cl, lacks, due to the confined space around the Te atom, any secondary interactions.

The ^1H- and ^{13}C-NMR spectra of $(2,6\text{-}Mes_2C_6H_3Te)_2O_5(Sn\text{-}t\text{-}Bu_2)_2$ and 2,4,6-t-$Bu_3C_6H_2TeO_2Sn$-t-Bu_2Cl show that the two *tert*-butyl groups are magnetically inequivalent confirming that the molecular structure is retained in solution.

In contrast, the ^{1}H- and ^{13}C-NMR of 8-$Me_2NC_{10}H_6TeO_2Sn$-*t*-Bu_2Cl were slightly broad, which is explained by a dynamic monomer-dimer equilibrium in solution. An osmometric molecular weight determination revealed a degree of association of 1.64.

In order to investigate their ability to fix carbon dioxide solutions of the respective compounds were treated with gaseous CO_2. However, no reaction was observed by means of IR- and NMR-spectroscopy.

9.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 33% of the experiments which lead to the synthesis of the compound 8-$Me_2NC_{10}H_6TeO_2Sn$-t-Bu_2Cl. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann and Dr. Malte Hesse.

X-Ray Crystallography: Prof. Dr. Jens Beckmann

ORGANOMETALLICS
Note

Organometallics **2009,** *28,* 4225–4228 4225
DOI: 10.1021/om900189s

Molecular Stannatelluroxanes

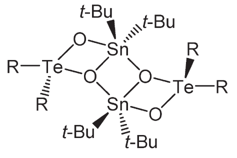
Jens Beckmann,* Jens Bolsinger, and Malte Hesse

Institut für Chemie und Biochemie, Freie Universität Berlin, Germany

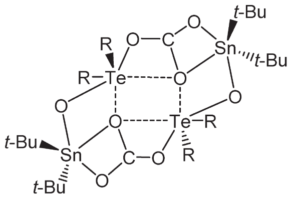
Received March 12, 2009

*Summary: The syntheses and structures are described of the molecular stannatelluroxanes 2,4,6-t-$Bu_3C_6H_2TeO_2Sn$-t-Bu_2Cl (**4**), 8-$Me_2NC_{10}H_6TeO_2Sn$-t-Bu_2Cl (**5**), and (2,6-$Mes_2C_6H_3Te)_2O_5(Sn$-t-$Bu_2)_2$ (**6**), which were obtained by the reaction of (t-$Bu_2SnO)_3$ with the respective aryltellurium trichlorides $RTeCl_3$ (R = 2,4,6-t-$Bu_3C_6H_2$, 8-$Me_2NC_{10}H_6$, 2,6-$Mes_2C_6H_3$). Compounds **4**−**6** were characterized by multinuclear NMR spectroscopy (^1H, ^{13}C, ^{119}Sn, ^{125}Te), ESI-TOF MS spectrometry, osmometric molecular weight determination, and X-ray crystallography.*

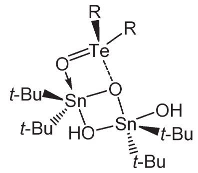
Organostannoxane clusters and polymers have been the focus of extensive research due to their fascinating structural diversity and applications in catalysis and material science.[1] Attempts to incorporate a second heavy element into the structure of organostannoxanes are motivated by the possibility to develop more advanced catalysts with multiple active centers. However, so far only very few compounds containing Sn−O−E linkages (E = heavy element) are known. We recently reported that the reaction of (*t*-$Bu_2SnO)_3$ with (*p*-$MeOC_6H_4)_2TeO$ using a Sn/Te ratio of 1:1 quantitatively provides the hypervalent stannatelluroxane [*p*-$MeOC_6H_4)_2TeOSn$*t*-$Bu_2O]_2$ (**1**).[2,3] Solutions of **1** rapidly absorb gaseous CO_2, giving a tetranuclear stannatelluroxane carbonate cluster [(*p*-$MeOC_6H_4)_2TeOSn$*t*-$Bu_2CO_3]_2$ (**2**).[2] Unlike most metal carbonates, **2** possesses three unevenly long C−O bonds due to the different coordination modes with the Sn and Te atoms, a useful characteristic when pursuing bond activation within carbonates. While salt-like carbonates are often thermally very stable, **2** liberates CO_2 upon heating above 90 °C. These properties make **2** a promising candidate for applications in the fixation and activation of CO_2. Another stannatelluroxane, [(*p*-$MeOC_6H_4)_2Te(OSn$-*t*-$Bu_2OH)_2$] (**3**), was obtained by the reaction of (*t*-$Bu_2SnO)_3$ with (*p*-$MeOC_6H_4)_2TeO$ using a Sn/Te ratio of 2:1 in the presence of moisture.[3] Two molecules of **3** interacted to give dimers in the solid state. The structural characterization of **2** and **3** has revealed the importance of hypervalent and secondary bonding for the fixation of CO_2, the degree of aggregation, and the supramolecular association.



1



2



3

R = *p*-$MeOC_6H_4$

In an effort to obtain deeper insight into the formation of stannatelluroxanes and their ability to absorb CO_2, we have now studied the reaction of di-*tert*-butyltin oxide with known aryltellurium trichlorides at various stoichiometric ratios (Scheme 1). The reaction of (*t*-$Bu_2SnO)_3$ with 2,4,6-*t*-$Bu_3C_6H_2TeCl_3$ and 8-$Me_2NC_{10}H_6TeCl_3$, respectively, using a Sn/Te ratio of 2:1 exclusively provided the dinuclear stannatelluroxanes 2,4,6-*t*-$Bu_3C_6H_2TeO_2Sn$*t*-Bu_2Cl (**4**) and 8-$Me_2NC_{10}H_6TeO_2Sn$-*t*-Bu_2Cl (**5**), respectively, and *t*-Bu_2SnCl_2. Under the same conditions, the reaction of (*t*-$Bu_2SnO)_3$ with 2,6-$Mes_2C_6H_3TeCl_3$ proceeded with complete oxide transfer and produced the dimeric aryltellurium oxo chloride [2,6-$Mes_2C_6H_3Te(O)Cl]_2$[4] and *t*-Bu_2SnCl_2. At a Sn/Te ratio of 5:2 the reaction of (*t*-$Bu_2SnO)_3$ with 2,6-$Mes_2C_6H_3TeCl_3$ afforded the tetranuclear stannatelluroxane (2,6-$Mes_2C_6H_3Te)_2O_5(Sn$-*t*-$Bu_2)_2$ (**6**). Further variation of the Sn/Te ratios provided no other stannatelluroxane products. Alternatively, **6** also was obtained by the condensation reaction of (*t*-$Bu_2SnO)_3$ with the aryltellurinic acid [2,6-$Mes_2C_6H_3Te(O)OH]_2$. Compounds **4**−**6** were isolated as colorless crystals in high yields and are rare examples of molecular oxides incorporating two heavy main group elements.

The molecular structures of **4**−**6** are shown in Figures 1−3, and selected bond parameters are collected in the captions of the figures. The spatial arrangement of the Sn atoms is

---

*Corresponding author. E-mail: beckmann@chemie.fu-berlin.de.

[1] Reviews and references cited therein: (a) Holmes, R. R. *Acc. Chem. Res.* **1989**, *22*, 190. (b) Jain, V. K. *Coord. Chem. Rev.* **1994**, *135*−*136*, 809. (c) Beckmann, J.; Jurkschat, K. *Coord. Chem. Rev.* **2001**, *215*, 267. (d) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.* **2002**, *235*, 1. (e) Chandrasekhar, V.; Gopal, K.; Thilagar, P. *Acc. Chem. Res.* **2007**, *40*, 420.

[2] Beckmann, J.; Dakternieks, D.; Duthie, A.; Lewcenko, N. A.; Mitchell, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 6683.

[3] Beckmann, J.; Dakternieks, D.; Duthie, A.; Mitchell, C. *Dalton Trans.* **2005**, 1563.

[4] Beckmann, J.; Finke, P.; Hesse, M.; Wettig, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 9982.

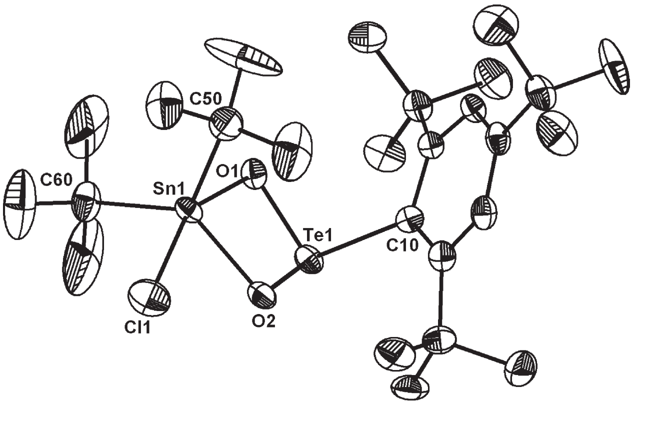
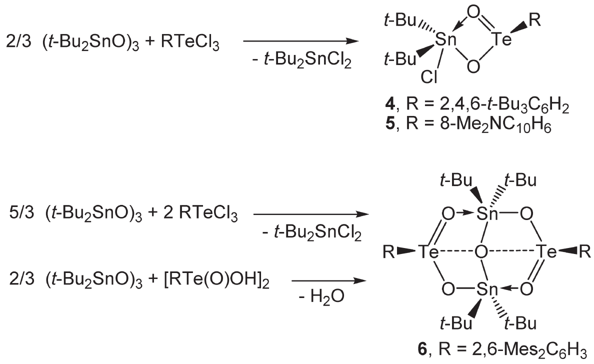


Figure 1. Molecular structure of **4** showing 30% probability displacement ellipsoids and the atom numbering. Selected bond parameters [Å, deg]: Sn1−O1 2.247(6), Sn1−O2 2.084(7), Sn1−Cl1 2.461(3), Sn1−C50 2.17(1), Sn1−C60 2.178(1), Te1−O1 1.855(6), Te1−O2 1.886(7), Te1−C10 2.138(9), O1−Sn1−O2 72.4(3), O1−Sn1−Cl1 155.0(2), O1−Sn1−C50 97.3(4), O1−Sn1−C60 90.4(4), O2−Sn1−Cl1 82.8(2), O2−Sn1−C50 118.6(4), O2−Sn1−C60 118.0(4), Cl1−Sn1−C50 96.4(3), Cl1−Sn1−C60 99.6(4), C50−Sn1−C60 122.5(4), O1−Te1−O2 86.4(3), O1−Te1−C10 97.2(3), O2−Te1−C10 100.0(3), Sn1−O1−Te1 98.1(3), Sn1−O2−Te1 103.0(3).

Scheme 1



distorted trigonal bipyramidal, and the Sn−O bond lengths are in the expected range for single bonds. The axial Sn−Cl bond lengths of **4** (2.461(3) Å) and **5** (2.517(3) Å) are somewhat longer than those in t-Bu$_2$SnCl$_2$ (2.334(1) and 2.335 Å).[5] Taking into account the stereochemically active lone pair, the spatial arrangement of the Te atoms is distorted tetrahedral for **4** (CO$_2$ donor set), distorted octahedral for **5** (CO$_2$ + NO donor set), and distorted trigonal bipyramidal for **6** (CO$_2$+O donor set), respectively. The primary Te−O bond lengths of **4** (1.855(6), 1.886(7) Å), **5** (1.900(6), 1.944(5) Å), and **6** (1.857(6)−1.874(7) Å) are significantly shorter than the standard Te−O single bond of [(4-MeOC$_6$H$_4$)$_2$TeO]$_n$ (2.025(2) and 2.100(2) Å),[6] pointing to a bond order of approximately 1.5. The intramolecular Te···N contact of **5** (2.533(8) Å) is longer than that in 8-Me$_2$NC$_{10}$H$_6$TeCl$_3$ (2.420(3) Å),[7] suggesting a reduced Lewis acidity of the Te atom. Besides the primary coordination sphere, **5** reveals two symmetry-related intermolecular secondary Te···O contacts (2.650(6) Å), which link two molecules into a centrosymmetric dimer in the crystal lattice. Compound **6** shows two intramolecular Te···O contacts (2.581(7) and 2.588(7) Å) to the Sn−O−Sn linkage (146.9(3)°). Compound **4** lacks any secondary interactions due to the confined space around the Te atom. Due to servere repulsion of the inorganic moiety with the *tert*-butyl groups in *ortho*-positions, the Te atom is not coplanar with the phenyl ring of the 2,4,5-tri-*tert*-butylphenyl substituent (largest deviation from the ideal plane 0.299(5) Å).[8]

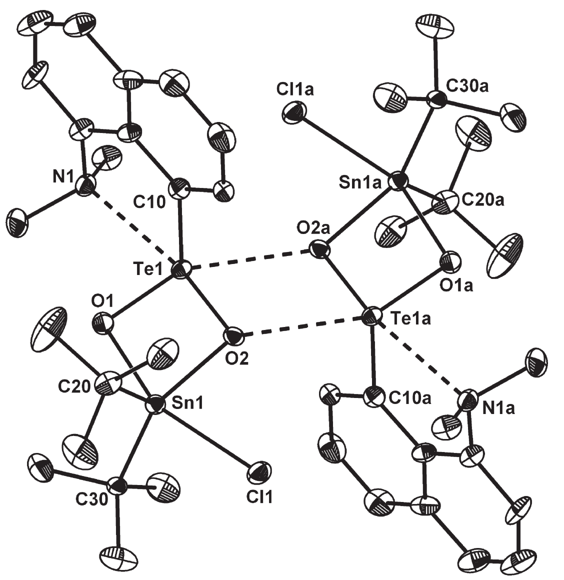


Figure 2. Molecular structure of **5** showing 30% probability displacement ellipsoids and the atom numbering. Symmetry code used to generate equivalent atoms: $a = 2-x, 1-y, 1-z$. Selected bond parameters [Å, deg]: Sn1−O1 2.165(6), Sn1−O2 2.075(5), Sn1−C20 2.210(8), Sn1−C30 2.160(8), Sn1−Cl1 2.517(4), Te1−O1 1.900(6), Te1−O2 1.944(5), Te1···O2a 2.650(6), Te1···N1 2.533(8), Te1−C10 2.123(8), O1−Te1−O2 82.8(2), O1−Te1−C10 99.6(3), O2−Te1−C10 95.8(3), O1−Sn1−O2 73.6(2), O1−Sn1−Cl1 155.8(2), O1−Sn1−C20 99.3(3), O1−Sn1−C30 92.0(3), O2−Sn1−Cl1 82.7(2), O2−Sn1−C20 117.1(3), O2−Sn1−C30 120.1(3),Cl1−Sn1−C30 95.9(2), Cl1−Sn1−C20 95.6(2), C20−Sn1−C30 122.6(3), Sn1−O1−Te1 100.9(2), Sn1−O2−Te1 102.6(2).

Compounds **4** and **6** are reasonably soluble in polar solvents such as CHCl$_3$ and THF, whereas **5** is only poorly soluble in most solvents. The ^{125}Te NMR spectrum (CDCl$_3$) of 2,4,6-t-Bu$_3$C$_6$H$_2$TeO$_2$Sn-t-Bu$_2$Cl (**4**) shows a signal at δ = 1748.6 with unresolved Sn satellites ($^2J(^{125}\text{Te}-^{119/117}\text{Sn})$ = 196 Hz), which is only slightly shifted compared to the parent compound 2,4,6-t-Bu$_3$C$_6$H$_2$TeCl$_3$ (δ = 1791.0).[8] The ^{119}Sn NMR spectrum (CDCl$_3$) of **4** displays a signal at δ = −128.3 with Te satellites ($^2J(^{119}\text{Sn}-^{125}\text{Te})$ = 196 Hz), which agrees well with the spatial arrangement of the pentacoordinated Sn atom and the C$_2$O$_2$Cl donor set. The ^{1}H and ^{13}C NMR spectra of **4** show that the two *tert*-butyl groups are magnetically inequivalent, which is in good agreement with the molecular structure established by X-ray crystallography. The ^{125}Te NMR spectrum (CDCl$_3$) of 8-Me$_2$N-C$_{10}$H$_6$TeO$_2$Sn-t-Bu$_2$Cl (**5**) shows a signal at δ = 1529.3

---

(5) Dakternieks, D.; Jurkschat, K.; Tiekink, E. R. T. *Main Group Met. Chem.* **1994**, *17*, 471.

(6) Beckmann, J.; Dakternieks, D.; Duthie, A.; Ribot, F.; Schürmann, M.; Lewcenko, N. A. *Organometallics* **2003**, *22*, 3257.

(7) Beckmann, J.; Bolsinger, J.; Duthie, A. Manuscript in preparation.

(8) Beckmann, J.; Heitz, S.; Hesse, M. *Inorg. Chem.* **2007**, *46*, 3275.

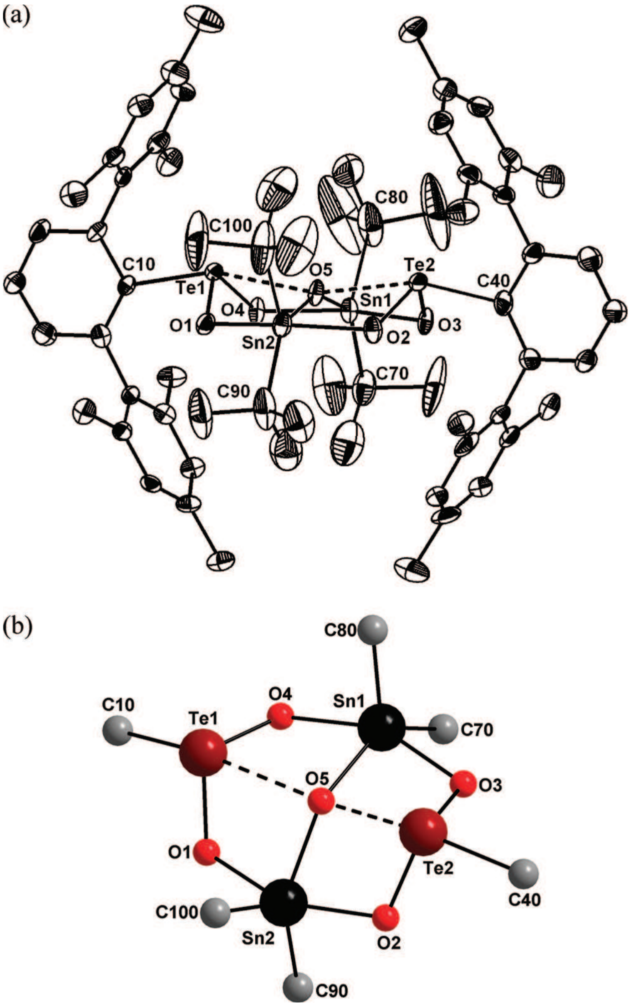


Figure 3. (a) Molecular structure of **6** showing 30% probability displacement ellipsoids and the atom numbering scheme and (b) inorganic core of **6**. Selected bond parameters [Å, deg]: Sn1−O3 2.165(6), Sn1−O4 2.174(6), Sn1−O5 1.997(5), Sn1−C70 2.10(1), Sn1−C80 2.21(1), Sn2−O1 2.162(7), Sn2−O2 2.142(7), Sn2−O5 2.016(5), Sn2−C90 2.07(1), Sn2−C100 2.24(2), Te1−O1 1.869(7), Te1−O4 1.857(6), Te1...O5 2.588(7), Te1−C10 2.199(6), Te2−O2 1.874(7), Te2−O3 1.858(7), Te2···O5 2.581(7), Te2−C40 2.169(7), O3−Sn1−O4 155.5(2), O3−Sn1−O5 79.3(2), O4−Sn1−O5 79.4(2), O3−Sn1−C70 93.1(3), O3−Sn1−C80 98.7(4), O4−Sn1−C70 92.8(3), O4−Sn1−C80 98.2(4), O5−Sn1−C70 133.1(4), O5−Sn1−C80 104.7(5), C70−Sn1−C80 122.1(6), O1−Sn2−O2 156.3(3), O1−Sn2−O5 79.6(2), O2−Sn2−O5 79.5(2), O1−Sn2−C90 91.6(3),O1−Sn2−C100 99.6(3), O2−Sn2−C90 94.2(3), O2−Sn2−C100 96.7(3), O5−Sn2−C90 132.2(4), O5−Sn2−C100 105.9(4), C90−Sn2−C100 121.9(5), O1−Te1−O4 105.1(3), O1−Te1−C10 96.5(3), O4−Te1−C10 98.1(3), O2−Te2−O3 105.6(3), O2−Te2−C40 98.6(3), O3−Te2−C40 97.1(3), Sn1−O5−Sn2 146.9(3), Sn1−O4−Te1 111.8(3), Sn1−O3−Te2 111.5(3), Sn2−O1−Te1 111.4(3), Sn2−O2−Te2 112.5(4).

($\omega_{1/2}$ = 42 Hz), which is shifted to higher frequencies compared to the parent compound 8-$Me_2NC_{10}H_6TeCl_3$ (δ = 1317.1 ($CDCl_3$)).[7] The ^{119}Sn NMR spectrum ($CDCl_3$) of **5** exhibits a signal at $\delta = -149.1$ ($\omega_{1/2}$ = 89 Hz), which is also consistent with the spatial arrangement of the pentacoordinated Sn atom and the C_2O_2Cl donor set. No satellites were observed due to the poor signal-to-noise ratio (acquisition time for each spectrum 24 h). Like the ^{119}Sn NMR signal, the ^{1}H and ^{13}C NMR chemical shifts of **5** were slightly broad, which is explained by a dynamic exchange process, namely, a monomer−dimer equilibrium in solution. This is supported by an osmometric molecular weight determination, which reveals a degree of association of 1.64 in $CHCl_3$. An attempt to measure a reasonable ^{125}Te and ^{119}Sn NMR spectrum of **5** at −20 °C failed due to the poor solubility. The ^{125}Te NMR ($CDCl_3$) of (2,6-$Mes_2C_6H_3Te)_2O_5$(Sn-*t*-$Bu_2)_2$ (**6**) shows a signal at δ = 1613.5 ($\omega_{1/2}$ = 42 Hz), which is shifted to higher frequencies when compared to [2,6-$Mes_2C_6H_3Te$(O)OH$]_2$ (δ = 1403).[4] The ^{119}Sn NMR spectrum ($CDCl_3$) of **6** shows a signal at $\delta = -253.3$ with Sn ($^{2}J(^{119}Sn-^{117}Sn)$ = 528 Hz) and Te satellites ($^{2}J(^{119}Sn-^{125}Te)$ = 32 Hz) that are consistent with the spatial arrangement of the pentacoordinated Sn atoms and the C_2O_3 donor set. While the magnitude of the $^{2}J(^{119}Sn-^{117}Sn)$ coupling agrees well with the wide Sn−O−Sn angle,[9] no explanation can be given for the small $^{2}J(^{119}Sn-^{125}Te)$ coupling at this point in time. The ^{1}H and ^{13}C NMR spectra show two sets of signals for the magnetically inequivalent *tert*-butyl groups, confirming that the molecular structure is retained in solution. Stannatelluroxanes **4**−**6** were also characterized by ESI-TOF MS spectrometry, a method that allows the detection of (trace amounts of) ionic species formed by autoionization in solution. For **4** and **5**, significant mass clusters were detected in the positive mode of the cations $[(RTe)_3t\text{-}Bu_2SnO_5]^+$, $[(RTe)_2t\text{-}Bu_2SnO_3(OH)]^+$, $[(RTe)t\text{-}Bu_2SnO(OH)Cl]^+$, and $[(RTe)t\text{-}Bu_2SnO_2]^+$ (R = 2,4,6-*t*-$Bu_3C_6H_2$, 8-$Me_2NC_{10}H_6$), respectively, whereas **6** showed a mass cluster for the cation $[(RTe)_2(t\text{-}Bu_2Sn)_2O_4(OH)]^+$ (R = 2,6-$Mes_2C_6H_3$).

In an effort to investigate their ability to fix carbon dioxide, solid and liquid samples of **4** and **6** in $CDCl_3$ were treated with gaseous CO_2 at room temperature. No reaction was observed by means of IR and NMR spectroscopy. Thus, unlike [*p*-$MeOC_6H_4)_2$TeOSn-*t*-$Bu_2O]_2$ (**1**),[2,3] no evidence for the formation of stannatelluroxane carbonates was found.

Experimental Section

General Considerations. The starting compounds (*t*-$Bu_2SnO)_3$,[10] 2,4,6-*t*-$Bu_3C_6H_2TeCl_3$,[8] 8-$Me_2NC_{10}H_6TeCl_3$,[7] 2,6-$Mes_2C_6H_3TeCl_3$, and [2,6-$Mes_2C_6H_3Te$(O)OH$]_2$[4] were prepared according to a literature procedure. The solution ^{1}H, ^{13}C, ^{119}Sn, and ^{125}Te NMR spectra were collected using a Jeol JNM-LA 400 FT spectrometer and a Jeol Eclipse + 500 FT spectrometer and are referenced against Me_4Si, Me_4Sn, and Me_2Te. Electrospray ionization time-of-flight ESI-TOF mass spectra were measured on an Agilent 6210 mass spectrometer (Agilent Technologies, Santa Clara, CA). Solvent flow rate was adjusted to 4 μL/min. The spray voltage and skimmer voltage were set to 4 kV and 150 V, respectively. Molecular weights were determined using a Knauer vapor pressure osmometer. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of 4−6. A solution or suspension of the appropriate aryltellurium trichloride (240 mg of 2,4,6-*t*-$Bu_3C_6H_2TeCl_3$, 202 mg of 8-$Me_2NC_{10}H_6TeCl_3$, 273 mg of 2,6-$Mes_2C_6H_3TeCl_3$; 0.50 mmol) and (*t*-$Bu_2SnO)_3$ (246 mg, 0.33 mmol for **4** and **5**; 620 mg, 0.83 mmol for **6**) in THF (60 mL) was stirred at rt for 6 h. The volume of the solution was reduced to

---

[9] Lockhart, T. P.; Puff, H.; Schuh, W.; Reuter, H.; Mitchell, T. N. *J. Organomet. Chem.* **1989**, *366*, 61.

[10] Puff, H.; Schuh, W.; Sievers, R.; Wald, W.; Zimmer, E. *J. Organomet. Chem.* **1984**, *260*, 271.

Table 1. Crystal Data and Structure Refinement of 4−6

	4	**5**·THF	**6**
formula	$C_{26}H_{47}ClO_2SnTe$	$C_{24}H_{38}ClNO_3SnTe$	$C_{64}H_{86}O_5Sn_2Te_2$
fw, g mol^{-1}	673.38	670.29	1427.91
cryst syst	monoclinic	triclinic	monoclinic
cryst size, mm	0.31 × 0.18 × 0.07	0.25 × 0.21 × 0.08	0.50 × 0.13 × 0.05
space group	$P2_1/n$	$P\bar{1}$	$C2/c$
a, Å	11.949(2)	8.56(1)	21.52(1)
b, Å	10.2751(8)	12.65(1)	21.417(5)
c, Å	25.423(3)	12.90(2)	29.85(1)
α, deg	90	100.4(1)	90
β, deg	91.64(1)	92.4(1)	96.22(4)
γ, deg	90	90.39(9)	90
V, Å^3	3120.1(7)	1373(3)	13676(9)
Z	4	2	8
ρ_{calcd}, Mg m^{-3}	1.433	1.622	1.387
T, K	150	150	150
μ(Mo Kα), mm^{-1}	1.839	2.093	1.608
F(000)	1352	664	5712
θ range, deg	1.86 to 25.25	2.08 to 29.20	2.22 to 29.29
index ranges	$-14 \le h \le 14$	$-11 \le h \le 11$	$-29 \le h \le 29$
	$0 \le k \le 12$	$-17 \le k \le 17$	$-29 \le k \le 24$
	$0 \le l \le 30$	$-17 \le l \le 17$	$-40 \le l \le 40$
no. of reflns collected	5643	14 890	65 721
completeness to θ_{max}	99.8%	98.2%	97.7%
no. indep reflns	5643	7303	18 258
no. obsd reflns with ($I > 2\sigma(I)$)	3258	2371	5397
no. refined params	275	280	730
GooF (F^2)	0.866	0.994	0.958
R_1 (F) ($I > 2\sigma(I)$)	0.0530	0.0375	0.0570
wR_2 (F^2) (all data)	0.1543	0.0844	0.1149
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001	< 0.001
largest diff peak/hole, e Å^{-3}	0.972/−1.600	0.602/−0.940	0.900/−0.713

10 mL under vacuum. Colorless single crystals of **4**, **5**·THF, and **6** were obtained within 12 h. The crystals of **5**·THF were dried for 2 h at 40 °C under vacuum to give an analytical sample of **5**.

2,4,6-*t*-Bu$_3$C$_6$H$_2$TeO$_2$Sn-*t*-Bu$_2$Cl (4). Yield: 272 mg, 0.41 mmol; 81%. ^{1}H NMR (CDCl$_3$): δ 7.37 (s, 2H; Ar), 1.49 (s, 18H; CH$_3$), 1.38 (s, 9H; CH$_3$), 1.24 (s, 18H; CH$_3$). ^{13}C NMR (CDCl$_3$): δ 156.7, 152.3, 149.8, 141.5, 125.5, 119.39 (Ar), 45.1, 42.1, 39.7, 34.7, 33.8, 31.5, 31.4, 30.4 (CMe$_3$). ^{119}Sn NMR (CDCl$_3$): δ −128.3 ($^2J(^{119}Sn{-}^{125}Te)$ = 196 Hz). ^{125}Te NMR (CDCl$_3$): δ 1748.6 ($^2J(^{125}Te{-}^{119/117}Sn)$ = 196 Hz). Anal. Calcd for $C_{26}H_{47}ClO_2SnTe$ (673.41): C, 46.37; H, 7.03. Found: C, 46.25; H, 6.78. ESI-TOF MS: m/z 1433.4 $[C_{62}H_{105}O_5Te_3Sn]^+$, 1044.1 $[C_{44}H_{77}O_4Te_2Sn]^+$, 675.1 $[C_{26}H_{48}O_2SnTeCl]^+$, 639.2 $[C_{26}H_{47}O_2SnTe]^+$.

8-Me$_2$NC$_{10}$H$_6$TeO$_2$Sn-*t*-Bu$_2$Cl (5). Yield: 147 mg, 0.25 mmol; 50%. ^{1}H NMR (CDCl$_3$): δ 8.68 (d, 2H; Ar), 8.05 (d, 2H; Ar), 7.87−7.81 (m, 4H; Ar), 7.59−7.57 (m, 4H; Ar), 3.34 (s, 12 H, NCH$_3$), 1.03 (s, 36 H, CCH$_3$). ^{13}C NMR (CDCl$_3$): δ 148.6, 140.9, 134.9, 131.9, 131.6, 131.3, 127.6, 127.4, 126.8, 119.7 (Ar), 47.9 (NMe$_2$), 40.9 (*C*Me$_3$), 29.8 (C*Me$_3$*). ^{119}Sn NMR (CDCl$_3$): δ −149.1 ($\omega_{1/2}$ = 89 Hz). ^{125}Te NMR (CDCl$_3$): δ 1529.3 ($\omega_{1/2}$ = 42 Hz). Anal. Calcd for $C_{20}H_{30}ClNO_2TeSn$ (598.22): C, 40.15; H, 5.05; N, 2.34. Found: C, 39.99; H, 4.84; N, 2.28. ESI-TOF MS: m/z 1208.0 $[C_{44}H_{54}N_3O_5SnTe_3]^+$, 895.0 $[C_{32}H_{43}N_2O_4SnTe_2]^+$, 600.0 $[C_{20}H_{31}NO_2SnTeCl]^+$, 564.0, $[C_{20}H_{30}NO_2SnTe]^+$. MW: 981 g mol^{-1} (c 10−25 mg/g CHCl$_3$).

(2,6-Mes$_2$C$_6$H$_3$Te)$_2$O$_5$(Sn*t*-Bu$_2$)$_2$ (6). Yield: 550 mg, 0.39 mmol, 77%. ^{1}H NMR (CDCl$_3$): δ 7.47 (t, 1H; Ar), 7.03 (d, 2H; Ar), 6.82 (s, 4H; Ar), 2.29 (s, 6H; CH$_3$), 2.0 (s, 12H; CH$_3$), 0.95 (s, 9H; CH$_3$), 0.88 (s, 9H; CH$_3$). ^{13}C NMR (CDCl$_3$): δ 146.3, 146.1, 137.5, 136.7, 136.4, 130.9, 129.3, 128.1 (Ar), 41.5, 35.5 (*C*Me$_3$), 30.2, 29.9 (C*Me$_3$*), 21.4, 21.0 (Ar*Me*). ^{119}Sn NMR (CDCl$_3$): δ −253.3 ($^2J(^{119}Sn{-}^{117}Sn)$ = 528 Hz, $^2J(^{119}Sn{-}O{-}^{125}Te)$ = 32 Hz). ^{125}Te NMR (CDCl$_3$): δ 1613.5 ($\omega_{1/2}$ = 42 Hz). Anal. Calcd for $C_{64}H_{86}O_5Sn_2Te_2$ (1427.98): C, 53.83; H, 6.07. Found: C, 53.86; H, 5.91. ESI-TOF MS: m/z 1429.3 $[C_{64}H_{87}O_5Sn_2Te_2]^+$.

Alternative Synthesis of 6. A solution of $[2,6\text{-}Mes_2C_6H_3Te(O)OH]_2$ (474 mg; 0.50 mmol) and $(t\text{-}Bu_2SnO)_3$ (246 mg; 0.33 mmol) in toluene (50 mL) was heated under reflux in a Dean−Stark apparatus for 2 h. The volume of the solution was reduced to 10 mL under vacuum. Colorless single crystals of **6**, which were obtained within 12 h, were isolated by filtration. Yield: 542 mg, 0.38 mmol, 76%.

X-ray Crystallography. Intensity data of **4**−**6** were collected on a STOE IPDS 2T area detector with graphite-monochromated Mo Kα (0.7107 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 and SHELXL-97 implemented in the program WinGX 2002.[11] Full-matrix least-squares refinements were done on F^2, using all data. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Disorder of the inorganic core of **6** was resolved with split occupancies of 0.75 (Te1, Te2, Sn1, Sn2, and O1−O5) and 0.25 (Te1′, Te2′, Sn1′, Sn2′, and O1′−O5′). Crystal and refinement details are collected in Table 1. Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers 733996 (**4**), 733997 (**5**), and 733998 (**6**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgment. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

---

(11) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

MANUSCRIPT VII

10 Carbon Dioxide Fixation with Dialkyltellurium(IV) Dihydroxide

Jens Beckmann, Jens Bolsinger and Andrew Duthie; *Z. Anorg. Allg. Chem.*, **2008**, *636*, 765–769

10.1 SYNOPSIS

The aim of this project was to examine the possibility of carbon dioxide fixation with simple dialkyl tellurium dihydroxides.

Freshly prepared aqueous solutions of $Me_2Te(OH)_2$[96] and $(CH_2)_4Te(OH)_2$[58] were purged with gaseous CO_2. Slow evaporation at room temperature afforded the dialkyltelluroxane carbonates $(Me_2TeOTeMe_2CO_3)_n$ and $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH \cdot 2H_2O$ as colorless single crystals in nearly quantitative yield.

The compounds contain two, respectively three crystallographically independent organotellurium sites and one carbonate moiety. The structures of the carbonate compounds can be described as 1D and 2D coordination polymers, respectively. Each structure features one $XR_2TeOTeR_2X$ unit similar to those found in other tetraorganotelluroxanes[21,22,58,59,63,95-104] and comprises secondary Te···O contacts.

Comparing the carbonate coordination of the new carbonate compounds with those of the previously known heavy *p*-block element carbonates[44,45,48,105-108] allows the classification of different coordination modes. The greatest involvement in metal coordination was observed for the polymeric trialkyltin carbonates[44], due to the high propensity of the organotin atoms to be hypercoordinated. The least involvement in the coordination was shown in the aryltin and arylantimony carbonates[45,107]. This is explained by the reduced Lewis acidity of the organotin and organoantimony atoms due to the presence of intramolecularly coordinated N donor ligands. All other cases including the newly synthesized compounds are intermediates of these modes.

The difference of the coordination types is reflected by vibrational spectroscopy[109]. The IR spectra of the newly synthesized compounds show strong absorptions at 1483 and 1305 ($(Me_2TeOTeMe_2CO_3)_n$) as well as 1640 and 1333 cm^{-1} ($(HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH \cdot 2H_2O)$), respectively. These absorptions are assigned to asymmetric and symmetric C–O stretching vibrations. It has to be noted, that comparable absorptions are absent in the IR spectra of the closely related

$IMe_2TeOTeMe_2I$ and $I(CH_2)_4TeOTe(CH_2)_4OTe(CH_2)_4I$[95]. The coupling between the asymmetric and symmetric C–O stretching vibration is smaller in $(Me_2TeOTeMe_2CO_3)_n$ than in $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH \cdot 2H_2O$, which compares well with the fact that the coordination of the carbonate to the tellurium atoms of $(Me_2TeOTeMe_2CO_3)_n$ is stronger in comparison.

Both compounds undergo electrolytic dissociation in D_2O, where they give basic solutions. The ^{125}Te NMR spectra only exhibit one broad signal, respectively.

10.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann.

X-Ray Crystallography: Prof. Dr. Jens Beckmann
^{125}Te MAS-NMR spectra and analysis thereof: Dr. Andrew Duthie

DOI: 10.1002/zaac.200900432

Carbon Dioxide Fixation with Dialkyltellurium(IV) Dihydroxides

Jens Beckmann,*[a] Jens Bolsinger,[a] and Andrew Duthie[b]

Keywords: Tellurium; Carbon dioxide fixation; NMR spectroscopy; X-ray diffraction; Carbonates

Abstract. Aqueous solutions of $Me_2Te(OH)_2$ and $(CH_2)_4Te(OH)_2$ readily absorb carbon dioxide giving rise to the formation of the dialkyltelluroxane carbonates $(Me_2TeOTeMe_2CO_3)_n$ (**1**) and $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH\cdot 2H_2O$ (**2**·$2H_2O$), which were characterised by ^{13}C MAS and ^{125}Te MAS NMR spectroscopy as well as X-ray crystallography. The spatial arrangement of the tellurium atoms is defined by C_2O_2 donor sets in the primary coordination sphere and one or two secondary Te···O contacts, which involve coordination of the carbonate moieties. In turn, the different Te–O coordination modes render a lack of symmetry to the carbonate moieties, which show significantly different C–O bond lengths, an important feature when contemplating the C–O bond activation in carbonates. The structural and spectroscopic parameters of **1** and **2** are discussed in comparison with other heavy *p*-block element carbonates. In solution, electrolytic dissociation of **1** and **2** takes place.

Introduction

Elevated CO_2 levels in the atmosphere are arguably the main course for the anthropogenic greenhouse effect, which leads to an average global warming and local climate changes. On the other hand, waste CO_2 may be an inexpensive, non-toxic C1-feedstock for the preparation of commodities, such as poly(propylene carbonate) (PPC), poly(cyclohexene carbonate) (PCHC), dimethyl carbonate (DMC) and diphenyl carbonate (DPC) [1].

Whereas a number of *s*-, *d*- and *f*-block metals are able to bind and activate CO_2 [2], *p*-block elements known to react with CO_2 are rarer. Notable exceptions include the organotin hydroxides and oxides Me_3SnOH, $(iBu_3Sn)_2O$ and $[(2\text{-}Me_2NCH_2C_6H_4)_2SnO]_2$ that readily absorb gaseous CO_2 to give rise to the well-defined organotin carbonates $[(Me_3Sn)_2CO_3]_n$, $[(iBu_3Sn)_2CO_3]_n$ [3], and $O[(2\text{-}Me_2NCH_2C_6H_4)_2Sn]_2CO_3$ [4]. The base hydrolysis of diorganotin dihalides in the presence of CO_2 directly afforded diorganotin carbonates, such as $[(tBu_2Sn)_3O(OH)_2CO_3\cdot 3MeOH]$ [5] and $[(Bz_2Sn)_5O_3(OH)_2CO_3]_2$ [6]. Tributyltin carbonate, $(Bu_3Sn)_2CO_3$, and other in situ prepared organotin carbonates were used as Lewis acid solid-liquid phase-transfer catalysts for the preparation of dialkyl carbonates [7]. Di- and triorganotin alkoxides $R_nSn(OR')_{4-n}$ (R = alkyl, R' = alkyl, aryl; *n* = 2, 3) undergo reaction with gaseous or supercritical CO_2 affording di- and triorganotin (alkoxy) carbonates, $R_2Sn(OR')(O_2COR')$ and $R_3Sn(O_2COR')$, some of which release DMC upon thermolysis [8–18]. Extensive research in this area allowed the isolation and full characterisation of some interesting organotin intermediates, such as $(Me_2Sn)_2(OMe)_2(OCO_2Me)_2$ [9], $(Bu_2Sn)_{10}O_6(OMe)_4(CO_3)_2$ [12], $(Bu_2Sn)_2(OiPr)_2(OCO_2iPr)_2$ and $(Bu_2Sn)_4O_2(OiPr)_2(OCO_2iPr)_2$ [13]. Very recently, the two diarylbismuth oxides $[tBuN(2\text{-}CH_2C_6H_4)_2Bi]_2O$ and $[(2\text{-}Me_2NCH_2C_6H_4)_2Bi]_2O$ were found to absorb CO_2 to give rise to diarylbismuth carbonates $[tBuN(2\text{-}CH_2C_6H_4)_2Bi]_2CO_3$ [14] and $[(2\text{-}Me_2NCH_2C_6H_4)_2Bi]_2CO_3$ [15]. The related diarylbismuth alkoxides $tBuN(2\text{-}CH_2C_6H_4)_2BiOR$ (R = Me, $CH_2CH_2NH_2$) also undergo reaction with CO_2 to afford the insertion products $tBuN(2\text{-}CH_2C_6H_4)_2BiOCO_2Me$ and $tBuN(2\text{-}CH_2C_6H_4)_2BiOCONHCH_2CH_2OH$, respectively [14]. A recent patent application claims the use of related azastibocines as carbon dioxide sensors [16]. An intramolecularly coordinated arylantimony(III) oxide $[2,6\text{-}(Me_2NCH_2)_2C_6H_3SbO]_2$ also reversibly absorbs CO_2 to give the arylantimony carbonate $2,6\text{-}(Me_2NCH_2)_2C_6H_3SbCO_3$ [17]. Aqueous solutions of trimethylantimony(V) dihydroxide, $Me_3Sb(OH)_2$, fix CO_2 and provide the hydrated trimethylantimony hydroxy carbonate $[(Me_3SbOH)_2CO_3\cdot 2H_2O]_n$ upon exposure to air moisture [18]. Recently, we discovered a cooperative effect when using the two organometallic oxides $(tBu_2SnO)_3$ and $(4\text{-}MeOC_6H_4)_2TeO$ for the CO_2 fixation, which lead to the isolation and full characterisation of a unique tetranuclear tellurastannoxane carbonate cluster $[(4\text{-}MeOC_6H_4)_2TeOSntBu_2CO_3]_2$ [19]. In continuation of this work, we now report on the CO_2 fixation with two simple dialkyltellurium dihydroxides, leading to the formation of dialkyltelluroxane carbonates.

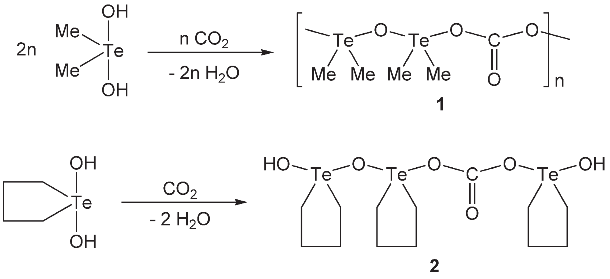
Discussion

Aqueous solutions of $Me_2Te(OH)_2$ [20] and $(CH_2)_4Te(OH)_2$ [21], freshly prepared in situ from the corresponding dialkyl-

---

* Prof. Dr. J. Beckmann
Fax: +49-30-838-52440
E-Mail: beckmann@chemie.fu-berlin.de
[a] Institut für Chemie und Biochemie
Freie Universität Berlin
Fabeckstraße 34–36
14195 Berlin, Germany
[b] School of Life and Environmental Sciences
Deakin University
Pigdons Road
Waurn Ponds 3217, Australia

tellurium diiodides and Ag_2O, were purged with gaseous CO_2. Slow evaporation at room temperature afforded the dialkyltelluroxane carbonates $(Me_2TeOTeMe_2CO_3)_n$ (**1**) and $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH{\cdot}2H_2O$ (**2**·$2H_2O$) in nearly quantitative yields as colourless single crystals (Scheme 1). Once isolated from the mother liquor, the crystal water of **2**·$2H_2O$ was lost within a few minutes to leave **2** as a colourless solid. The crystal structures of **1** and **2**·$2H_2O$ are shown in Figure 1 and Figure 2 and selected bond parameters are listed in the caption of the figures. Compounds **1** and **2** contain two and three crystallographically independent organotellurium sites, respectively, and one carbonate moiety. The ^{125}Te MAS NMR spectrum of **1** shows two equally intense signals at δ_{iso} = 1192 and 1026.



Scheme 1.

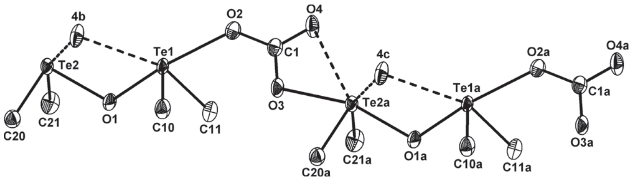


Figure 1. Crystal structure of $(Me_2TeOTeMe_2CO_3)_n$ (**1**) showing 50 % probability ellipsoids and the crystallographic numbering scheme. Symmetry codes used to generate equivalent atoms: a = *x*, *y*, *z* + 1; b = *x* + 0.5, –*y* + 1.5, *z* – 0.5; c = *x* + 0.5, –*y* + 1.5, *z* + 0.5). Selected bond parameters /Å ,°: Te1–O1 1.953(5), Te1–O2 2.382(5), Te1···O4b 2.932(7), Te1–C10 2.107(8), Te1–C11 2.105(8), Te2–O1 2.058(5), Te2a-O3 2.211(5), Te2···O4b 2.88(1), Te2a···O4 2.904(6), Te2–C20 2.093(8), Te2–C21 2.115(8), C1–O2 1.282(9), C1–O3 1.326(9), C1–O4 1.244(9), O1–Te1–O2 173.1(2), O1–Te1–C10 92.5(3), O1–Te1–C11 88.5(3), O2–Te1–C10 86.1(3), O2–Te1–C11 84.9(3), C10–Te1–C11 93.8(3), O1a-Te2a-O3 162.7(2), O1–Te2–C20 87.4(3), O1–Te2–C21 84.2(3), O3–Te2a–C20a 80.8(3), O3–Te2a–C21a 85.1(3), C20–Te2–C21 98.7(3), Te1–O1–Te2 118.7(3).

The ^{13}C MAS NMR spectrum of **1** exhibits five signals at δ_{iso} = 165.3, 25.5, 24.6, 22.8 and 21.0, which were assigned to the carbonate moiety and the four magnetically inequivalent methyl groups, respectively. The ^{125}Te MAS NMR spectrum of **2** shows three equally intense signals at δ_{iso} = 1215, 1173 and 1131, whereas the ^{13}C MAS NMR spectrum reveals three signals at δ_{iso} = 164.9, 48.4 and 32.6 with the latter two being broad and unresolved. The spatial arrangement of all tellurium atoms is distorted trigonal bipyramidal when taking into account the stereochemically active lone pair and the primary coordination sphere defined by a C_2O_2 donor set. Each structure features one $XR_2TeOTeR_2X$ unit similar to those found in other tetraorganotelluroxanes [20–34]. As observed in other $OR_2TeOTeR_2O$ units, the shortest Te–O bond lengths of **1** [1.953(5) and 2.058(5) Å] were observed for the oxygen atoms situated in the centre of the Te–O–Te linkages, whereas the opposite axial Te–O bond lengths [2.211(5) and 2.382(6) Å] associated with the coordination of the carbonate moiety are considerably longer. The Te–O–Te linkage of **2** is more asymmetric, which is reflected in the uneven Te–O bond lengths [1.911(4) and 2.186(3) Å]. The Te–O bond lengths of **2** related to the hydroxy groups [2.015(4) and 2.039(3) Å] are considerably shorter than those associated with the coordination of the carbonate moiety [2.265(3) and 2.88(1) Å]. The Te–O–Te angles of **1** [118.7(3)°] and **2** [127.91(8)°] fall in the range of other tetraorganotelluroxanes [21–33]. The coordination sphere of the tellurium atoms is completed by one (Te1 of **1**) and two (Te2 of **1** and Te1, Te2, Te3 of **2**) secondary Te···O contacts [2.88(1)–2.904(6) Å for **1** and 3.007(5)–3.488(5) Å for **2**] that are up to 17 % shorter than the sum of the van-der-Waals radii (3.5 Å) [35]. It is to note that such secondary Te···O contacts are commonly observed for Te^{IV} compounds, as exemplified in the recently reported crystal structures of $Te(OCH_3)_4$ and $Te(OCH_2CF_3)_4$ [36]. The two water molecules (O7 and O8) and the two hydroxy groups (O1 and O6) of **2** are involved in hydrogen bonds. The O···O distances [2.758(6)–2.896(9) Å] allow the classification of medium strength hydrogen bonding [37]. Considering all types of interactions, the structures of **1** and **2** can be described as 1D and 2D coordination polymers,

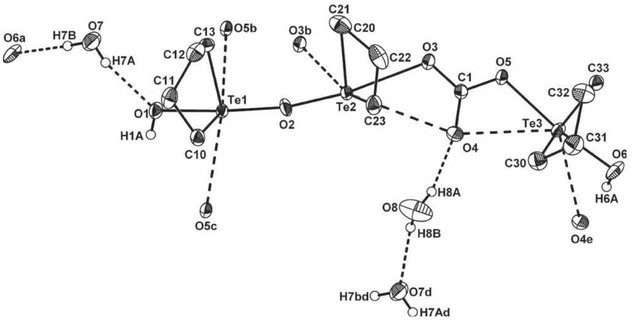
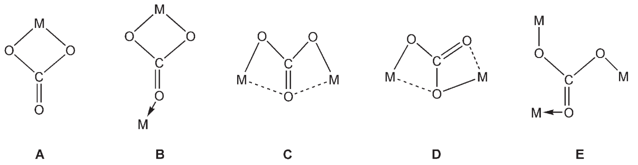


Figure 2. Crystal structure of $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH{\cdot}2H_2O$ (**2**·$2H_2O$) showing 50 % probability ellipsoids and the crystallographic numbering scheme. Symmetry codes used to generate equivalent atoms: a = *x* – 2, *y* – 1, *z*; b = –*x* – 1, –*y*, –*z* – 1; c = *x* – 1, *y*, *z*; d = *x* + 1, *y* + 1, *z*; e = –*x*, –*y* + 1, –*z* + 1). Selected bond parameters /Å, °: Te1–O1 2.039(3), Te1–O2 2.186(3), Te1···O5b 3.488(5), Te1···O5c 3.248(5), Te1–C10 2.130(5), Te1–C13 2.115(5), Te2–O2 1.911(4), Te2–O3 2.568(5), Te2···O3b 3.324(6), Te2···O4 3.414(4), Te2–C20 2.116(5), Te2–C23 2.138(5), Te3···O4 3.007(5), Te3···O4e 3.421(5), Te3–O5 2.265(3), Te3–O6 2.015(4), Te3–C30 2.123(6), Te3–C33 2.121(5), C1–O3 1.281(6), C1–O4 1.259(6), C1–O5 1.312(6), O6a···O7 2.814(9), O1···O7 2.758(6), O4···O8 2.896(9), O7d···O8 2.88(1), O1–Te1–O2 166.81(13), O2–Te2–O3 167.64(14), O1–Te1–C10 89.10(17), O1–Te1–C13 85.36(16), O2–Te1–C10 80.16(17), O2–Te1–C13 86.10(16), C10–Te1–C13 85.18(19), O2–Te2–C20 92.12(17), O2–Te2–C23 90.79(18), C20–Te2–C23 85.6(2), O5–Te3–O6 167.57(13), O5–Te3–C30 86.51(18), O5–Te3–C33 81.73(17), O6–Te3–C30 88.9(2), O6–Te3–C33 86.45(18), C30–Te3–C33 86.0(2), Te1–O2–Te2 127.91(8).

Table 1. Classification and C–O bond lengths /Å of heavy *p*-block element carbonates.



Entry	Compound	Type	Shortest C–O bond	Medium C–O bond	Longest C–O bond
1	$[(Me_3Sn)_2CO_3]_n$ [3]	E	1.263(7)	1.289(7)	1.301(7)
2	$[(i Bu_3Sn)_2CO_3]_n$ [3]	E	1.23(1)	1.30(2)	1.31(2)
			1.25(2)	1.30(2)	1.32(2)
3	$O[(2\text{-}Me_2NCH_2C_6H_4)_2Sn]_2CO_3$ [4]	A	1.215(8)	1.312(2)	1.322(2)
4	$2,6\text{-}(Me_2NCH_2)_2C_6H_3SbCO_3$ [17]	A	1.223(5)	1.312(5)	1.314(5)
5	$[(Me_3SbOH)_2CO_3{\cdot}2H_2O]_n$ [18]	D	1.235(6)	1.314(6)	1.318(5)
6	$[t BuN(2\text{-}CH_2C_6H_4)_2Bi]_2CO_3$ [14]	C	1.255(5)	1.286(4)	1.312(4)
7	$[(2\text{-}Me_2NCH_2C_6H_4)_2Bi]_2CO_3$ [15]	C	1.24(1)	1.293(9)	1.32(1)
8	$[(2\text{-}Me_2NCH_2C_6H_4)_2Bi]_2CO_3{\cdot}C_6H_6$ [15]	D	1.24(1)	1.282(9)	1.299(9)
9	$[(4\text{-}MeOC_6H_4)_2TeOSnt Bu_2CO_3]_2$ [19]	B	1.259(3)	1.278(3)	1.329(3)
10	$(Me_2TeOTeMe_2CO_3)_n$ (**1**)	D	1.244(9)	1.282(9)	1.326(9)
11	$HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH$ (**2**)	C	1.259(6)	1.281(6)	1.312(6)

Table 2. Crystal data and structure refinement for **1** and **2**·$2H_2O$.

	1	**2**·$2H_2O$
Formula	$C_5H_{12}O_4Te_2$	$C_{13}H_{30}O_8Te_3$
Formula weight /g·mol^{-1}	391.35	697.17
Crystal system	monoclinic	triclinic
Crystal size /mm	0.49 × 0.32 × 0.08	0.43 × 0.25 × 0.12
Space group	$P2_1/n$	$P\bar{1}$
a /Å	6.741(2)	9.611(8)
b /Å	16.504(5)	11.23(1)
c /Å	9.324(3)	11.45(1)
α/°		102.97(7)
β/°	109.257(6)	106.35(7)
γ/°		113.91(7)
V /Å^3	979.3(5)	1000(2)
Z	4	2
$D_{calcd.}$ /Mg·m^{-3}	2.654	2.314
T /K	173	150
μ /mm^{-1}	5.929	4.380
F(000)	712	656
θ range /deg	2.47 to 25.00	2.01 to 25.00
Index ranges	$-8 \le h \le 9$	$-13 \le h \le 9$
	$-23 \le k \le 23$	$-15 \le k \le 15$
	$-12 \le l \le 13$	$-15 \le l \le 15$
No. of reflns collcd	11402	10246
Completeness to θ_{max}	99.8 %	98.5 %
No. of indep reflns/R_{int}	1715	3470
No. of reflns obsd with (I>2σ (I))	1681	3229
No. refined Param.	100	234
GooF (F^2)	1.253	1.274
R_1 (F) (I>2σ (I))	0.0350	0.0275
wR_2 (F^2) (all Data)	0.0948	0.0800
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001
Largest diff peak/hole /e·Å^{-3}	2.393 / –1.453	0.839 / –2.225

respectively. The 1D polymeric chain of **1** propagates along the crystallographic *c*-axis. The three crystallographically independent $(CH_2)_4Te$ moieties of **2** describe puckered five-membered C_4Te ring structures with one carbon atom in β-position to the tellurium atom showing the largest deviation from the ideal plane (0.301–0.315 Å). The comparison of the carbonate coordination in **1** and **2** with those of the previously known heavy *p*-block element carbonates [3, 4, 14, 15, 17–19] allows the classification of different coordination modes, which are collected together with the related C–O bond lengths in Table 1. The greatest involvement in metal coordination was observed for the polymeric trialkyltin carbonates (type E, entries 1 and 2) [3], which complies with the high propensity of the organotin atoms to be hypercoordinated. In turn, the aryltin and arylantimony carbonates (type A, entries 3 and 4) [4, 17] show the least involvement in the coordination, which coincides with the presence of the intramolecularly coordinated N-donor ligands that effectively reduce the Lewis acidity of the organotin and organoantimony atoms. All other cases including **1** and **2** (entries 5–11) are intermediates of these modes. Because of the lack of symmetry, the C–O bond lengths differ substantially, however, no relation could be established between the divergence of C–O bond lengths and the types of coordination modes. It is interesting to note that the sum of C–O bond lengths varies only marginally in the range from 3.821(9) Å (entry 8, type D) [15] to 3.867(6) Å (entry 5, type D) [18]. This is presumably the reason why the ^{13}C MAS NMR spectroscopic signals of **1** (δ_{iso} = 165.3, entry 10, type D), **2** (δ_{iso} = 164.9, entry 11, type C), $[(Me_3Sn)_2CO_3]_n$ (δ_{iso} = 163.8, entry 1, type E) [3], $[(i Bu_3Sn)_2CO_3]_n$ (δ_{iso} = 163.3, entry 2, type E) [3] and $[(4\text{-}MeOC_6H_4)_2TeOSnt Bu_2CO_3]_2$ (δ_{iso} = 165.6, entry 1, type E) [19] are very similar. Nonetheless, the difference of the coordination types is reflected by vibrational spectroscopy [38]. The IR spectra of **1** and **2** show strong absorptions at 1483 and 1305 as well as 1640 and 1333 cm^{-1}, respectively, which were assigned to asymmetric and symmetric C–O stretching vibrations. Similar absorptions are absent in the IR spectra of the closely related $IMe_2TeOTeMe_2I$ and $I(CH_2)_4TeOTe(CH_2)_4OTe(CH_2)_4I$ [34]. The coupling between the asymmetric and symmetric C–O stretching vibration is smaller in **1** (178 cm^{-1}) than **2** (307 cm^{-1}), which complies with the fact that the coordination of the carbonate to the tellurium atoms of **1** (entry 10, type D) is stronger than that of **2** (entry 11, type C). The thermal analysis of **2** indicates a mass loss between 20 and 110 °C that is associated with the release of the two mole equivalents of water. The mass loss related with the liberation of CO_2 slowly starts at approximately 110 °C for **1** and **2**, however, the mass loss incident appears to be overran by the thermal decomposition, which starts before the melting points of 218 (**1**) and 183 °C (**2**) are reached.

Compounds **1** and **2** are readily soluble in D_2O, where they undergo electrolytic dissociation to give basic solutions. The ^{125}Te NMR spectra of **1** and **2** show broad signals at $\delta = 1049.9$ ($\omega_{1/2} = 1200$ Hz) and 1271.6 ($\omega_{1/2} = 998$ Hz). The carbonate ions give rise to ^{13}C NMR spectroscopic resonances at $\delta =$ 163.5 and 163.7, respectively.

Experimental Section

General

Me_2TeI_2 and $(CH_2)_4TeI_2$ were prepared according to the literature [20, 21]. The solution NMR spectra were recorded at 500.16 (^{1}H), 125.77 (^{13}C) and 126.26 MHz (^{125}Te) with a Jeol Eclipse+ 500 FT and a Jeol JNM-LA 400 FT spectrometer. Chemicals shift are referenced to $TeMe_2$ and $SiMe_4$. The ^{13}C and ^{125}Te CP MAS NMR spectra were obtained at 100.53 and 126.26 MHz with a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 5 and 10 kHz. Recycle delays of 5 (^{13}C) and 30 s (^{125}Te) were used and typically 5000 to 10000 transitions were accumulated to obtain reasonable signal-to-noise ratios. Referencing against $SiMe_4$ (^{13}C) and $TeMe_2$ (^{125}Te) was achieved with solid adamantane (δ 38.56 / 29.50) and $Te(OH)_6$ (δ_{iso} 692.2 / 685.5) as secondary references. The ^{125}Te isotropic chemical shifts δ_{iso} were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies. Infrared spectra were recorded using a Nexus FT-IR spectrometer with a Smart DuraSamplIR. The thermal analyses were carried out with a Netzsch Thermo Microbalance TG 209. Microanalyses were obtained with a Vario EL elemental analyser.

Syntheses

$(Me_2TeOTeMe_2CO_3)_n$ (1) and $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH$ (2): A solution of the appropriate dialkyltellurium(IV) dihydroxide, prepared in situ from the corresponding R_2TeI_2 (620 mg for R = Me and 660 mg for R = C_4H_8; 1.5 mmol) [20, 21] and freshly prepared Ag_2O (1.50 g, 10.7 mmol) in water (50 mL), was purged with carbon dioxide for 45 min. Evaporation of the water yielded **1** and **2** as colourless and slightly brown solids in nearly quantitative yield. Colourless crystals of **1** and **2**·$2H_2O$ were obtained after recrystallisation from water and slow evaporation of an aqueous solution, respectively.

1: Yield 251 mg, 0.64 mmol; 86 %. Mp. 218 °C (dec.). $C_5H_{12}O_4Te_2$ (391.35): C, 15.35; H, 3.09; Found: C, 14.95, H, 3.23 %. **^{1}H NMR** (D_2O): $\delta = 2.46$. **^{13}C NMR** (D_2O): $\delta = 163.5$ (CO_3), 20.8 ($^1J(^{13}C–^{125}Te)$ 96 Hz; CH_3). **^{125}Te NMR** (D_2O): $\delta = 1049.9$ ($\omega_{1/2} = 1200$ Hz). **^{13}C MAS NMR** $\delta_{iso} = 165.3$ (CO_3), 25.5, 24.6, 22.8, 21.0. **^{125}Te MAS NMR** $\delta_{iso} = 1192$, 1026. **IR** (KBr): $\tilde{\nu} = $ 3021m, 3009m, 2940m,sh, 2924m, 2788w, 2520w, 2461w, 2441w, 2419w, 2341w, 1793w, 1755m, 1727m, 1698w, 1483s, 1413s,sh, 1305s, 1236s, 1225s, 1210s, 1106m, 1073m, 1045s, 905m, 889m, 861m, 843s, 823sh, 715m, 687s, 635vs, 562s, 548s, 439s cm^{-1}.

2: Yield 304 mg, 0.46 mmol; 91 %. Mp. 183 °C (dec.). $C_{13}H_{26}O_6Te_3$ (667.89): C, 23.62; H, 3.96. Found: C 23.54, H 3.68 %. **^{1}H NMR** (D_2O): $\delta = 3.02$ (t, 12 H), 2.44 (q, 12 H). **^{13}C NMR** (D_2O): $\delta = 163.7$ (1C; CO_3), 45.9 (($^1J(^{13}C–^{125}Te)$ 86 Hz; 6C; CH_2), 32.3 (6 C; CH_2). **^{125}Te NMR** (D_2O): $\delta = 1271.6$ ($\omega_{1/2} = 998$ Hz). **^{13}C MAS NMR** $\delta_{iso} =$ 164.9, 48.4, 32.6. **^{125}Te MAS NMR** $\delta_{iso} = 1215$, 1173, 1131. **IR** (KBr): $\tilde{\nu} = $ 3505m, 3431m,sh, 3316m, 3218m, 3001m, 2954m, 2929m, 2859m, 2369w, 1754vw, 1734vw, 1675m, 1640s, 1463s, 1451s, 1438s,sh, 1412s, 1401s, 1333vs, 1308s, 1248m, 1190m, 1150m, 1104m, 1090m, 1047m, 1039m, 1033m, 956m, 947m, 871w, 849m, 818m, 753m,sh, 744m, 707m, 665vs, 583m, 576m,sh, 552s cm^{-1}.

X-ray Crystallography

Intensity data were collected with Bruker SMART 1000 CCD (**1**) and STOE IPDS 2T (**2**·$2H_2O$) diffractometers with graphite-monochromated Mo-K_α (0.7107 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002 [39]. Full-matrix least-squares refinements on F^2, using all data were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model and were refined isotropically. The hydrogen atoms attached to the oxygen atoms of **2**·$2H_2O$ were located during the last refinement cycle and refined isotropically. Crystal and refinement data are collected in Table 2. Figures were created using DIAMOND [40]. Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC numbers CCDC-748957 (**1**) and CCDC-748958 (**2**·2 H_2O). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgement

The *Deutsche Forschungsgemeinschaft* (DFG) is gratefully acknowledged for financial support.

References

[1] a) A.-A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951; b) M. Shi, Y.-M. Shen, *Curr. Org. Chem.* **2003**, *7*, 737; c) G. W. Coates, D. R. Moore, *Angew. Chem. Int. Ed.* **2004**, *43*, 6618; d) I. Omae, *Catal. Today* **2006**, *115*, 33; e) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365; f) D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388; g) T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312.

[2] a) D. H. Gibson, *Chem. Rev.* **1996**, *96*, 2063; b) X. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27.

[3] J. Kümmerlen, A. Sebald, H. Reuter, *J. Organomet. Chem.* **1992**, *427*, 309.

[4] Z. Padělková, H. Vaňkátová, I. Císařová, M. S. Nechaev, T. A. Zevaco, O. Walter, A. Růžička, *Organometallics* **2009**, *28*, 2629.

[5] a) H. Reuter, Ph. D. Thesis, University of Bonn, Germany **1986**; b) D. Ballivet-Tkatchenko, R. Burgat, S. Chambrey, L. Plasseraud, P. Richard, *J. Organomet. Chem.* **2006**, *691*, 1498.

[6] G.-L. Zheng, J.-F. Ma, J. Yang, Y.-Y. Li, X.-R. Hao, *Chem. Eur. J.* **2004**, *10*, 3761.
[7] T. Fujinami, S. Sato, S. Skai, *Chem. Lett.* **1981**, 749.
[8] A. G. Davies, P. G. Harrison, *J. Chem. Soc. C* **1967**, 1313.
[9] J.-C. Choi, T. Sakakura, T. Sako, *J. Am. Chem. Soc.* **1999**, *121*, 3793.
[10] D. Ballivet-Tkatchenko, O. Douteau, S. Stutzmann, *Organometallics* **2000**, *19*, 4563.
[11] D. Ballivet-Tkatchenko, T. Jerphagnon, R. Ligabue, L. Plasseraud, D. Poinsot, *Appl. Catal. A* **2003**, *255*, 93.
[12] D. Ballivet-Tkatchenko, S. Chambrey, R. Keiski, R. Ligabue, L. Plasseraud, P. Richard, H. Turunen, *Catal. Today* **2006**, *115*, 80.
[13] D. Ballivet-Tkatchenko, H. Chermette, L. Plasseraud, O. Walter, *Dalton Trans.* **2006**, 5167.
[14] S.-F. Yin, J. Maruyama, T. Yamashita, S. Shimada, *Angew. Chem.* **2008**, *120*, *Angew. Chem. Int. Ed.* **2008**, *47*, 6590.
[15] H. J. Breunig, L. Königsmann, E. Lork, M. Nema, N. Philipp, C. Silvestru, A. Soran, R. A. Varga, R. Wagner, *Dalton Trans.* **2008**, 1831.
[16] S. Shimada, S. Yin, 5,6,7,12-tetrahydrodibenzo[c,f][1,5]azastibocines as carbon dioxide sensors and their preparation, Japanese patent application JP 2008255049 A, **2008**.
[17] L. Dostál, R. Jambor, A. Růžiĉka, M. Erben, R. Jirásko, E. Cernoškova, J. Holeĉek, *Organometallics* **2009**, *28*, 2633.
[18] G. Lang, K. W. Klinkhammer, C. Recker, A. Schmidt, *Z. Anorg. Allg. Chem.* **1998**, *624*, 689.
[19] J. Beckmann, D. Dakternieks, A. Duthie, N. A. Lewcenko, C. Mitchell, *Angew. Chem.* **2004**, *116*, *Angew. Chem. Int. Ed.* **2004**, *43*, 6683.
[20] R. H. Vernon, *J. Chem. Soc.* **1920**, *117*, 86.
[21] P. C. Srivastava, S. Bajpai, C. Ram, R. Kumar, R. J. Butcher, *J. Organomet. Chem.* **2007**, *692*, 2482.
[22] M. M. Mangion, M. R. Smith, E. A. Meyers, *J. Heterocycl. Chem.* **1973**, *10*, 543.
[23] N. W. Alcock, W. D. Harrison, *J. Chem. Soc., Dalton Trans.* **1982**, 1421.
[24] N. W. Alcock, W. D. Harrison, C. Howes, *J. Chem. Soc., Dalton Trans.* **1984**, 1709.
[25] K. Kobayashi, N. Deguchi, E. Horn, N. Furukawa, *Angew. Chem.* **1998**, *110*, *Angew. Chem. Int. Ed.* **1998**, *37*, 984.
[26] H. W. Roesky, R. J. Butcher, S. Bajpai, P. C. Srivastava, *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *161*, 135.
[27] K. Kobayashi, K. Tanaka, H. Izawa, Y. Arai, N. Furukawa, *Chem. Eur. J.* **2001**, *7*, 4272.
[28] K. Kobayashi, H. Izawa, N. Furukawa, K. Yamaguchi, E. Horn, *Chem. Commun.* **2001**, 1428.
[29] R. Oilunkaniemi, R. S. Laitinen, M. Ahlgrén, *Z. Naturforsch.* **2001**, *56b*, 215.
[30] J. Beckmann, D. Dakternieks, A. Duthie, N. A. Lewcenko, C. Mitchell, M. Schürmann, *Z. Anorg. Allg. Chem.* **2005**, *631*, 1856.
[31] T. M. Klapötke, B. Krumm, P. Mayer, K. Polborn, I. Schwab, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2677.
[32] T. M. Klapötke, B. Krumm, P. Mayer, M. Scherr, *Z. Naturforsch.* **2006**, *61b*, 528.
[33] J. Beckmann, J. Bolsinger, A. Duthie, *Aust. J. Chem.* **2008**, *61*, 172.
[34] J. Beckmann, J. Bolsinger, J. Spandl, *J. Organomet. Chem.* **2008**, *693*, 957.
[35] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.
[36] R. Betz, M. Stapel, M. Pfister, F. W. Roeßner, M. M. Reichvilser, P. Klüfers, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2391.
[37] T. Steiner, *Angew. Chem.* **2002**, *114*, *Angew. Chem. Int. Ed.* **2002**, *41*, 49.
[38] a) G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227; b) G. B. Deacon, F. Huber, R. J. Phillips, *Inorg. Chim. Acta* **1985**, *104*, 41.
[39] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.
[40] *DIAMOND V3.1d*, Crystal Impact GbR, K. Brandenburg, H. Putz, **2006**.

Received: September 9, 2009

MANUSCRIPT VIII

11 New Insights into the Formation and Structure of Diaryl Tritellurides

Jens Beckmann, Jens Bolsinger and Andrew Duthie; *Organometallics,* **2009**, 28, 4610-4612

11.1 SYNOPSIS

Diorgano ditellurides, RTeTeR (R=alkyl, aryl), are versatile starting materials in organotellurium chemistry, such as for the preparation of organic charge-transfer complexes and ion-radical salts possessing high conductivity[110]. Usually ditellurides are produced by the reaction of organolithium or organomagnesium reagents with tellurium powder followed by air oxidation. Sometimes rather unstable diorgano tritellurides, RTeTeTeR (R=alkyl, aryl) could be formed by this procedure in varying amounts[111-113].

The number of structurally characterized diorgano tritellurides is still limited to two examples[111,112], and their reactivity remains unexplored[110]. In order to synthesize monoorganotellurium compounds containing a 8-dimethylaminonaphthyl group, a necessary precursor was (8-dimethylaminonaphthyl) ditelluride, for which a procedure similar to that already published by *Singh et al.* was used[114].

It was possible to isolate through fractioned crystallization the ditelluride RTeTeR and the tritelluride RTeTeTeR separately. The yield of the tritelluride depends on the reaction conditions. The ratio between the ditelluride and the tritelluride is dependent on the stoichiometry of 8-dimethylamino-1-naphthyllithium diethyl etherate and Te powder and on the oxidation conditions. Longer oxidation times and the use of pure oxygen instead of air favor higher amounts of the ditelluride.

The tritelluride is only moderately stable in solution and slowly decomposes in solution into elemental Te (as mirror on the glass wall) and unaccounted byproducts. However, in the solid state the tritelluride is indefinitely stable and can be even handled in air for short periods of time.

Consistent with the three crystallographically independent Te sites, the ^{125}Te MAS-NMR spectrum of the tritelluride reveals three signals at approximately the same intensity. Although the ditelluride has two crystallographically independent Te sites, the ^{125}Te MAS-NMR spectrum shows only one broad signal. In solution at room temperature, the tritelluride is characterized by two ^{125}Te NMR signals with an integral ratio of 2:1, whereas the ditelluride shows the expected one signal.

In light of the limited stability of tritellurides in solution at room temperature and the established ^{125}Te NMR parameters, it is proposed that the second of the two ^{125}Te NMR chemical shifts reported for bis-2-(p-tolyliminomethyl)phenyl tritelluride is erroneously assigned and due to the corresponding ditelluride[115].

In an effort to suppress the decomposition, a low-temperature ^{125}Te NMR spectrum of an analytically pure crystalline sample of the tritelluride was recorded in CD_2Cl_2 at -90 °C. The spectrum shows two major signals at with an integral ratio of 2:1 for the tritelluride. Besides the two major signals of the tritelluride the spectrum reveals three signals, which were assigned to the ditelluride and bis[8-(dimethylamino)naphthyl] tetratelluride, respectively. The tritelluride RTeTeTeR is apparently in equilibrium with the ditelluride RTeTeR and the tetratelluride RTeTeTeTeR. This is the first spectroscopic evidence for the existence of tetratellurides.

Such an equilibrium state implies that the Te-Te bonds are kinetically labile on the laboratory time scale. This finding is comparable with the observed formation of asymmetric species in a mixture of two different diaryl ditellurides[116] or the reversible dissociation of mixed valent tellurenyl(II) bromides into the respective monomers[117].

11.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann.

X-Ray Crystallography: Prof. Dr. Jens Beckmann
^{125}Te MAS-NMR spectra and analysis thereof: Dr. Andrew Duthie

4610 *Organometallics* **2009,** *28,* 4610–4612
DOI: 10.1021/om900494d

ORGANOMETALLICS
Note

New Insights into the Formation and Structure of Diaryl Tritellurides

Jens Beckmann,*[,a] Jens Bolsinger,[a] and Andrew Duthie[b]

[a]*Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstrasse 34-36, 14195 Berlin, Germany, and* [b]*School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia*

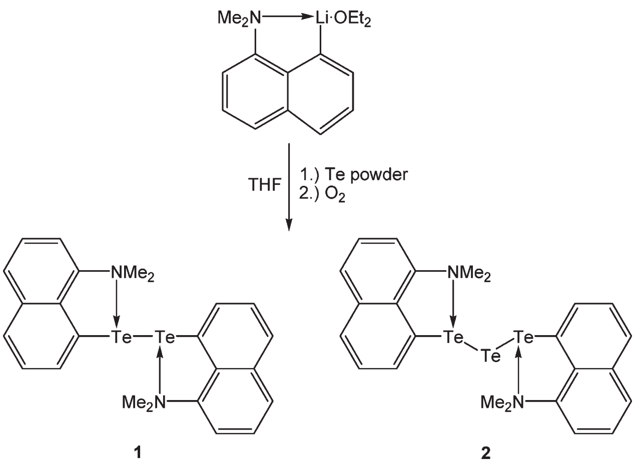
Received June 11, 2009

*Summary: The reaction of 8-dimethylamino-1-naphthyllithium diethyl etherate with tellurium powder and subsequent O_2 oxidation was reinvestigated. Besides the previously reported bis[8-(dimethylamino)naphthyl] ditelluride (**1**), the new bis[8-(dimethylamino)naphthyl] tritelluride (**2**) was isolated in 42% yield and fully characterized. Low-temperature ^{125}Te NMR spectroscopy provides evidence to suggest that analytically pure **2** is in equilibrium with **1** and bis[8-(dimethylamino)naphthyl] tetratelluride (**2a**).*

Diorgano ditellurides, RTeTeR (R = alkyl, aryl), are versatile starting materials in organotellurium chemistry, such as for the preparation of organic charge-transfer complexes and ion-radical salts possessing high conductivity.[1] Common routes for the preparation of ditellurides involve the reaction of organolithium or organomagnesium reagents with tellurium powder followed by air oxidation or, alternatively, the reduction of organotellurium(IV) halides. Occasionally, these procedures also give rise to the formation of rather unstable diorgano tritellurides, RTeTeTeR (R = alkyl, aryl), in varying amounts.[2−4]

Although a rational synthesis was developed by the reaction of organotellurenyl(II) halides with telluride ions,[5] the number of structurally characterized diorgano tritellurides is still limited to two examples,[2,3] and their reactivity remains unexplored.[1] Our interest in organotelluroxane chemistry[6] required the preparation of (8-dimethylaminonaphthyl) ditelluride (**1**), for which we used a procedure similar to that already published by Singh et al.[7] Thus, the reaction of 8-dimethylamino-1-naphthyllithium diethyl etherate with Te powder in THF followed by vigorous air oxidation for 10 min provided a reaction mixture consisting of a deeply colored solution containing the ditelluride RTeTeR (**1**) and the tritelluride RTeTeTeR (**2**) in varying ratios (R = $8\text{-}Me_2NC_{10}H_6$). The ratio between **1** and **2** depends on the stoichiometry of 8-dimethylamino-1-naphthyllithium diethyl etherate and Te powder and was determined by integration of the ^{125}Te NMR signals of the crude reaction mixture. For an $8\text{-}Me_2NC_{10}H_6Li\cdot Et_2O$ to Te ratio of 1:1,[7] 1:1.5, and 1:2, the ratio between the ditelluride **1** and the tritelluride **2** varied from 97:3 to 53:47 to 31:69, respectively (Scheme 1). The ratio between **1** and **2** also depends on the oxidation conditions. Longer oxidation times and the use of pure oxygen instead of air favor higher amounts of the ditelluride **1**. Fractional crystallization of these mixtures affords at first pure tritelluride **2** and then pure ditelluride **1** as crystalline solids. Crops of **1** and **2** can be easily distinguished by the characteristic orange and dark red color. The maximum isolated yield of **2** was 42%. Like the three previously reported members of this compound class, the tritelluride **2** is only moderately stable and slowly decomposes in solution into **1**, elemental Te (as mirror on the glass wall), and unaccounted byproducts. The decomposition can be monitored by ^{125}Te NMR spectroscopy. However, in the solid state **2** is indefinitely stable and can be even handled in air for short periods of time.

Scheme 1



The molecular structure of **2** is shown in Figure 1, and selected bond parameters are collected in the caption. The essential bond parameters of the ditelluride **1**[7] and the tritelluride **2** are very similar.

The average Te−Te bond lengths of **1** (2.765(1) Å) and **2** (2.760(1) Å) are somewhat longer than in diphenyl ditelluride (2.712(2) Å)[8] and 1-naphthyl ditelluride (2.7110(6) Å).[9]

---

*To whom correspondence should be addressed. E-mail: beckmann@chemie.fu-berlin.de. Fax: ++49-30838- 52440.

[1] Sadekov, I. D.; Minkin, V. I. *Sulfur Rep.* **1997**, *19*, 285.

[2] Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hübner, T. *J. Chem. Soc., Chem. Commun.* **1985**, 1800.

[3] (a) Hamor, T. A.; Al-Salim, N.; West, A. A.; McWhinnie, W. R. *J. Organomet. Chem.* **1986**, *310*, C5. (b) Al-Salim, N.; West, A. A.; McWhinnie, W. R.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2363.

[4] Klapötke, T. M.; Krumm, B.; Nöth, H.; Gálvez-Ruiz, J. C.; Polborn, K.; Schwab, I.; Suter, M. *Inorg. Chem.* **2005**, *44*, 5254.

[5] Maslakov, A. G.; Greaves, M. R.; McWhinnie, W. R.; McWhinnie, S. L. W. *J. Organomet. Chem.* **1994**, *468*, 125.

[6] Beckmann, J.; Finke, P.; Hesse, M.; Wettig, B. *Angew. Chem., Int. Ed.* **2008**, *47*, 9982.

[7] Menon, S. C.; Singh, H. B.; Jasinski, J. M.; Jasinski, J. P.; Butcher, R. J. *Organometallics* **1996**, *15*, 1707.

[8] Llabres, G.; Dideberg, O.; Dupont, L. *Acta Crystallogr.* **1972**, *B28*, 2438.

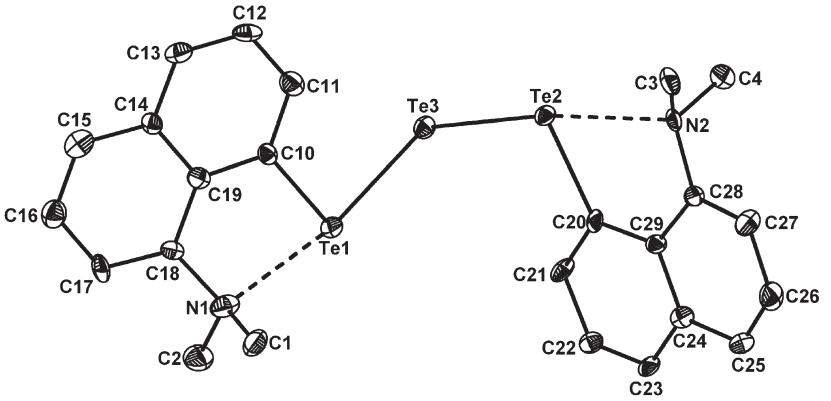


Figure 1. Molecular structure of **2** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, deg]: Te1−C10 2.16(1), Te1−Te3 2.764(1), Te1−N1 2.68(1), Te2−C20 2.16(1), Te2−Te3 2.757(1), Te2−N2 2.66(1), C20−Te2−Te3 99.0(3), Te2−Te3−Te1 105.80(4), C10−Te1−Te3 100.4(3), N1−Te1−Te3 170.5(3), N2−Te2−Te3 169.1(2).

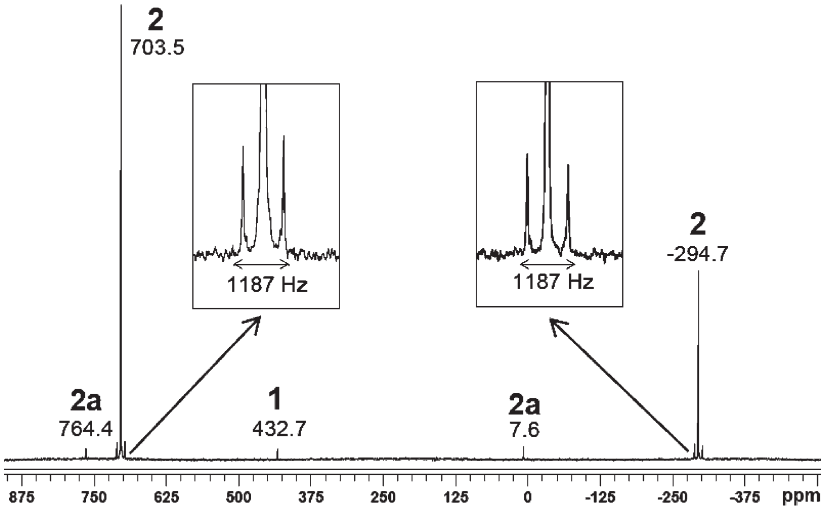


Figure 2. ^{125}Te NMR spectrum (CD_2Cl_2) of **2** at −90 °C.

The Raman spectrum of **2** shows a very intense band at $\tilde{\nu}$ = 172 cm^{-1}, which was assigned to the Te−Te stretching vibrations. Diphenyl ditelluride and 1-naphthyl ditelluride give rise to similar bands at $\tilde{\nu}$ = 202 and 188 cm^{-1}, respectively.[10] Together, the Te−Te bond lengths and stretching vibrations suggest that the Te−Te bonds are weaker in **1** and **2** compared to diaryl ditellurides lacking intramolecular N-coordination. The average Te···N bond length in **2** (2.67(1) Å) is slightly shorter than in **1** (2.721(5) Å). The Te1−Te3−Te2 angle in **2** being 105.80(4)° is close to the expected tetrahedral angle. Unlike **1**, individual molecules of **2** are associated via secondary Te2a···Te3 contacts of 3.750(7) Å in the crystal lattice (symmetry code used to generate equivalent atoms: a = 0.5−x, 0.5+y, 0.5−z), which are presumably the reason for the darker color. Consistent with the three crystallographically independent Te sites, the ^{125}Te MAS NMR spectrum of **2** reveals three signals at δ_{iso} = 731, 597, and −203 with approximately the same intensity.

Although **1** has two crystallographically independent Te sites, the ^{125}Te MAS NMR spectrum shows only one broad signal at δ_{iso} = 430 with a $\omega_{1/2}$ = 30. In solution at room temperature, the tritelluride **2** is characterized by two ^{125}Te NMR signals with an integral ratio of 2:1 at δ = 717.7 and −243.5 ($CDCl_3$), 711.3 and −260.3 (CD_2Cl_2), 716.5 and −249.8 (D_8-THF), and 717.5 and −249.6 (D_8-toluene). Notably, the signals at around δ = −250 are slightly broader than those at around δ = 715. In solution at room temperature, the ditelluride **1** is characterized by one ^{125}Te NMR signal at δ = 456.3 ($CDCl_3$), 454.1 (CD_2Cl_2), 448.2 (D_8-THF), and 454.3 (D_8-toluene). In light of the limited stability of tritellurides in solution at room temperature and the established ^{125}Te NMR parameters of **1** and **2**, we propose that the second of the two ^{125}Te NMR chemical shifts reported for bis-2-(*p*-tolyliminomethyl)phenyl tritelluride (δ = 740.5 and 432.1) is erroneously assigned and due to the corresponding ditelluride.[5] In an effort to suppress the decomposition, a low-temperature ^{125}Te NMR spectrum of an analytically pure crystalline sample of **2** was recorded in CD_2Cl_2 at −90 °C (acquisition time 2 h), which is shown in Figure 2. The spectrum shows two slightly shifted signals at δ = 703.5 and −294.7 with an integral ratio of 2:1 for the tritelluride **2**. Both signals show $^{1}J(^{125}\text{Te}-^{125}\text{Te})$ couplings of 1187 Hz, which are substantially larger than those of unsymmetrical diaryl ditellurides ranging between 170 and

---

[9] Lang, E. S.; Burrow, R. A.; Silveira, E. T. *Acta Crystallogr.* **2002**, *C58*, o397.

[10] Joo, S.-W. *J. Raman Spectrosc.* **2006**, *37*, 1244.

207 Hz.[11] Besides the two major signals of **2** (total integral 96%), the spectrum reveals three signals at $\delta = 432.7$, 764.4, and 7.6, which were assigned to the ditelluride **1** (integral 1.4%) and bis[8-(dimethylamino)naphthyl] tetratelluride (**2a**, total integral 2.6%), respectively. The tritelluride RTeTeTeR (**2**) is apparently in equilibrium with the ditelluride RTeTeR (**1**) and the tetratelluride RTeTeTeTeR (**2a**) with a ratio of 1:0.02:0.02 (R = 8-$Me_2NC_{10}H_6$). While the first diorganoditelluride diselenide, $(Me_3Si)_3CTeSeSeTeC(SiMe_3)_3$ has already been reported,[1] this is the first spectroscopic evidence for the existence of tetratellurides. An equilibrium state between **1**, **2**, and **2a** implies that the Te−Te bonds are kinetically labile on the laboratory time scale. This idea is supported by the observation that mixtures of two different diaryl ditellurides RTeTeR and R′TeTeR′ form asymmetric species RTeTeR′ (e.g., R = 4-ClC_6H_4, R′= 4-MeC_6H_4)[11] and that the mixed valent tellurenyl(II) bromides $R_2TeTeBr_2R$ undergo reversible dissociation into RTeBr monomers (R = Ph, 2,6-$Mes_2C_6H_3$).[12]

Experimental Section

General Procedures. Dimethylnaphthylamine, butyllithium, and Te powder were purchased from commercial sources and used as received. The ^1H, ^{13}C and ^{125}Te NMR spectra were recorded using a Jeol GX270 spectrometer and are referenced to $SiMe_4$ (^1H, ^{13}C) and Me_2Te (^{125}Te). The ^{125}Te MAS NMR spectra were obtained using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 7 and 10 kHz (experimental conditions: pulse 6 s (30), recycle delay 60 s). The isotropic chemical shifts (δ_{iso}) were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced against Me_2Te using solid $Te(OH)_6$ as the secondary reference (δ_{iso} 692.2 / 685.5). Raman spectra were recorded using a Bruker RFS 100/S spectrometer with a Nd:YAG laser. Microanalyses were obtained from a Vario EL elemental analyzer.

Procedure Optimized for the Synthesis of 2. Tellurium powder (3.06 g, 24.0 mmol) was added in small portions to a solution of 8-$Me_2NC_{10}H_6Li \cdot Et_2O$ (3.0 g, 12.0 mmol) in dry THF (80 mL). The deep red mixture was stirred overnight and was then purged with a vigorous stream of air for 10 min. The dark gray residue was separated by filtration, half of the solvent was removed under vacuum, and dry MeCN (20 mL) was added to the remaining dark red solution. Fractional crystallization under exclusion of light and air afforded analytically pure **2** as deep red crystals, which were separated by filtration. Concentration of the mother liqueur provided at first a crop consisting of a mixture of **1** and **2** (520 mg) and then a crop of analytically pure **1** as orange crystals, which were also separated by filtration.

2 (1.82 g, 2.52 mmol; 42%): ^1H NMR ($CDCl_3$): δ 8.34 (d, 2H; Ar); 7.70 (dd, 4H; Ar); 7.41 (t, 2H; Ar); 7.35 (m, 4H; Ar); 2.81(s, 12H; NCH_3). ^{13}C NMR ($CDCl_3$): δ 149.4, 138.0, 134.8, 131.9, 127.6, 126.8, 126.6, 125.4, 118.1, 103.34 (Ar), 48.2 (NCH_3). ^{125}Te-NMR ($CDCl_3$): δ 717.7 (s, 2Te) and −243.5 (s, 1Te). Raman: $\tilde{\nu}$ 3046s, 3023sh, 2989w, 2975w, 2936m, 2900w, 2879w, 2863w, 2829w, 2783w, 1584w, 1554m, 1489w, 1449w, 1419w, 1359sh, 1352s, 1142w, 1078w, 1020w, 857w, 789w, 717w, 599w, 533w, 492w, 345w, 324w, 254w, 233w, 213w, 172vs, 153s, 120m, 96s. Anal. Calcd for $C_{24}H_{24}N_2Te_3$ (723.26): C 39.86, H 3.34, N 3.87. Found: C 40.15, H 3.28, N 3.84.

1 (440 mg, 0.74 mmol; 12%): ^1H and ^{13}C NMR spectra were identical to those published.[7] ^{125}Te NMR ($CDCl_3$): δ 456.3. Anal. Calcd for $C_{24}H_{24}N_2Te_2$ (595.73): C 48.39, H 4.06, N 4.70. Found: C 48.13, H 4.19, N 4.58.

Crystallography. Crystal data and structure solution: $C_{24}H_{24}N_2Te_3$, $M_r = 723.25$, monoclinic, $P2_1/n$, $a = 9.661(5)$ Å, $b = 9.432(5)$ Å, $c = 25.760(5)$ Å, $\beta = 94.358(5)°$, $V = 2341(2)$ Å^3, $Z = 4$, $D_x = 2.053$ Mg/m^3, $F(000) = 1352$, $\mu = 3.727$ mm^{-1}, $T = 173$ K. Intensity data were collected on a Bruker SMART 1000 CCD diffractometer fitted with Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.71073$ Å) to a maximum of $\theta_{max} = 26.37°$ via ω scans (completeness 99.5% to θ_{max}). Data were reduced and corrected for absorption using the programs SAINT and SADABS.[13] The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX 2002.[14] Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model (including free rotation about C−C) and were refined isotropically. $R_1 = 0.0567$ for 3220 [$I > 2\sigma(I)$] and $wR_2 = 0.1762$ for 4759 independent reflections. GooF = 1.108. The max. and min. residual electron densities were 1.580 and − 3.127 e Å^{-3}. The figure was prepared using the DIAMOND program.[15] Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 737075 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgment. Mrs. Irene Brüdgam (Freie Universität Berlin) is thanked for the X-ray data collection. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

---

[11] Granger, P.; Chapelle, S.; McWhinnie, W. R.; Al-Rubaie, A. *J. Organomet. Chem.* **1981**, *220*, 149.

[12] Beckmann, J.; Hesse, M.; Poleschner, H.; Seppelt, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 8277.

[13] *SMART*, *SAINT* and *SADABS*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1999.

[14] Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

[15] *DIAMOND* V2.1d; Crystal Impact, K. Brandenburg & M. Berndt GbR , **2002**.

MANUSCRIPT IX

12 Intramolecularly Coordinated Telluroxane Clusters and Polymers

Jens Beckmann, Jens Bolsinger and Andrew Duthie; *Chem. Eur. J.,* **2011**, 17, 930-940

12.1 SYNOPSIS

Despite the pioneering work of *Lederer* nearly a century ago[11], little new information concerning this elementary compound class was published thereafter. Most previously known tellurinic acids, $[RTe(O)(OH)]_n$ or their corresponding anhydrides $[RTeO_{1.5}]_n$, are ill-defined, amorphous substances with random polymeric structures. However, the preparation of the first well-defined molecular tellurinic acid $[2,6\text{-}Mes_2C_6H_3Te(O)(OH)]_2$ (Mes=mesityl) by a base hydrolysis route using the kinetic stabilization of a bulky *m*-terphenyl substituent, which limits the condensation and aggregation process, was achieved in our work group[51].

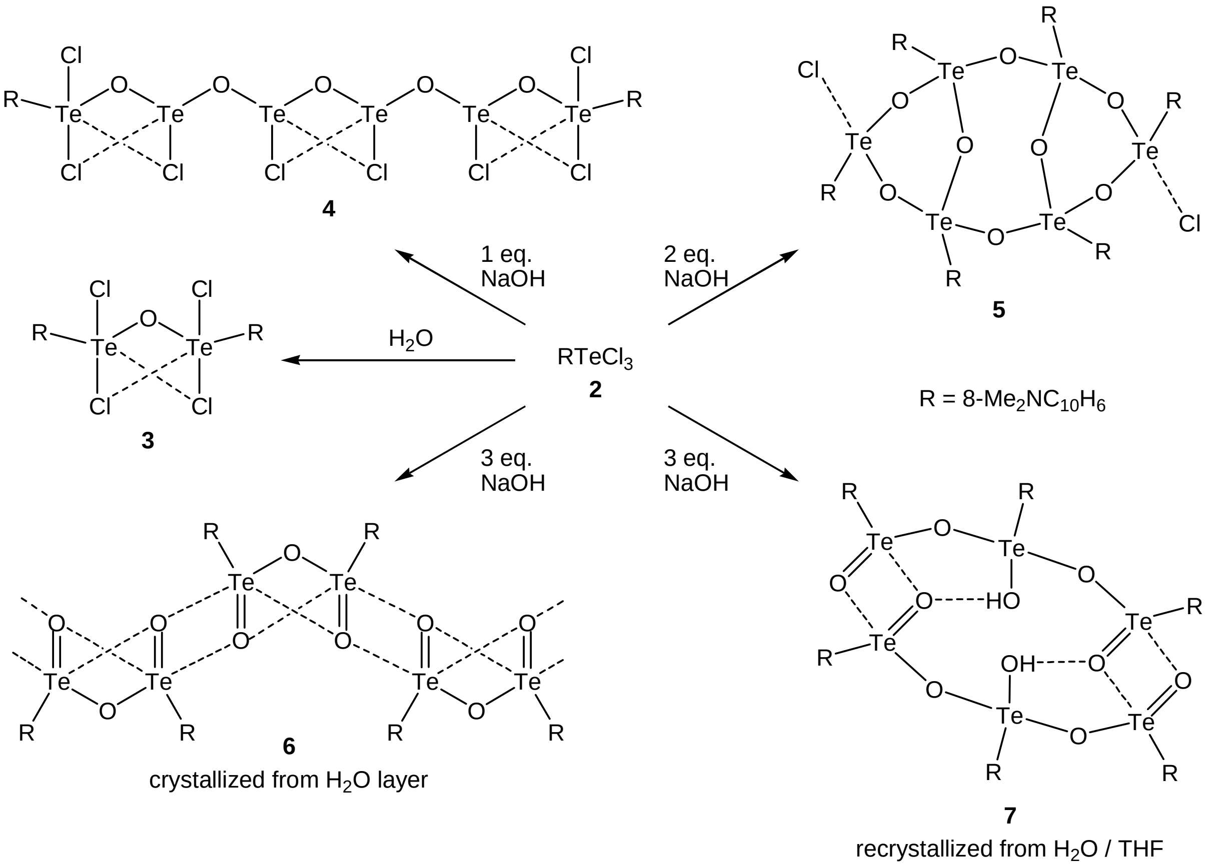
Therefore, the effect of the intramolecular coordination on the results of a similar base hydrolysis route was studied. The base hydrolysis of an intramolecularly coordinated aryltellurium trichloride containing a rigid N donor ligand, namely, the 8-dimethylaminonaphthyl substituent, turned out to be a rational approach for the synthesis of a series of well-defined telluroxane clusters and polymers.

The aryltellurenyl chloride $8\text{-}Me_2NC_{10}H_6TeCl$ and aryltellurium trichloride $8\text{-}Me_2NC_{10}H_6TeCl_3$ were generally obtained by a stoichiometrically controlled chlorination of the intramolecularly coordinated diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$[114,118] with SO_2Cl_2.

The aryltellurenyl monochloride is a polymorph, crystallizing from MeOH in a monoclinic and from $CHCl_3$ in a triclinic modification. The monoclinic and triclinic modifications comprise two and four crystallographically independent, albeit similar conformers, which give rise to the formation of dimers through secondary Te···Te interactions, whereas the aryltellurium trichloride forms centrosymmetric dimers through secondary Te···Cl interactions.

The average bond length of Te-Cl points to a considerable *trans*-effect of the N donor ligand, since the aryltellurenyl monochloride comprises a significantly longer Te-Cl average bond length than that of the kinetically stabilized aryltellurenyl chloride, $2,4,6\text{-}t\text{-}Bu_3C_6H_2TeCl$[119]. The equatorial and axial Te-Cl bond lengths of the aryltellurenyl trichloride are somewhat shorter than the average in the aryltellurenyl monochloride, which is probably due to the higher Lewis acidity.

The hydrolysis experiments of the aryltellurium trichloride 8-$Me_2NC_{10}H_6TeCl_3$ were performed in a two-layer system consisting of chloroform and water or aqueous sodium hydroxide solutions, respectively (Scheme 10).



R = 8-$Me_2NC_{10}H_6$

crystallized from H_2O layer

recrystallized from H_2O / THF

Scheme 10: Base hydrolysis of 8-$Me_2NC_{10}H_6TeCl_3$

In the absence of base, the hydrolysis of the aryltellurenyl trichloride provided the dinuclear telluroxane (8-$Me_2NC_{10}H_6Te)_2OCl_4$. The average Te-O bond length and Te-O-Te angle agrees well with the average values found in $[(4\text{-}Me_2NC_6H_4)_2Te]_2OCl_2$[64]. Two of the four Te-Cl bonds are involved in intramolecular secondary Te···Cl contacts with the respective adjacent tellurium atom.

The hydrolysis of the aryltellurium trichloride 8-$Me_2NC_{10}H_6TeCl_3$ with 1 equivalent NaOH gave rise to the formation of the hexanuclear telluroxane (8-$Me_2NC_{10}H_6Te)_6O_5Cl_8$. However, the size of the obtained crystals and possible twinning preluded the establishment of a crystal structure. Based on the elemental analysis and the spectroscopic data an open-chain hexanuclear structure is proposed for this telluroxane. This proposal is consistent with the established solid state structures of the further base hydrolysis product [(8-$Me_2NC_{10}H_6Te)_2O_3]_n$ (see below) and the structures of (8-$Me_2NC_{10}H_6Te)_2OCl_4$ and [(4-$Me_2NC_6H_4)_2Te]_2OCl_2$[64].

The hydrolysis with 2 equivalent of NaOH produced another hexanuclear telluroxane (8-$Me_2NC_{10}H_6Te)_6O_8Cl_2\cdot 8CHCl_3$, comprising a tricyclic arrangement of the telluroxane ring, in a very low yield. A much better yield was obtained by the reaction of the trichloride 8-$Me_2NC_{10}H_6TeCl_3$ with (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$.

The Te-O bond lengths cover a large range, with the average being close to the average single bond length of polymeric [(4-$MeOC_6H_4)_2TeO]_n$[19]. The average tellurium chlorine bond length is significantly longer than the respective average values of the trichloride 8-$Me_2NC_{10}H_6TeCl_3$, suggesting a rather ionic Te···Cl bond.

The hydrolysis of the aryltellurium trichloride 8-$Me_2NC_{10}H_6TeCl_3$ with 3 equivalent of NaOH gave two products, namely [(8-$Me_2NC_{10}H_6Te)_2O_3]_n$ and (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$. Slow evaporation of the aqueous layer yielded the product [(8-$Me_2NC_{10}H_6Te)_2O_3\cdot 7/3\ H_2O]_n$, whereby the nearly complete removal of the water under vacuum and recrystallization of the residue from THF/hexane afforded the product (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2\cdot 4THF\cdot 6H_2O$.

These compounds can be regarded as condensation products of the same elusive aryltellurinic acid and are only reasonably soluble in polar solvents, such as water and THF. They are interconvertible by crystallization from H_2O and THF/hexane, respectively, and give identical spectra in solution. The fact that only one signal was found in the ^{125}Te NMR spectrum in D_2O suggests that the aggregation and disaggregation processes are fast on the NMR spectroscopic time scale. The low temperature ^{125}Te NMR spectrum ([D_4]THF, -80 °C) indicates that the aggregation and disaggregation processes cannot entirely be frozen under these conditions. An osmotic molecular weight determination points to an average degree of aggregation of 2.5.

Consistently, the ESI-TOF MS spectrum reveals indicative cations with up to three tellurium atoms, but surprisingly, a mass cluster was also found for the cation $[(RTe)_3O_5]^+$, which apparently suggests that one of the three tellurium atoms was oxidized from IV to VI under ESI-TOF MS conditions.

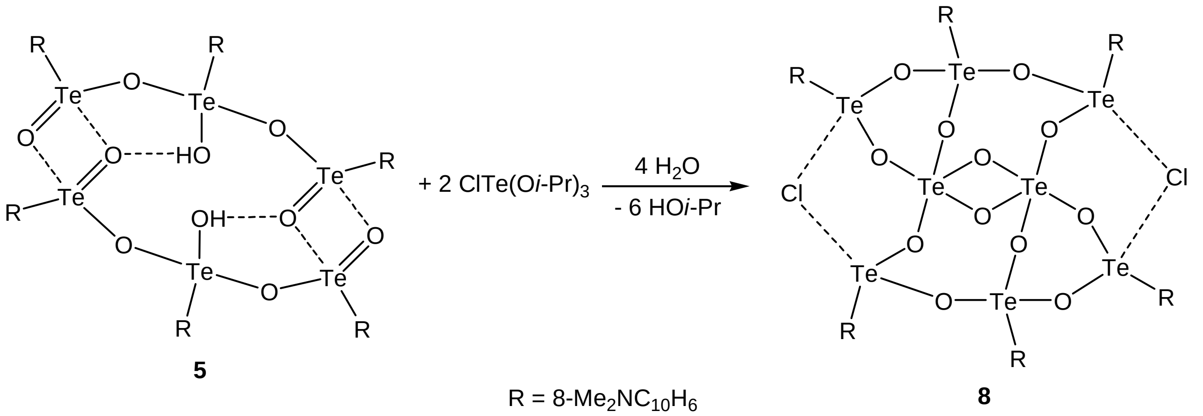
The crystal structure of $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3\cdot 7/3\ H_2O]_n$ features two crystallographically independent, albeit similar 1D Te-O double strings comparable to the supramolecular association of $[(4\text{-}Me_2NC_6H_4)_2Te]_2OCl_2$[64]. The Te-O contacts cover the whole range from elongated formal double bonds, short and long single bonds to secondary interactions.

The molecular structure of $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2\cdot 4THF\cdot 6H_2O$ comprises a centrosymmetric 12-membered telluroxane ring. The majority of primary Te-O contacts have bond lengths that fall in the range of single bonds, however, the Te1-O1 and Te3-O4 bonds are significantly shorter than the majority of Te-O contacts and compare well with the average elongated formal Te-O double bonds of $(Ph_2TeO)_2$[74].

The 8-dimethylaminonaphthyl group ('stiff-arm ligand') is considered to be quite rigid[120]. Surprisingly, the Te···N bond lengths vary substantially in the synthesized compounds. The (average) Te···N bond lengths of the aryltellurenyl(II) chloride and the aryltellurium(IV) trichloride are significantly shorter than those of the diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ and the diaryltritelluride $(8\text{-}Me_2NC_{10}H_6Te)_2Te$[114,118] indicating strong attractive interactions.

Amongst the aryltellurium(IV) compounds, the (average) Te···N bond lengths increase when going from aryltellurium(IV) trichloride to $(8\text{-}Me_2NC_{10}H_6Te)_2OCl_4$, $(8\text{-}Me_2NC_{10}H_6Te)_6O_5Cl_8$, $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2\cdot 4THF\cdot 6H_2O$ and $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3\cdot 7/3\ H_2O]_n$, which suggests that the Lewis acidity of the Te atoms is successively reduced with an increasing degree of hydrolysis and aggregation.

The octanuclear telluroxane cluster $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ was obtained by the reaction of $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ with $ClTe(OiPr)_3$[133] in the presence of water (Scheme 11).



Scheme 11: Synthesis of $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$

It has to be noted that during the course of this work, *Singh et al.* communicated a comparable heptanuclear organotelluroxane cluster $[2\text{-}(PhNN)C_6H_4Te]_6TeO_{11}$ provided by base hydrolysis of an intramolecularly coordinated aryltellurium trichloride[121].

The inorganic Te atoms comprise a four-membered Te_2O_2 ring and the Te···Cl bond length is, like the respective bond length in $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$, significantly longer than the average values of $8\text{-}Me_2NC_{10}H_6TeCl_3$ and $(8\text{-}Me_2NC_{10}H_6Te)_2OCl_4$, which also points to a rather ionic Te···Cl bond.

The water molecules play an integral role for the intermolecular association of $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$. Adjacent molecules are linked in the crystal lattice by two crystallographically independent water molecules via a medium strength hydrogen bonding[71].

Thus, base hydrolysis of the intramolecularly coordinated aryltellurium trichloride $8\text{-}Me_2NC_{10}H_6TeCl_3$ proved to be a rational strategy for the synthesis of the discrete molecular telluroxane clusters $(8\text{-}Me_2NC_{10}H_6Te)_6O_5Cl_8$, $(8\text{-}Me_2NC_{10}H_6Te)_6O_8Cl_2$ and $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ and the well-defined telluroxane polymer $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$, which is the first structurally characterized aryltellurinic anhydride. The degree of aggregation within these compounds is higher than in the kinetically stabilized compounds $[2,6\text{-}Mes_2C_6H_3Te(O)Cl]_2$ and $[2,6\text{-}Mes_2C_6H_3Te(O)(OH)]_2$ prepared by the base hydrolysis of $2,6\text{-}Mes_2C_6H_3TeCl_3$ under similar conditions[51]. Furthermore, the reaction of $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ with $Cl(O\textit{i}\text{-}Pr)_3$ in the presence of water produced the telluroxane cluster $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_{12}$, with the inorganic Te sites being more highly coordinated than the Te atoms of α- and β-TeO_2.

12.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann.

X-Ray Crystallography: Prof. Dr. Jens Beckmann
^{125}Te MAS-NMR spectra and analysis thereof: Dr. Andrew Duthie

CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201002371

Intramolecularly Coordinated Telluroxane Clusters and Polymers

Jens Beckmann,*[a] Jens Bolsinger,[a] and Andrew Duthie[b]

In memory of Professor Dr. med. Hans-Rüdiger Ritter von Baeyer

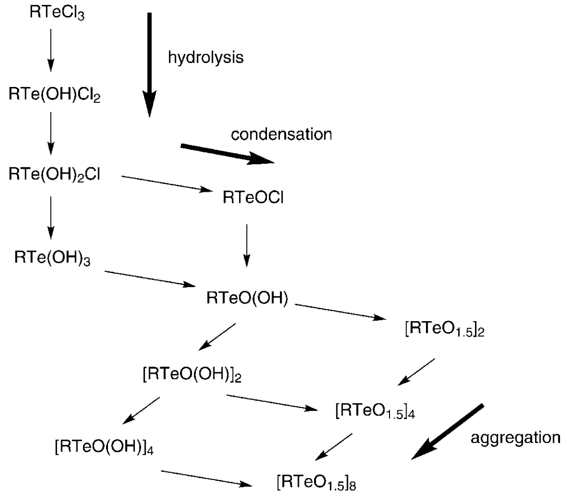
Abstract: The stoichiometrically controlled chlorination of the diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ with SO_2Cl_2 afforded the aryltellurinyl chloride $8\text{-}Me_2NC_{10}H_6TeCl$ (**1**) and the aryltellurium trichloride $8\text{-}Me_2NC_{10}H_6TeCl_3$ (**2**). Alternatively, **1** was obtained by the reaction of the aryltellurenyl diethyldithiacarbamate $8\text{-}Me_2NC_{10}H_6Te(S_2CNEt_2)$ with hydrochloric acid. The base hydrolysis of **2** provided the novel telluroxanes $(8\text{-}Me_2NC_{10}H_6Te)_2OCl_4$ (**3**), $(8\text{-}Me_2NC_{10}H_6Te)_6O_5Cl_8$ (**4**), $(8\text{-}Me_2NC_{10}H_6Te)_6O_8Cl_2$ (**5**), $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$ (**6**) and $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**7**) depending on the reaction conditions applied. The reaction of **7** with $ClTe(OiPr)_3$ in the presence of water gave rise to the telluroxane $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (**8**). The crystal and molecular structures of **1**–**3** and **5**–**8** were determined by X-ray crystallography. The telluroxane clusters and polymers **6**–**8** hold potential as model compounds for alkali tellurite glasses $(M_2O)_x(TeO_2)_{1-x}$ (M = Li, Na, K) for which no precise structural data are available.

Keywords: cluster compounds · hydrolysis · polymers · tellurium · telluroxanes

Introduction

The interest in aryltellurinic(IV) acids dates back to the pioneering work of Lederer nearly 100 years ago, but still little is known about the structure and reactivity of this elementary compound class.[1] Although the corresponding sulfinic and seleninic acids RE(O)OH (E = S, Se; R = alkyl, aryl) are well-defined molecular compounds, most previously known tellurinic acids, $[RTe(O)(OH)]_n$ or their corresponding anhydrides $[RTeO_{1.5}]_n$ are ill-defined, amorphous substances with random polymeric structures. A common route for the preparation of tellurinic acids involves the base hydrolysis of tellurium trichlorides $RTeCl_3$, which usually proceeds with condensation and aggregation when the organic substituents are small (Scheme 1).[2]

Recently, we achieved the preparation of the first well-defined molecular tellurinic acid $[2,6\text{-}Mes_2C_6H_3Te(O)(OH)]_2$ (Mes = mesityl) by the base hydrolysis route using the kinetic stabilisation of a bulky *m*-terphenyl substituent, which limits the condensation and aggregation process.[3]



Scheme 1. Base hydrolysis route for the preparation of tellurinic acids and related anhydrides.

---

[a] Prof. Dr. J. Beckmann, Dipl.-Chem. J. Bolsinger
Institut für Chemie und Biochemie
Freie Universität Berlin, Fabeckstrasse 34–36
14195 Berlin (Germany)
and
Universität Bremen
Institut für Anorganische und Physikalische Chemie
Loebener Strasse Gebäude NW2
Postfach 330440, 28334 Bremen (Germany)
Fax: (+49) 421-218-9863160
E-mail: j.beckmann@uni-bremen.de

[b] Dr. A. Duthie
School of Life and Environmental Sciences
Deakin University
Pigdons Road, Waurn Ponds 3217 (Australia)

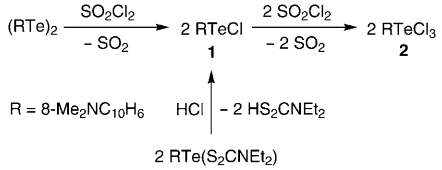
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201002371.

A few years ago, Giolando et al. reported on the structural characterisation of the unique dodecanuclear telluroxane cluster $[Li(THF)_4]\{(iPrTe)_{12}O_{16}Br_4[Li(THF)Br]_4Br\}\cdot 2\,THF$, which was accidentally obtained by the air oxidation of isopropyl hex-1-ynyl telluride in the presence of LiBr in THF.[4] Although a rational synthesis of this compound is still unknown, the oligomeric structure pointed to a potentially rich telluroxane cluster chemistry that remained yet to be explored.

Well-defined telluroxane clusters may be useful as model compounds for alkali tellurite glasses $(M_2O)_x(TeO_2)_{1-x}$ (M = Li, Na, K),[4] which are promising optical materials characterised by a high refractive index, good and wide IR transmittance and a large third-order non-linear optical susceptibility.[5] These remarkable properties arise from the free electron pair in the structural motifs of the Te^{IV} sites. Although the network builder (TeO_2) itself is only a conditional glass former, the alkali modifier (M_2O) gives rise to stable and chemically durable glasses with x in the range from 10 to 25 mol% for M = Li, K and even 35 mol% for M = Na. The modifier can be used to change the number of TeO_4 and TeO_3 structural units and thus, the glass-transition temperature and non-linear optical response. Despite the significant progress in the interpretation of solid-state ^{125}Te NMR spectroscopic data[6] and the structural determination of a few related crystalline phases,[7] precise structural data of tellurite glasses remain elusive due to the amorphous nature of these materials.

In continuation of our previous work,[3] we have now studied the base hydrolysis of an intramolecularly coordinated aryltellurium trichloride containing a rigid N-donor ligand, namely, the 8-dimethylaminonaphthyl substituent, which turned out to be a rational approach for the synthesis of a series of well-defined telluroxane clusters and polymers. During the course of our study, Singh et al. communicated the hydrolysis of a similar intramolecularly coordinated aryltellurium trichloride, namely, $2\text{-}(PhNN)C_6H_4TeCl_3$, which gave rise to the formation of a discrete heptanuclear organotelluroxane cluster $[2\text{-}(PhNN)C_6H_4Te]_6TeO_{11}$ (see below).[8]

Results and Discussion



Scheme 2. Synthesis of $8\text{-}Me_2NC_{10}H_6TeCl_3$ (**2**).

The stoichiometrically controlled chlorination of the intramolecularly coordinated diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$[9] with SO_2Cl_2 proceeded in two steps and afforded aryltellurenyl chloride $8\text{-}Me_2NC_{10}H_6TeCl$ (**1**) and aryltellurium trichloride $8\text{-}Me_2NC_{10}H_6TeCl_3$ (**2**) as orange and slightly yellow crystalline solids in 86 and 39% yield, respectively (Scheme 2). Alternatively, aryltellurenyl chloride **1** was obtained by the reaction of aryltellurenyl diethyldithiacarbamate, $8\text{-}Me_2NC_{10}H_6Te(S_2CNEt_2)$,[10] with hydrochloric acid in 62% yield (Scheme 2). Aryltellurenyl chloride **1** is a polymorph, crystallising from MeOH in a monoclinic modification ($\rho_{calcd} = 1.860\ mg\,cm^{-1}$) and from $CHCl_3$ in a triclinic modification ($\rho_{calcd} = 1.795\ mg\,cm^{-1}$). The monoclinic and triclinic modifications comprise two and four crystallographically independent, albeit similar conformers of **1**.

The molecular structures **1** and **2** are shown in Figures 1 and 2 and selected bond parameters are collected in the caption of the figures.

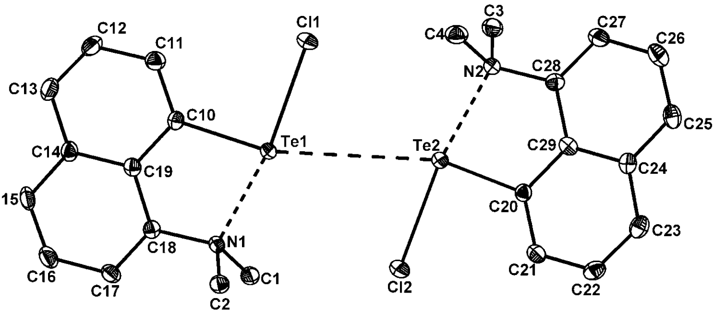


Figure 1. Molecular structure of monoclinic $8\text{-}Me_2NC_{10}H_6TeCl$ (**1**) showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å]: Te1–C10 2.098(4), Te1–Cl1 2.546(2), Te1···N1 2.340(3), Te2–C20 2.107(4), Te2–Cl2 2.526(2), Te2···N2 2.360(3), Te1···Te2 3.87(1).

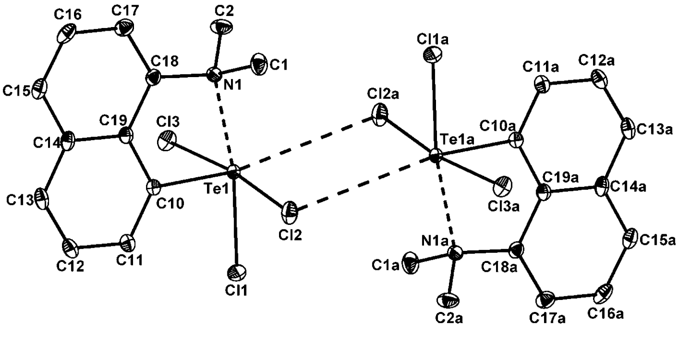
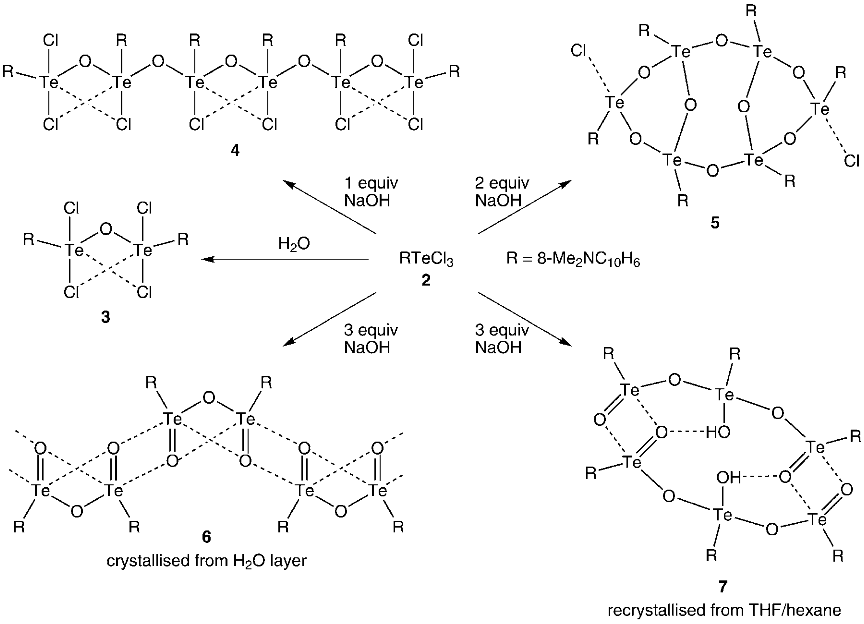


Figure 2. Molecular structure of $8\text{-}Me_2NC_{10}H_6TeCl_3$ (**2**) showing 30% probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: $a = -x, -y, -z$). Selected bond parameters [Å]: Te1–C10 2.105(3), Te1–Cl1 2.442(2), Te1–Cl2 2.529(2), Te1–Cl3 2.488(2), Te1···N1 2.420(3), Te1···Cl2a 3.515(8).

The spatial arrangement of the Te atoms of **1** and **2** is distorted square planar (coordination number (CN) = 2+2, CCl+NTe donor set) and distorted octahedral (CN = 4+2, CCl_3+NCl donor set), respectively. The average Te–Cl bond length of **1** (2.536(2) Å) is significantly longer than that of the kinetically stabilised aryltellurenyl chloride, $2,4,6\text{-}tBu_3C_6H_2TeCl$ (2.334(1) Å),[11] which points to a considerable *trans* effect of the N-donor ligand. Due to the higher Lewis acidity, both the equatorial (2.442(2) Å) and axial (2.488(2) and 2.529(2) Å) Te−Cl bond lengths of **2** are somewhat shorter than the average in **1** (2.536(2) Å). In both polymorphs of aryltellurenyl chloride **1**, the conformers give rise to the formation of dimers through secondary Te···Te interactions that range from 3.7382(4) to 3.8810(5) Å, whereas the aryltellurium trichloride **2** forms centrosymmetric dimers through secondary Te···Cl interactions of 3.515(8) Å in the solid state. The ^{125}Te cross-polarisation magic angle spinning (CP MAS) NMR spectra of (monoclinic) **1** and **2** show signals at $\delta = 845$ and 1355 ppm, respectively. Compounds **1** and **2** are soluble in reasonably polar solvents, such as $CHCl_3$ and THF, but only poorly soluble in less polar solvents, such as hexane and toluene. In solution, **1** and **2** are characterised by ^{125}Te NMR spectroscopic ($CDCl_3$) chemical shifts of $\delta = 1595.0$ and 1317.1 ppm. For comparison, the ^{125}Te NMR spectroscopic chemical shifts of the sterically encumbered aryltellurenyl chloride 2,4,6-tBu$_3$C$_6$H$_2$TeCl ($\delta = 1791.0$ ppm) and the aryltellurium trichloride 2,4,6-tBu$_3$C$_6$H$_2$TeCl$_3$ ($\delta = 1179.0$ ppm) were observed significantly more highfield.[11] While the solution and solid-state ^{125}Te NMR spectroscopic chemical shifts of **2** are reasonably similar, the large discrepancy of **1** is highly unusual. In the absence of another explanation, we tentatively attribute this large chemical-shift discrepancy to the absence and presence of the Te···Te secondary interactions in solution and in the solid state, respectively.



Scheme 3. Base hydrolysis of 8-Me$_2$NC$_{10}$H$_6$TeCl$_3$ (**2**).

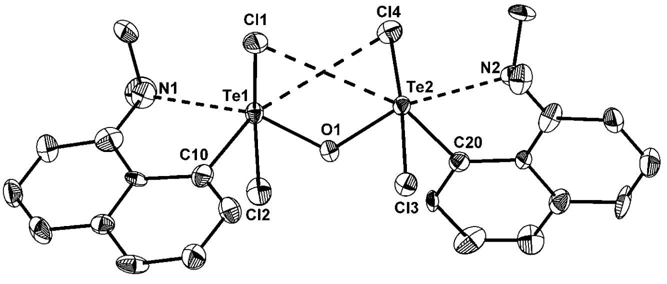


Figure 3. Molecular structure of (8-Me$_2$NC$_{10}$H$_6$Te)$_2$OCl$_4$ (**3**) showing 30 % probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters ([Å] and [°]): Te1−C10 2.12(2), Te1−O1 1.96(1), Te1−Cl1 2.551(5), Te1−Cl2 2.470(5), Te1···Cl4 3.482(5), Te1···N1 2.55(1), Te2−C20 2.11(1), Te2−O1 1.97(1), Te2···Cl1 3.543(6), Te2−Cl3 2.479(4), Te2−Cl4 2.562(5), Te2···N2 2.55(1); Te1-O1-Te2 125.4(5).

The hydrolysis experiments of the aryltellurium trichloride 8-Me$_2$NC$_{10}$H$_6$TeCl$_3$ (**2**) were performed in a two-layer system consisting of chloroform and water or aqueous sodium hydroxide solutions, respectively. The products were isolated either from evaporation of the $CHCl_3$ or the aqueous layer. Sometimes, the products crystallised directly from the reaction mixture and were filtered off.

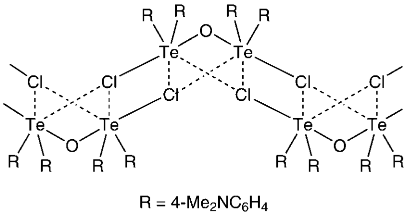
In the absence of base, the hydrolysis of **2** provided the dinuclear telluroxane (8-Me$_2$NC$_{10}$H$_6$Te)$_2$OCl$_4$ (**3**), which directly crystallised from the reaction mixture as high-melting slightly yellow prisms in 51 % yield (Scheme 3). The molecular structure of **3** is shown in Figure 3 and selected bond parameters are collected in the caption of the figure. It comprises two crystallographically independent, albeit similar acentric conformers.

The spatial arrangement of the Te atoms is distorted octahedral (CN = 4+2, COCl$_2$+NCl donor set). The average Te−O bond length of 1.97(1) Å is slightly shorter than the average 'single bond lengths' observed for polymeric [(4-MeOC$_6$H$_4$)$_2$TeO]$_n$ (2.063(2) Å)[12] and agrees well with the average value found in [(4-Me$_2$NC$_6$H$_4$)$_2$Te]$_2$OCl$_2$ (1.985(3) Å).[13]

The average Te-O-Te angle of 126.0(5)° resembles those of [(4-MeOC$_6$H$_4$)$_2$TeO]$_n$ (126.0(1)°)[12] and [(4-Me$_2$NC$_6$H$_4$)$_2$Te]$_2$OCl$_2$ (121.0(1)°).[13] The Te1−Cl1 and Te2−Cl4 bond lengths of 2.551(5) and 2.562(5) Å are slightly longer than the Te1−Cl2 and Te2−Cl3 bond lengths of 2.470(5) and 2.479(4) Å, respectively. This is presumably due to the intramolecular secondary Te1···Cl4 and Te2···Cl1 contacts of 3.482(5) and 3.543(6) Å, respectively (Figure 3). Compound **3** is reasonably soluble in common organic solvents. In solution, **3** is characterised by a ^{125}Te NMR spectroscopic chemical shift ($CDCl_3$) of $\delta = 1359.7$ ppm (1355.6 ppm at −60 °C), which differs only marginally from that of the starting material 8-$Me_2NC_{10}H_6TeCl_3$ (**2**) in $CDCl_3$ (δ = 1317.1 ppm). The ESI-TOF MS spectrum (MeCN, positive mode) of **3** shows related tri- and dinuclear cations $[(RTe)_3O_3Cl_2]^+$ (*m*/*z* 1013.9) and $[(RTe)_2O_2Cl]^+$ (*m*/*z* 663.0) that presumably formed by further hydrolysis processes under MS conditions (R = 8-$Me_2NC_{10}H_6$).

The hydrolysis of the aryltellurium trichloride 8-$Me_2NC_{10}H_6TeCl_3$ (**2**) with 1 equiv NaOH gave rise to the formation of the hexanuclear telluroxane (8-$Me_2NC_{10}H_6Te)_6O_5Cl_8$ (**4**), obtained from the $CHCl_3$ layer and crystallised from THF/hexane as small colourless needles in 43 % yield. Unfortunately, the size of the crystals and possible twinning precluded establishing the molecular structure of **4** by X-ray crystallography. The telluroxane **4** is quite soluble in most organic solvents. The ^{125}Te NMR spectrum ($CDCl_3$, −60 °C) of **4** revealed three equally intense signals at δ = 1408.7, 1380.2 and 1330.8 ppm, however, no reasonable ^{125}Te NMR spectrum was obtained at room temperature. The IR spectrum of **4** shows no OH-stretching vibration. ESI-TOF MS spectrum (MeCN, positive mode) of **4** reveals the closely related hexanuclear telluroxane cation $[(RTe)_6O_6Cl_5]^+$ (*m*/*z* 2058.8) as well as the lighter telluroxane cations $[(RTe)_5O_5Cl_4]^+$ (*m*/*z* 1709.9), $[(RTe)_4O_4Cl_3]^+$ (*m*/*z* 1362.9), $[(RTe)_4O_5Cl]^+$ (*m*/*z* 1307.0), $[(RTe)_3O_3Cl_2]^+$ (*m*/*z* 1013.9), $[(RTe)_3O_4]^+$ (*m*/*z* 958.0) and $[(RTe)_2O_2Cl]^+$ (*m*/*z* 663.0), which may be formed by means of autoionisation and hydrolysis processes under MS conditions (R = 8-$Me_2NC_{10}H_6$). Based on the elemental analysis and the spectroscopic data at hand we propose an open-chain hexanuclear structure for **4** (Scheme 3). This proposal is consistent with the established solid-state structures of **3**, **6** and $[(4\text{-}Me_2NC_6H_4)_2Te]_2OCl_2$ (Scheme 4).[13] Furthermore, spectroscopic evidence was presented for the existence of the molecular oligotelluroxanes of the type $[R_2TeO(TeR_2O)_nTeR_2]^{2+}$ (R = 4-MeC_6H_4, n = 1–4).[14]

The hydrolysis of the aryltellurium trichloride 8-$Me_2NC_{10}H_6TeCl_3$ (**2**) with 2 equiv of NaOH produced high-melting colourless crystals of the hexanuclear telluroxane (8-$Me_2NC_{10}H_6Te)_6O_8Cl_2\cdot 8\,CHCl_3$ (**5**·8 $CHCl_3$) that were isolated in 2 % yield by addition of hexane to the $CHCl_3$ layer (Scheme 3). Once isolated from the mother liquor, the solvate **5**·8 $CHCl_3$ rapidly lost all solvent molecules to give **5** as a microcrystalline solid. The same telluroxane chloroform solvate **5**·8 $CHCl_3$ was also obtained by the reaction of 8-$Me_2NC_{10}H_6TeCl_3$ (**2**) with (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**7**) in $CHCl_3$ in 53 % yield. The molecular structure of **5**·8 $CHCl_3$ is shown in Figure 4 and selected bond parameters are collected in the caption of the figure. It reveals the tricyclic arrangement of the telluroxane ring. The spatial arrangement of the three crystallographically independent Te atoms is distorted trigonal bipyramidal (CN = 3+2, CO_2+NCl donor set for Te1 and CO_3+N donor sets for Te2 and Te3). The Te−O bond lengths cover a large range from 1.902(3) to 2.243(3) Å, with the average of 2.027(3) Å being close to the average 'single bond length' of polymeric $[(4\text{-}MeOC_6H_4)_2TeO]_n$ (2.063(2) Å).[12] Interestingly, the Te···Cl bond length of 3.051(8) Å is significantly longer than the average values of **2** (2.486(2) Å) and **3** (2.516(5) Å), which suggests that the Te···Cl bond is rather ionic. Compound **5** is



Scheme 4. Supramolecular association of $(4\text{-}Me_2NC_6H_4)_4Te_2OCl_2$.[13]

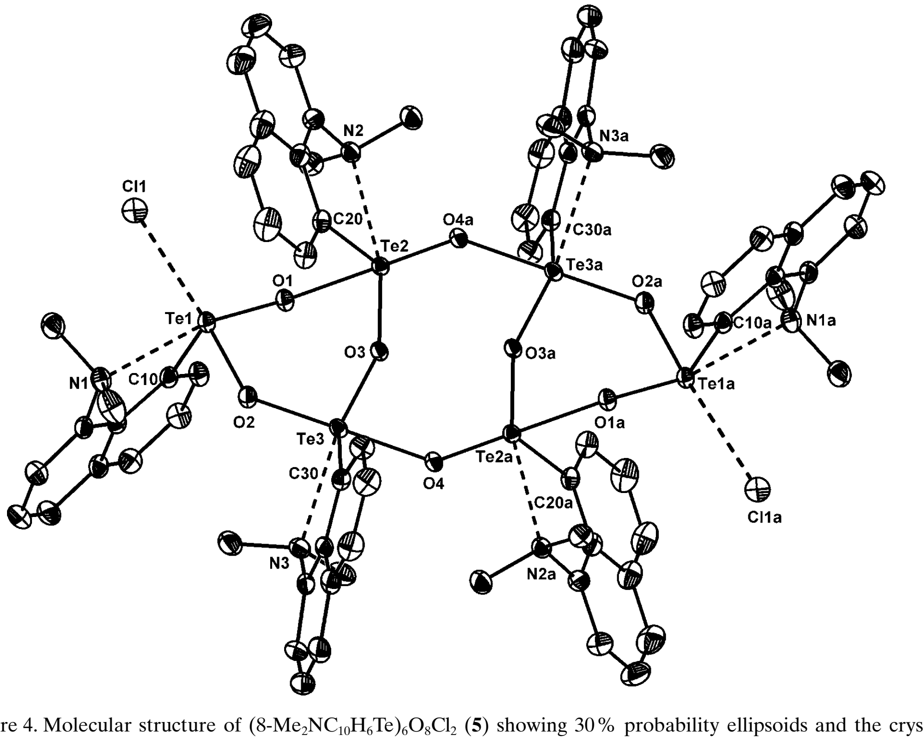


Figure 4. Molecular structure of (8-$Me_2NC_{10}H_6Te)_6O_8Cl_2$ (**5**) showing 30 % probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: $a = -x, -y, -z$). Selected bond parameters ([Å] and [°]): Te1−C10 2.120(4), Te1−O1 1.902(3), Te1−O2 1.936(3), Te1···Cl1 3.074(2), Te1···N1 2.601(6), Te2−C20 2.118(4), Te2−O1 2.243(3), Te2−O3 1.994(3), Te2−O4a 1.971(3), Te2···N2 2.570(5), Te3−C30 2.126(4), Te3−O2 2.107(3), Te3−O3 1.964(3), Te3−O4 2.096(3), Te3···N3 2.619(3); Te1-O1-Te2 127.8(1), Te1-O2-Te3 117.3(1).

only sparingly soluble in most solvents. Unfortunately, the ^{1}H NMR spectrum (CDCl$_3$) of **5** shows only broad signals. The ESI-TOF MS spectrum (MeCN, positive mode) of **5** exhibits only lighter telluroxane cations $[(\mathrm{RTe})_4\mathrm{O}_5\mathrm{Cl}]^+$ (*m*/*z* 1307.0), $[(\mathrm{RTe})_3\mathrm{O}_4]^+$ (*m*/*z* 958.0), $[(\mathrm{RTe})_2\mathrm{O}_2\mathrm{Cl}]^+$ (*m*/*z* 663.0), $[(\mathrm{RTe})_2\mathrm{O}_2(\mathrm{OH})]^+$ (*m*/*z* 645.0), $[(\mathrm{RTe})(\mathrm{OH})_2]^+$ (*m*/*z* 334.0) and $[\mathrm{RTeO}]^+$ (*m*/*z* 316.0), which are very similar to those found for **4** (R = 8-Me$_2$NC$_{10}$H$_6$).

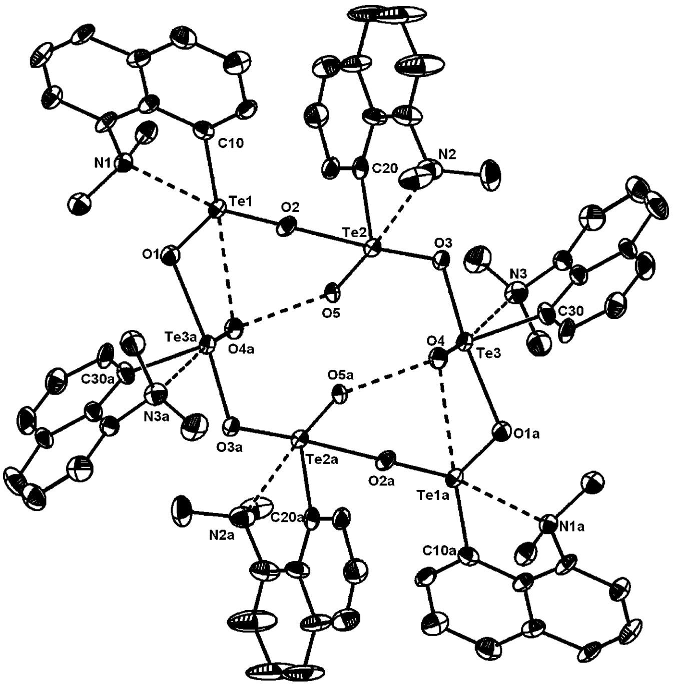


Figure 6. Molecular structure of (8-Me$_2$NC$_{10}$H$_6$Te)$_6$O$_8$(OH)$_2$ (**7**) showing 30 % probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: *a* = −*x*, −*y*, −*z*). Selected bond parameters ([Å] and [°]): Te1–C10 2.142(9), Te1–O1 1.875(5), Te1–O2 1.929(6), Te1···N1 2.598(8), Te2–C20 2.137(9), Te2–O2 2.257(5), Te2–O3 1.978(5), Te2–O5 1.922(6), Te2···N2 2.639(7), Te3–C30 2.109(8), Te3–O1a 2.273(6), Te3–O3 2.010(6), Te3–O4 1.877(5), Te3···N3 2.703(9); Te1-O1-Te3a 109.8(3), Te1-O2-Te2 127.6(3), Te2-O3-Te3 114.7(2).

The hydrolysis of the aryltellurium trichloride 8-Me$_2$NC$_{10}$H$_6$TeCl$_3$ (**2**) with 3 equiv of NaOH gave two products, namely, $[(8\text{-Me}_2\text{NC}_{10}\text{H}_6\text{Te})_2\text{O}_3]_n$ (**6**) and (8-Me$_2$NC$_{10}$H$_6$Te)$_6$O$_8$(OH)$_2$ (**7**), both of which were isolated from the aqueous layer (Scheme 3). Slow evaporation of the aqueous layer afforded high-melting colourless prisms of $[(8\text{-Me}_2\text{NC}_{10}\text{H}_6\text{Te})_2\text{O}_3\cdot{}^{7}\!/_{3}\,\text{H}_2\text{O}]_n$ ($[\mathbf{6}\cdot{}^{7}\!/_{3}\,\text{H}_2\text{O}]_n$) in 25 % yield. When the water was removed almost completely under vacuum and the solid residue was recrystallised from THF/hexane, high-melting colourless prisms of (8-Me$_2$NC$_{10}$H$_6$Te)$_6$O$_8$(OH)$_2$·4THF·6H$_2$O (**7**·4THF·6H$_2$O) were obtained in 61 % yield. Compounds **6** and **7** can be regarded as condensation products of the same elusive aryltellurinic acid. The crystal and molecular structures of **6**·$^{7}\!/_{3}$ H$_2$O and **7**·4THF·6H$_2$O are shown in Figures 5 and 6 and selected bond parameters are collected in the caption of the figures. The crystal structure of **6**·$^{7}\!/_{3}$ H$_2$O features two crystallographically independent, albeit similar 1D Te–O double strings, reminiscent of the supramolecular association of [(4-Me$_2$NC$_6$H$_4$)$_2$Te]$_2$OCl$_2$ (Scheme 4).[13] The spatial arrangement of the three independent Te atoms is distorted octahedral (CN = 3+3, CO$_2$+NO$_2$ donor set). The four Te–O contacts cover the whole range from elongated 'formal' double bonds (Te1–O2 1.890(5) Å), short and long single bonds (Te1–O1 1.976(3) Å, Te1–O2b 2.311(5) Å) to secondary interactions (Te1–O2a 3.319(5) Å). The molecular structure of **7**·4THF·6H$_2$O comprises a centrosymmetric 12-membered telluroxane ring.

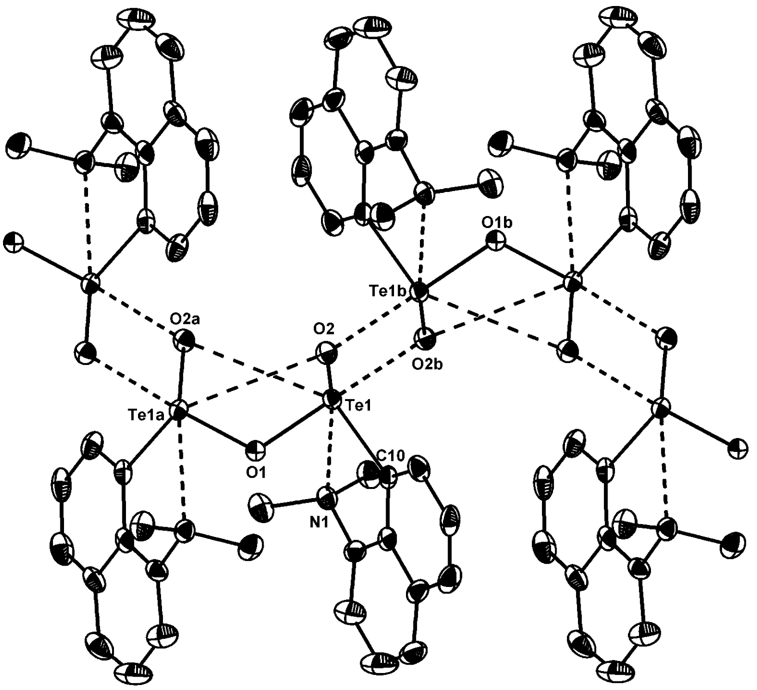


Figure 5. Crystal structure of $[(8\text{-Me}_2\text{NC}_{10}\text{H}_6\text{Te})_2\text{O}_3]_n$ (**6**) showing 30 % probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: *a* = −*x*, −*y*, 0.5−*z*; *b* = −*x*, −*y*, −*z*). Selected bond parameters ([Å] and [°]): Te1–C10 2.133(7), Te1–O1 1.976(3), Te1–O2 1.890(5), Te1···O2a 3.319(5), Te1–O2b 2.311(5), Te1···N1 2.718(6); Te1-O1-Te1a 120.6(3).

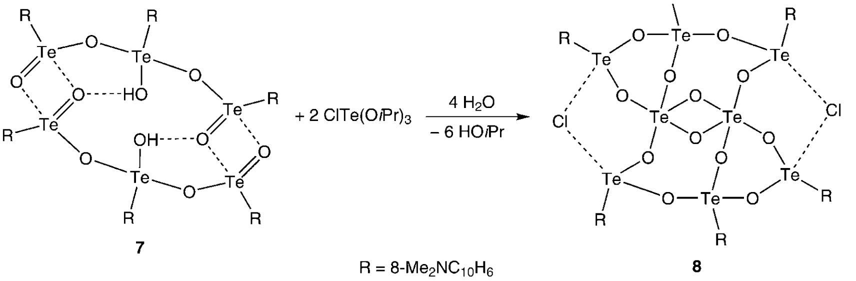
The spatial arrangement of the three crystallographically independent Te atoms is distorted trigonal bipyramidal (CN = 3+2, CO$_2$+NO donor set for Te1; CN = 4+1, CO$_3$+N donor sets for Te2 and Te3). The majority of primary Te–O contacts have bond lengths that fall in the range between 1.922(6) and 2.273(6) Å (average 2.062(6) Å) and can be regarded as single bonds. However, the Te1−O1 and Te3−O4 bonds of 1.875(5) and 1.877(5) Å, respectively, are significantly shorter than the majority of Te−O contacts and compare well with the average elongated 'formal' Te−O double bonds of $(Ph_2TeO)_2$ (1.89(1) Å).[15] One of the related O atoms acts as both a donor for an intramolecular secondary Te1···O4a contact of 2.897(6) Å and an acceptor for an intramolecular hydrogen bridge (O5···O4a 2.532(7) Å). In the solid state, the two 1D Te−O double strings of **6** and the 12-membered telluroxane rings of **7** are associated by three crystallographically independent water molecules (see Figure S4 and S5 of the Supporting Information). The O···O distances lie in the range from 2.72(1) to 2.89(1) Å and 2.84(6) to 3.05(3) Å, respectively, and are indicative for medium-strength hydrogen bonding.[16] The two crystallographically independent THF molecules fill the voids in the crystal lattice, but are neither associated by hydrogen bonding nor involved in coordination to the Te atoms. Despite the three crystallographically independent Te sites, the ^{125}Te CP MAS NMR spectrum of **6** shows only two signals at $\delta_{iso} = 1357$ and 1448 ppm, with an approximate integral ratio of 1:1. No solid-state ^{125}Te NMR spectrum was obtained for **7**. Compounds **6** and **7** are only reasonably soluble in polar solvents, such as water and THF. They are interconvertible by crystallisation from H_2O and THF/hexane, respectively, and give identical spectra in solution. The ^{125}Te NMR spectrum (D_2O) shows a single broad signal at $\delta = 1530.6$ ppm. An osmometric molecular weight determination in H_2O revealed a molecular weight of 878 g mol^{-1}, which accounts for an average degree of aggregation of 2.5. Consistently, the ESI-TOF MS spectrum (H_2O, positive mode) reveals indicative cations with up to three Te atoms $[(RTe)_3O_4]^+$ (*m*/*z* 958.0), $[(RTe)_2O_2(OH)]^+$ (*m*/*z* 645.0) and $[(RTe)(OH)_2]^+$ (*m*/*z* 334.0).

Surprisingly, a mass cluster was also found for the cation $[(RTe)_3O_5]^+$ (*m*/*z* 974.0), which apparently suggests that one of the three tellurium atoms was oxidised from IV to VI under ESI-TOF MS conditions ($R = 8\text{-}Me_2NC_{10}H_6$). The deliberate oxidation of aryltellurinic acids and related compounds to aryltelluronic acids will be the subject of forthcoming papers.[17] In light of the molecular weight determination and the ESI-TOF MS spectrum, the fact that only one signal was found in the ^{125}Te NMR spectrum in D_2O suggests that the aggregation and disaggregation processes are fast on the NMR spectroscopic timescale. No reasonable ^{125}Te NMR spectrum was obtained in [D$_4$]THF at room temperature, presumably because the signals are too broad. The ^{125}Te NMR spectrum ([D$_4$]THF, −80 °C) exhibits seven signals at $\delta = 1471.1$, 1459.0, 1393.7, 1366.4 (broad), 1364.2 (broad), 1356.5 (broad) and 1316.2 ppm, which could not be integrated satisfactorily (10 mm tube, acquisition time 4 h). Apparently, the aggregation and disaggregation processes cannot entirely be frozen under these conditions.

The 8-dimethylaminonaphthyl group ('stiff-arm ligand') is considered to be quite rigid.[18] Surprisingly, the Te···N bond lengths vary substantially in **1**–**7**. The (average) Te···N bond lengths of the aryltellurenyl(II) chloride **1** (2.350(3) Å) and the aryltellurium(IV) trichloride **2** (2.420(3) Å) are significantly shorter than those of the diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ (2.721(5) Å) and the diaryltritelluride $(8\text{-}Me_2NC_{10}H_6Te)_2Te$ (2.67(1) Å),[9] thereby indicating strong attractive interactions. Amongst the aryltellurium(IV) compounds, the (average) Te···N bond lengths increase when going from **2** (2.420(3) Å) to **3** (2.55(1) Å), **4** (2.600(6) Å), **7** (2.647(9) Å) and **6** (2.718(6) Å), which suggests that the Lewis acidity of the Te atoms is successively reduced with an increasing degree of hydrolysis and aggregation.

Very recently, Singh et al. communicated that the base hydrolysis of the aryltellurium trichloride $2\text{-}(PhNN)C_6H_4TeCl_3$ provided the heptanuclear telluroxane cluster $[2\text{-}(PhNN)C_6H_4Te]_6TeO_{11}$, which contains six organotellurium sites and also one inorganic Te^{IV} atom.[8] Although not explicitly mentioned by the authors, the inorganic Te^{IV} atom might be formed by an uncontrolled Te−C bond cleavage in the presence of base. Alternatively, the purity of $2\text{-}(PhNN)C_6H_4TeCl_3$ might have been compromised by a small amount of unaccounted (^{1}H and ^{13}C NMR-silent) $TeCl_4$, which was co-hydrolysed.

In a similar manner, we obtained a small crop of crystals that were identified as the octanuclear telluroxane cluster $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (**8**) containing six organotellurium sites and two inorganic Te^{IV} atoms. In our case, the diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ used as starting material was contaminated by a small amount of the diaryltritelluride $(8\text{-}Me_2NC_{10}H_6Te)_2Te$.[9] The chlorination of this impure $(8\text{-}Me_2NC_{10}H_6Te)_2$ provided a mixture of the aryltellurium trichloride $8\text{-}Me_2NC_{10}H_6TeCl_3$ (**2**) with $TeCl_4$, which was used for the hydrolysis experiment. The reaction of $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**7**) with ClTe(O*i*Pr)$_3$[19] in the presence of water turned out to be a more rational synthesis of the same octanuclear telluroxane cluster $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (**8**), and was obtained as colourless high-melting crystals in 48 % yield (Scheme 5).



7

R = $8\text{-}Me_2NC_{10}H_6$

8

Scheme 5. Synthesis of $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (**8**).

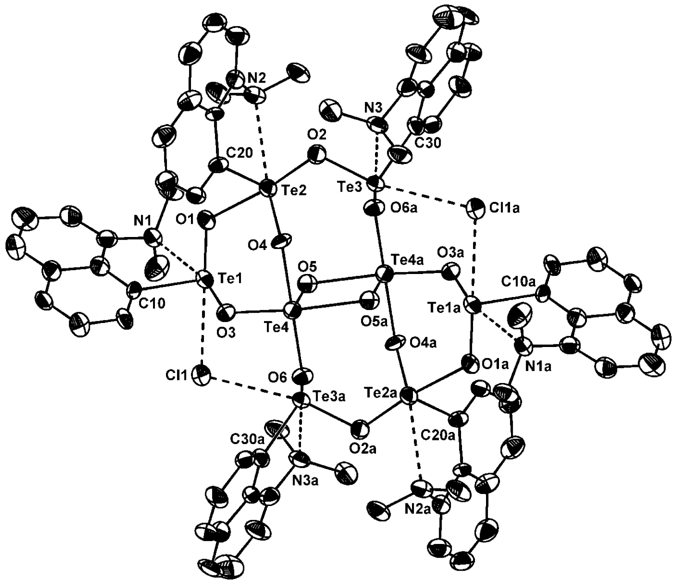


Figure 7. Molecular structure of $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (**8**) showing 30 % probability ellipsoids and the crystallographic numbering scheme (symmetry code used to generate equivalent atoms: $a = -x, -y, -z$). Selected bond parameters ([Å] and [°]): Te1−C10 2.12(1), Te1−O1 1.892(9), Te1−O3 1.94(1), Te1···Cl1 3.051(8), Te1···N1 2.60(1), Te2−C20 2.10(1), Te2−O1 2.166(9), Te2−O2 2.06(1), Te2−O4 1.89(1), Te2···N2 2.71(2), Te3−C30 2.12(2), Te3−O2 1.90(1), Te3−O6a 1.908(9), Te3···Cl1a 3.08(1), Te3···N3 2.61(1), Te4−O3 1.98(1), Te4−O4 2.104(9), Te4−O5 1.92(1), Te4−O5a 2.24(1), Te4−O6 2.073(9); Te1-O1-Te2 125.4(5), Te1-O3-Te4 120.9(5), Te2-O2-Te3 117.9(5), Te2-O4-Te4 128.1(5), Te3-O6a-Te4a 132.5(5), Te4-O5-Te4a 103.0(4).

The molecular and crystal structure of **8**·4 H_2O is shown in Figure 7 and selected bond parameters are collected in the caption of the figure. The spatial arrangement of the organometallic Te sites is trigonal bipyramidal (CN = 3+2, CO_2+NCl donor set for Te1 and Te3 and CN = 4+1, CO_3+N donor set for Te2).

As for compounds **4** and **5**, the Te−O bond lengths of the organometallic Te sites cover a large range from 1.892(9) to 2.166(9) Å with the average being 2.29(1) Å. The spatial arrangement of the symmetry-related inorganic Te sites are distorted square pyramidal (CN = 5, O5 donor set) or distorted octahedral when taking into account the stereochemically active lone pair. Notably, the structural motif of the inorganic Te atoms cannot be found in the crystal structures of α- and β-TeO_2, which adopt distorted trigonal bipyramidal arrangements.[20] We speculate that similar square pyramidal Te sites might also be present in alkali tellurite glasses $(M_2O)_x(TeO_2)_{1-x}$ (M = Li, Na, K; $0.10 < x < 0.35$).[5] The inorganic Te atoms comprise a four-membered Te_2O_2 ring and the Te−O bond lengths also cover a rather large range from 1.92(1) to 2.24(1) Å, with the average of 2.06(1) Å being slightly longer than those of α-TeO_2 (av. 2.00 Å) and β-TeO_2 (2.01 Å), respectively.[20] The Te···Cl bond length of **8** (3.06(1) Å) is like that in **5** (3.051(8) Å), significantly longer than the average values of **2** (2.486(2) Å) and **3** (2.516(5) Å), which also suggests that the Te···Cl bond is rather ionic. The water molecules of **8**·4 H_2O play an integral role for the intermolecular association (see Figure S6 in the Supporting Information). Each of the two crystallographically independent water molecules is involved in medium-strength hydrogen bonding (O5···O8 3.05(3), O7b···O8 2.84(6) and O4···O7 2.95(8) Å)[16] and links adjacent molecules of **8** in the crystal lattice. Unfortunately, all attempts to obtain a reasonable ^{125}Te MAS NMR spectrum of **8** failed. Once crystallised from the mother liquor, **8** is only poorly soluble in most common organic solvents. The ^1H NMR spectrum ($CDCl_3$) of **8** reveals only very broad signals for the 8-dimethylaminonapththyl group. No qualitative change was observed when the ^1H NMR spectrum was recorded at −60 °C. The ESI-TOF MS spectrum (MeCN, positive mode) of **8** is shown in Figure 8 and comprises seven indicative mass clusters that were assigned to the cations $[(RTe)_6Te_2O_{12}Cl]^+$ (*m*/*z* 2270.7), $[(RTe)_5Te_2O_{11}]^+$ (*m*/*z* 1921.7), $[(RTe)_5TeO_9]^+$ (*m*/*z* 1759.9), $[(RTe)_4Te_2O_8(OH)_3]^+$ (*m*/*z* 1626.8), $[(RTe)_3Te_2O_8]^+$ (*m*/*z* 1277.8), $[(RTe)_3TeO_6]^+$ (*m*/*z* 1117.9) and the dication $[(RTe)_6Te_2O_{12}]^{2+}$ (*m*/*z* 1117.9; R = 8-$Me_2NC_{10}H_6$). While ESI-TOF MS spectroscopy allows no conclusion about the concentration of these ions in solution, the detected mass clusters as well as the broad ^1H NMR spectroscopic signals suggest that other telluroxane clusters may be in equilibrium with **8**.

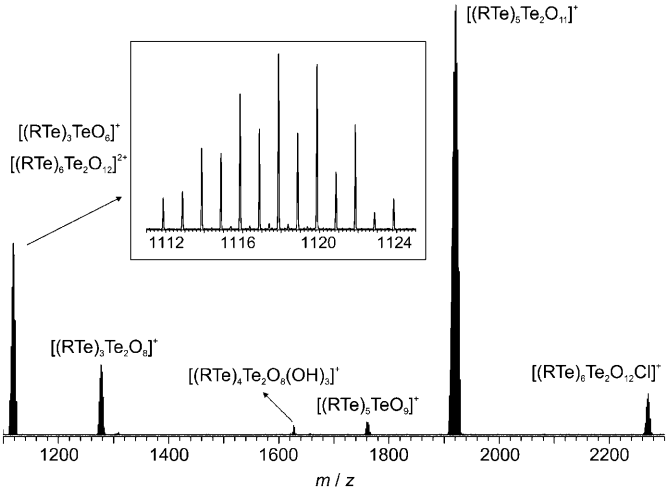


Figure 8. ESI-TOF MS spectrum (THF, positive mode) of $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (**8**).

Conclusion

The base hydrolysis of the intramolecularly coordinated aryltellurium trichloride 8-$Me_2NC_{10}H_6TeCl_3$ (**2**) proved to be a rational strategy for the synthesis of the discrete molecular telluroxane clusters $(8\text{-}Me_2NC_{10}H_6Te)_6O_5Cl_8$ (**4**), $(8\text{-}Me_2NC_{10}H_6Te)_6O_8Cl_2$ (**5**) and $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**7**) and the well-defined telluroxane polymer $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$ (**6**), which is the first structurally characterised aryltellurinic anhydride. The degree of aggregation within these compounds is higher than in the kinetically stabilised compounds [2,6-$Mes_2C_6H_3Te(O)Cl]_2$ and [2,6-$Mes_2C_6H_3Te(O)(OH)]_2$ prepared by the base hydrolysis of 2,6-$Mes_2C_6H_3TeCl_3$ under similar conditions.[3] The reaction of **7** with $ClTe(OiPr)_3$ in the presence of water produced the telluroxane cluster (8-$Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (**8**), containing both organometallic and inorganic Te sites, with the latter being more highly coordinated than the Te atoms of α- and β-TeO_2. The chloride-free hydrolysis products [(8-$Me_2NC_{10}H_6Te)_2O_3]_n$ (**6**) and (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**7**) are interconvertible by crystallisation from H_2O and THF/hexane, respectively, and span a wide range of Te−O bond lengths, accounting for (formal) Te=O double bonds, short and long Te−O single bonds as well as Te⋯O secondary interactions. The telluroxane clusters (8-$Me_2NC_{10}H_6Te)_6O_8Cl_2$ (**5**) and (8-$Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (**8**) show no secondary Te⋯O interactions, but rather long Te⋯Cl contacts. Further studies on the reactivity of **1**–**8** and related compounds are currently underway.

Experimental Section

General: (8-$Me_2NC_{10}H_6Te)_2$,[9] 8-$Me_2NC_{10}H_6Te(S_2CNEt_2)$[10] and $ClTe(OiPr)_3$[19] were prepared according to literature procedures. The ^{1}H, ^{13}C and ^{125}Te NMR spectra were recorded using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ and Me_2Te. The ^{125}Te CP MAS NMR spectra were obtained using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 8 and 10 kHz. A 30 s recycle delay was used and typically 5000 to 10000 transitions were accumulated to obtain adequate signal-to-noise ratios. The isotropic chemical shifts (δ_{iso}) were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced using solid $Te(OH)_6$ as the secondary reference ($\delta_{iso}=692.2/685.5$ ppm). Infrared (IR) spectra were recorded using a Nexus FTIR spectrometer with a Smart DuraSamplIR. Electrospray ionisation time-of-flight (ESI-TOF) MS spectra were measured on an Agilent 6210 mass spectrometer, Agilent Technologies, Santa Clara, CA, USA. Solvent flow rate was adjusted to 4 μL min^{-1}. The spray voltage and skimmer voltage were set to 4 kV and 150 V, respectively. The drying gas flow rate was set to 1 bar. Molecular weights were determined using a Knauer vapour pressure osmometer. Microanalyses were obtained from a Vario EL elemental analyser.

Synthesis of 8-$Me_2NC_{10}H_6TeCl$ (1)

Method A: SO_2Cl_2 (0.023 mL, 0.67 mmol) was slowly added at 0 °C to a solution of (8-$Me_2NC_{10}H_6Te)_2$ (200 mg, 0.33 mmol) in THF (20 mL). The mixture was stirred overnight at RT. The solvent was completely removed under vacuum and the solid residue recrystallised from CH_2Cl_2 (30 mL)/hexane (20 mL) to afford orange crystals of **1** (193 mg, 0.56 mmol, 86 %; m.p. 148–152 °C).

Method B: Concentrated HCl solution (2 mL) was added to a solution of 8-$Me_2NC_{10}H_6Te(S_2CNEt_2)$ (900 mg, 2.02 mmol) in MeOH (30 mL) and CH_2Cl_2 (20 mL) and was stirred overnight. The yellow-green precipitate was collected by filtration and dissolved in $CHCl_3$ (50 mL). After filtration to remove a small amount of insoluble material, the solvent was completely removed under vacuum and the solid residue recrystallised from CH_2Cl_2 (30 mL)/hexane (20 mL) to afford orange crystals of **1** (420 mg, 1.26 mmol, 62 %).

^{1}H NMR ($CDCl_3$): $\delta=8.09$ (d, 1H; Ar), 7.77 (d, 1H; Ar), 7.69 (d, 1H; Ar), 7.56 (t, 1H; Ar), 7.48 (t, 1H; Ar), 7.40 (d, 1H; Ar), 3.23 ppm (s, 6H; Me); ^{13}C NMR ($CDCl_3$): $\delta=148.3$, 135.1, 131.5, 130.0, 128.9, 128.1, 125.9, 125.7, 118.2, 117.7 (Ar), 52.9 ppm (Me); ^{125}Te NMR ($CDCl_3$): $\delta=1595.0$ ppm; ^{125}Te CP MAS NMR: $\delta_{iso}=845$ ppm; elemental analysis calcd (%) for $C_{12}H_{12}ClNTe$ (333.28): C 43.25, H 3.63, N 4.20; found: C 43.03, H 3.20, N 4.05.

Synthesis of 8-$Me_2NC_{10}H_6TeCl_3$ (2): SO_2Cl_2 (1.00 mL, 5.05 mmol) was slowly added at 0 °C to a solution of (8-$Me_2NC_{10}H_6Te)_2$ (2.0 g, 4.04 mmol) in THF (40 mL). The mixture was stirred for 30 min at RT before the yellow-brown precipitate was collected by filtration and air dried. Recrystallisation from THF/hexane (30 mL/20 mL) afforded slightly yellow crystals of **2** (1.30 g, 3.21 mmol, 39 %). M.p. 282–292 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta=8.85$ (d, 1H; Ar), 8.10 (d, 1H; Ar), 7.92 (d, 1H; Ar), 7.88 (t, 1H; Ar), 7.64 (m, 2H; Ar), 3.35 ppm (s, 6H, Me); ^{1}H NMR ([D$_6$]DMSO): $\delta=8.70$ (d, 1H; Ar), 8.31 (d, 1H; Ar), 8.12 (d, 1H; Ar), 8.10 (t, 1H; Ar), 7.98 (t, 1H; Ar), 7.79 (d, 1H; Ar), 3.38 ppm (s, 6H; Me); ^{13}C NMR ([D$_6$]DMSO): $\delta=146.7$, 141.5, 134.8, 131.3, 128.7, 128.53, 128.45, 128.38, 127.8, 121.4 (Ar), 50.5 ppm (Me); ^{125}Te NMR ([D$_6$]DMSO): $\delta=1358.4$ ppm; ^{125}Te NMR ($CDCl_3$): $\delta=1317.1$ ppm; ^{125}Te CP MAS NMR: $\delta_{iso}=1355$ ppm; elemental analysis calcd (%) for $C_{12}H_{12}Cl_3NTe$ (404.19): C 35.66, H 2.99, N 3.47; found: C 35.60, H 2.90, N 3.36.

Synthesis of (8-$Me_2NC_{10}H_6Te)_2OCl_4$ (3): Water (5 mL) was added to a stirred suspension of **2** (404 mg, 1.0 mmol) in $CHCl_3$ (5 mL) and the reaction mixture was stirred at RT. After approximately 1 h, the entire solid had dissolved and the organic layer turned orange. The pH value of the aqueous layer was 1.0. A colourless precipitate started to form after approximately 5 h and was collected after 2 d by filtration (234 mg). The precipitate was redissolved in THF (50 mL) and hexane (10 mL) to give a slightly orange solution. Slow evaporation of the solvent furnished slightly yellow prisms of **3** (192 mg, 0. 254 mmol, 51 %). M.p. 257–261 °C (decomp); ^{1}H NMR ($CDCl_3$): $\delta=9.02$ (d, 1H; Ar), 8.03 (d, 1H; Ar), 7.89–7.85 (m, 2H; Ar), 7.60 (m, 2H; Ar), 3.19 ppm (s, 6H; Me). ^{1}H NMR ($CDCl_3$, −60 °C): $\delta=8.98$ (d, 1H; Ar), 8.06 (d, 1H; Ar), 7.90–7.87 (m, 2H; Ar), 7.63 (m, 2H; Ar), 3.19 ppm (s, 6H; Me); ^{13}C NMR ($CDCl_3$, −40 °C (signals broad)): $\delta=146.5$, 142.0, 135.0, 131.0, 129.4, 128.9, 128.5, 128.0, 126.6, 119.9 (Ar, br.), 48.9 ppm (Me); ^{125}Te NMR ($CDCl_3$): $\delta=1359.7$ ppm; ^{125}Te NMR ($CDCl_3$, −40 °C): $\delta=1355.6$ ppm; ^{125}Te CP MAS NMR: $\delta_{iso}=1356$, 1376 ppm (1:1); elemental analysis calcd (%) for $C_{24}H_{24}Cl_4N_2OTe_2$ (753.47): C 38.26, H 3.21, N 3.72; found: C 38.65, H 3.28, N 3.59; ESI-TOF MS (MeCN, positive mode): *m/z*: 1013.9 $[C_{36}H_{36}Cl_2N_3O_3Te_3]^+$, 663.0 $[C_{24}H_{24}ClN_2O_2Te_2]^+$.

Synthesis of (8-$Me_2NC_{10}H_6Te)_6O_5Cl_8$ (4): A solution of NaOH (40 mg; 1.0 mmol) in H_2O (5 mL) was added to a stirred suspension of **2** (404 mg, 1.0 mmol) in $CHCl_3$ (5 mL) at RT. After approximately 1 h, the entire solid had dissolved and the $CHCl_3$ layer turned into a slightly orange solution. The pH value of the aqueous layer was 2.7. The precipitation of a colourless solid began after approximately 6 h and was collected by vacuum filtration after 2 d (156 mg). The crude product was redissolved in THF (50 mL) and hexane (10 mL) to give a clear orange solution. Slow evaporation of the solvent provided small colourless needles of **4** (156 mg, 0.072 mmol; 43 %). M.p. 264–267 °C (decomp); ^{1}H NMR ($CDCl_3$, −60 °C): $\delta=8.67$ (d, 1H; Ar), 8.29 (d, 1H; Ar), 8.19 (d, 1H; Ar), 8.15 (d, 1H; Ar), 8.05–7.98 (m, 2H; Ar), 7.94–7.75 (m, 5H; Ar), 7.69–7.66 (m, 3H; Ar), 7.53–7.51 (m, 2H; Ar), 7.44–7.40 (m, 2H; Ar), 3.40 (br s, 3H; Me), 3.07 (br s, 3H; Me), 3.05 (br s, 3H; Me), 2.91 (br s, 6H; Me), 2.71 ppm (br s, 3H; Me); ^{125}Te NMR ($CDCl_3$, −60 °C): $\delta=1408.7$, 1380.2, 1330.8 ppm; elemental analysis calcd (%) for $C_{72}H_{72}Cl_8N_6O_5Te_6$ (2150.80): C 40.21, H 3.37, N 3.91; found: C 39.96, H 3.48, N 3.67; ESI-TOF MS (MeCN, positive mode): *m/z*: 2058.8 $[C_{72}H_{72}Cl_5N_6O_6Te_6]^+$, 1709.9 $[C_{60}H_{60}Cl_4N_5O_5Te_5]^+$, 1362.9 $[C_{48}H_{48}Cl_3N_4O_4Te_4]^+$, 1307.0 $[C_{48}H_{48}ClN_4O_5Te_4]^+$, 1013.9 $[C_{36}H_{36}Cl_2N_3O_3Te_3]^+$, 958.0 $[C_{36}H_{36}N_3O_4Te_3]^+$, 663.0 $[C_{24}H_{24}ClN_2O_2Te_2]^+$.

Synthesis of (8-$Me_2NC_{10}H_6Te)_6O_8Cl_2$ (5)

Method A: A solution of NaOH (80 mg, 2 mmol) in water (5 mL) was added to a stirred suspension of **2** (404 mg, 1.00 mmol) in $CHCl_3$ (5 mL). After approximately 15 min the entire solid had dissolved and the $CHCl_3$ layer turned into a slightly orange solution. The pH value of the aqueous layer was 3.9. Stirring was continued for 2 d before the layers were separated. Hexane (10 mL) was added to the organic layer and slow evaporation of the solvent yielded colourless prisms of **5** (38 mg, 0.019 mmol; 2 %; m.p. 255–258 °C (decomp)).

Table 1. Crystal data and structure refinement of **1**–**8**.

	1 (monoclinic)	**1** (triclinic)	**2**	**3**
formula	$C_{12}H_{12}ClNTe$	$C_{12}H_{12}ClNTe$	$C_{12}H_{12}Cl_3NTe$	$C_{24}H_{24}Cl_4N_2OTe_2$
M_r [g mol^{-1}]	333.28	333.28	404.18	753.45
crystal system	monoclinic	triclinic	triclinic	triclinic
crystal size [mm]	0.40 × 0.09 × 0.03	0.30 × 0.15 × 0.04	0.15 × 0.15 × 0.03	0.30 × 0.25 × 0.20
space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [Å]	9.026(5)	11.140(2)	8.008(5)	12.104(2)
b [Å]	17.473(5)	14.039(2)	8.007(5)	15.363(2)
c [Å]	15.666(5)	16.349(2)	11.590(5)	17.338(2)
α [°]	90	79.043(3)	88.671(5)	108.46(1)
β [°]	105.528(5)	79.477(3)	78.643(5)	90.02(1)
γ [°]	90	86.526(3)	69.860(5)	101.97(1)
V [Å^3]	2380(2)	2467.1(6)	683.2(7)	2984.0(7)
Z	8	8	2	4
ρ_{calcd} [Mg m^{-3}]	1.860	1.795	1.965	1.677
T [K]	173	173	173	150
m (Mo$_{K\alpha}$) [mm^{-1}]	2.690	2.595	2.740	2.332
$F(000)$	1280	1280	388	1448
θ range [°]	1.78 to 27.53	1.77 to 30.51	1.79 to 30.52	0.99 to 25.50
index ranges	$-11 \leq h \leq 11$	$-15 \leq h \leq 15$	$-8 \leq h \leq 8$	$-14 \leq h \leq 14$
	$-22 \leq k \leq 19$	$-20 \leq k \leq 17$	$-16 \leq k \leq 16$	$-18 \leq k \leq 17$
	$-20 \leq l \leq 19$	$-23 \leq l \leq 23$	$-17 \leq l \leq 19$	$0 \leq l \leq 20$
no. reflns collected	22 988	30 749	8547	10 016
completeness to θ_{max} [%]	99.4	96.8	97.0	95.2
no. indep. reflns	5457	14 590	4062	10 016
no. obsd reflns with ($I > 2\sigma(I)$)	4088	12 876	3439	5024
no. refined params	271	541	154	643
GOF (F^2)	1.062	1.111	1.080	0.895
R_1 (F) ($I > 2\sigma(I)$)	0.0320	0.0266	0.0319	0.0711
wR_2 (F^2) (all data)	0.0721	0.0818	0.0867	0.1794
$(\Delta/s)_{max}$	< 0.001	< 0.001	< 0.001	< 0.001
largest diff peak/hole [e Å^{-3}]	1.012/−0.828	3.743/−1.370	2.340/−0.501	1.400/−1.008

	5·8 $CHCl_3$	**6**·$^7/_3$ H_2O	**7**·4 THF·6 H_2O	**8**·4 H_2O
formula	$C_{80}H_{80}Cl_{26}N_6O_8Te_6$	$C_{72}H_{86}N_6O_{16}Te_6$	$C_{88}H_{118}N_6O_{20}Te_6$	$C_{72}H_{80}Cl_2N_6O_{16}Te_8$
M_r [g mol^{-1}]	2940.80	2057.07	2345.48	2377.12
crystal system	triclinic	monoclinic	triclinic	triclinic
crystal size [mm]	0.29 × 0.16 × 0.10	0.32 × 0.14 × 0.04	0.24 × 0.11 × 0.09	0.20 × 0.14 × 0.10
space group	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	11.899(3)	28.083(3)	9.94(1)	8.5320(9)
b [Å]	15.952(3)	27.967(2)	15.07(1)	16.432(2)
c [Å]	16.606(4)	10.0341(9)	16.18(2)	17.435(2)
α [°]	109.802(5)	90.00	98.58(8)	93.238(8)
β [°]	108.554(5)	106.670(7)	100.11(9)	101.756(8)
γ [°]	101.953(5)	90.00	96.93(8)	95.884(8)
V [Å^3]	2631(1)	7549(1)	2332(4)	2373.0(4)
Z	1	4	1	1
ρ_{calcd} [Mg m^{-3}]	1.856	1.797	1.660	1.658
T [K]	173	150	150	150
m (Mo$_{K\alpha}$) [mm^{-1}]	1.856	2.356	1.921	2.535
$F(000)$	1420	3944	1146	1124
θ range [°]	0.99 to 27.50	2.10 to 29.22	2.68 to 29.19	2.68 to 25.02
index ranges	$-15 \leq h \leq 15$	$-32 \leq h \leq 38$	$-13 \leq h \leq 13$	$-10 \leq h \leq 9$
	$-20 \leq k \leq 17$	$-38 \leq k \leq 38$	$-20 \leq k \leq 20$	$-19 \leq k \leq 19$
	$-21 \leq l \leq 20$	$-32 \leq l \leq 32$	$-22 \leq l \leq 18$	$-0 \leq l \leq 20$
no. reflns collected	34 681	44 606	24 999	8310
completeness to θ_{max} [%]	99.1	99.3	98.4	99.2
no. indep. reflns	11 981	10 179	12 420	8310
no. obsd reflns with ($I > 2\sigma(I)$)	9565	4407	5034	4109
no. refined params	613	452	541	469
GOF (F^2)	1.119	0.931	0.892	0.898
R_1 (F) ($I > 2\sigma(I)$)	0.0352	0.0419	0.0537	0.0713
wR_2 (F^2) (all data)	0.1082	0.0757	0.1187	0.1862
$(\Delta/s)_{max}$	< 0.001	< 0.001	< 0.001	< 0.001
largest diff peak/hole [e Å^{-3}]	1.300/−0.947	0.678/−0.927	1.028/−1.661	1.575/−0.856

Method B: A Solution of **2** (31.0 mg; 0.077 mmol) in hot THF (10 mL) was added to a stirred solution of **7** (200.0 mg, 1.026 mmol) in hot THF (30 mL). Crystallisation started after a few min at RT and produced colourless needles of **5** (122 mg, 0.061 mmol; 53 %).

^{1}H NMR ($CDCl_3$, very broad signals): $\delta = 9.20$, 8.45, 7.99–7.74, 7.41 (12H; Ar), 2.8–1.9 ppm (12H; Me); IR: $\tilde{\nu} = 3527$, 3395 cm^{-1}; elemental analysis calcd (%) for $C_{72}H_{72}Cl_2N_6O_8Te_6$ (1985.88): C 43.55, H 3.65, N 4.23; found: C 42.85, H 2.52, N 4.04; ESI-TOF MS (MeCN, positive mode): *m*/*z*: 1307.0 $[C_{48}H_{48}ClN_4O_5Te_4]^+$, 958.0 $[C_{36}H_{36}N_3O_4Te_3]^+$, 663.0 $[C_{24}H_{24}ClN_2O_2Te_2]^+$, 645.0 $[C_{24}H_{25}N_2O_3Te_2]^+$, 334.0 $[C_{12}H_{14}NO_2Te]^+$, 316.0 $[C_{12}H_{12}NOTe]^+$.

Synthesis of $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$ (6) and $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (7): A solution of NaOH (120 mg, 3 mmol) in water (5 mL) was added to a stirred suspension of **2** (404 mg, 1.0 mmol) in $CHCl_3$ (5 mL). After approximately 15 min the entire solid had dissolved and the $CHCl_3$ layer turned into a slightly orange solution. The pH value of the aqueous layer was 6.9. Stirring was continued for 2 d before the layers were separated. Slow evaporation of the aqueous layer provided colourless prisms of **6** (83 mg, 0.042 mmol; 25 %; m.p. 220–225 °C). In another experiment the solvent was completely removed under vacuum. The solid residue was extracted with hot THF (3×50 mL). In this way, the crude product was separated from the insoluble inorganic salts. Hexane (10 mL) was added to the slightly orange solution in THF and slow evaporation of the solvent afforded colourless prisms of **7** (203 mg, 0.100 mmol, 61 %; m.p. 221–225 °C). Before drying: compound **6**: ^{125}Te CP MAS NMR: $\delta_{iso} =$ 1357.3 and 1448.5 ppm (1:1); IR: $\tilde{\nu} = 3464$, 3355, 3233 cm^{-1}; compound **7**: IR (KBr): $\tilde{\nu} = 3467$, 3341 cm^{-1}.

Compounds **6** and **7** were dried under a high vacuum at 100 °C for 4 h, however, in both cases the analytical samples still contained 2 equiv of water. After drying, both samples appear to be identical. After drying: compound **6**: elemental analysis calcd (%) for $C_{72}H_{76}N_6O_{11}Te_6$ (1967.0): C 43.96, H 3.89, N 4.27; found: C 43.81, H 3.75, N 4.19; compound **7**: elemental analysis calcd (%) for $C_{72}H_{76}N_6O_{11}Te_6$ (1967.0): C 43.96, H 3.89, N 4.24; found: C 43.84, H 3.95, N 4.12.

In solution, **6** and **7** gave identical spectroscopic data. ^{1}H NMR (D_2O): $\delta = 8.40$ (d, 1H; Ar), 8.22 (d, 1H; Ar), 7.99 (d, H; Ar), 7.85 (t, 1H; Ar), 7.79 (d, 1H; Ar), 7.70 (t, 1H; Ar), 2.89 ppm (s, 3H; Me); ^{13}C NMR (D_2O): $\delta = 148.2$, 135.8, 132.6, 130.9, 130.4, 128.3, 128.1, 128.0, 121.1 (Ar), 46.4 ppm (Me); ^{125}Te NMR (D_2O): $\delta = 1530.6$ ppm; ESI-TOF MS (H_2O, positive mode): *m*/*z*: 974.0 $[C_{36}H_{36}N_3O_5Te_3]^+$, 958.0 $[C_{36}H_{36}N_3O_4Te_3]^+$, 645.0 $[C_{24}H_{25}N_2O_3Te_2]^+$, 334.0 $[C_{12}H_{14}NO_2Te]^+$.

Synthesis of $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ (8): A solution of $ClTe(O\mathit{i}Pr)_3$ (59 mg, 0.20 mmol) in THF (20 mL) was added to a hot solution of **7** (204 mg, 0.10 mmol) in THF (50 mL). The solution was left to stand so that atmospheric moisture could slowly hydrolyse the $ClTe(O\mathit{i}Pr)_3$. After a few minutes a colourless solid precipitated, which was redissolved in $CHCl_3$ (50 mL) and hexane (10 mL). Slow evaporation of the solvent provided colourless prisms of **8** (110 mg, 0.048 mmol, 48 %; m.p. 272–274 °C (decomp)). No reasonable NMR spectra were obtained. Elemental analysis calcd (%) for $C_{72}H_{72}Cl_2N_6O_{12}Te_8$ (2305.08): C 37.52, H 3.15, N 3.65; found: C 37.25, H 3.24, N 3.29; ESI-TOF MS (THF, positive mode): *m*/*z*: 2270.7 $[C_{72}H_{72}ClN_6O_{12}Te_8]^+$, 1921.8 $[C_{60}H_{60}N_5O_{11}Te_7]^+$, 1759.9 $[C_{60}H_{60}N_5O_9Te_6]^+$, 1626.8 $[C_{48}H_{48}Cl_3ClN_4O_9Te_6]^+$, 1277.8 $[C_{36}H_{36}N_3O_8Te_5]^+$, 1117.9 $[C_{36}H_{36}N_3O_6Te_4]^+$, 1117.9 $[C_{72}H_{72}ClN_6O_{12}Te_8]^{2+}$.

Crystallography: Intensity data were collected on a Bruker SMART 1000 CCD area detector (**1**, **2**, **5**) and a Stoe IPDS 2T area detector (**3**, **6**, **7**, **8**) equipped with graphite-monochromated $Mo_{K\alpha}$ (0.7107 Å) radiation. Data were reduced and corrected for absorption using commercial Bruker and Stoe software. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[21] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. H atoms attached to C atoms were included in geometrically calculated positions for all structures using a riding model and were refined isotropically. H atoms attached to O atoms were not located during the refinement and are therefore omitted. The two crystallographically independent molecules of **3** are disordered. The atoms Te1–Te4 and Cl1–Cl8 were refined over two positions with split occupancies of 85 and 15 %. Two of the four crystallographically independent $CHCl_3$ molecules of $\mathbf{5}\cdot 8\,CHCl_3$ are disordered. The atoms Cl3–Cl7 were refined over two positions with split occupancies of 50 %. Figure were created with DIAMOND.[22] Table 1 contains the crystal data and structure refinement data for compounds **1**–**8**. CCDC-793288 (**1** (monoclinic)), 793289 (**1** (triclinic)), 793290 (**2**), 793291 (**3**), 793292 ($\mathbf{5}\cdot 8\,CHCl_3$), 793293 ($\mathbf{6}\cdot {}^7\!/_3\,H_2O$), 793294 ($\mathbf{7}\cdot 4\,THF\cdot 6\,H_2O$) and 793295 ($\mathbf{8}\cdot 4\,H_2O$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Irene Brüdgam and Dr. Malte Hesse (Freie Universität Berlin) are thanked for the X-ray data collection. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

---

[1] K. Lederer, *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 1345–1350.

[2] a) L. Reichel, E. Kirschbaum, *Justus Liebigs Ann. Chem.* **1936**, *523*, 211–223; b) N. Petragnani, G. Vicentini, *Bol. Quim. Peru.* **1959**, *5*, 75–84; c) P. Thavornyutikarn, W. R. McWhinnie, *J. Organomet. Chem.* **1973**, *50*, 135–143; d) J. Bergman, J. Siden, K. Maartmann-Moe, *Tetrahedron* **1984**, *40*, 1607–1610; e) D. H. R. Barton, J.-P. Finet, M. Thomas, *Tetrahedron* **1986**, *42*, 2319–2324.

[3] J. Beckmann, P. Finke, M. Hesse, B. Wettig, *Angew. Chem.* **2008**, *120*, 10130–10133; *Angew. Chem. Int. Ed.* **2008**, *47*, 9982–9984.

[4] H. Citeau, K. Kirschbaum, O. Conrad, D. M. Giolando, *Chem. Commun.* **2001**, 2006–2007.

[5] a) R. El-Mallawany, *Mater. Chem. Phys.* **1998**, *53*, 93–120; b) R. El-Mallawany, *Mater. Chem. Phys.* **1999**, *60*, 103–131; c) R. El-Mallawany, *Mater. Chem. Phys.* **2000**, *63*, 109–115; d) J. C. McLaughlin, S. L. Tagg, J. W. Zwanziger, D. R. Haeffner, S. D. Shastri, *J. Non-Cryst. Solids* **2000**, *274*, 1–8; e) J. C. McLaughlin, S. L. Tagg, J. W. Zwanziger, *J. Phys. Chem. B* **2001**, *105*, 67–75.

[6] a) S. Sakida, S. Hayakawa, T. Yoku, *J. Non-Cryst. Solids* **1999**, *243*, 13–25; b) D. Holland, J. Bailey, G. Ward, B. Turner, P. Tierney, R. Dupree, *Solid-State NMR* **2005**, *27*, 16–27.

[7] C. R. Becker, S. L. Tagg, J. C. Huffman, J. W. Zwanziger, *Inorg. Chem.* **1997**, *36*, 5559–5564, and references cited therein.

[8] K. Srivastava, S. Sharma, H. B. Singh, U. P. Singh, R. J. Butcher, *Chem. Commun.* **2010**, *46*, 1130–1132.

[9] a) S. C. Menon, H. B. Singh, J. M. Jasinksi, J. P. Jasinski, R. J. Butcher, *Organometallics* **1996**, *15*, 1707–1712; b) J. Beckmann, J. Bolsinger, A. Duthie, *Organometallics* **2009**, *28*, 4610–4612.

[10] A. Panda, G. Mugesh, H. B. Singh, R. J. Butcher, *Organometallics* **1999**, *18*, 1986–1993.

[11] J. Beckmann, S. Heitz, M. Hesse, *Inorg. Chem.* **2007**, *46*, 3275–3282.

[12] J. Beckmann, D. Dakternieks, A. Duthie, F. Ribot, M. Schürmann, N. A. Lewcenko, *Organometallics* **2003**, *22*, 3257–3261.

[13] J. Beckmann, J. Bolsinger, A. Duthie, *Aust. J. Chem.* **2008**, *61*, 172–182.

[14] a) K. Kobayashi, N. Deguchi, O. Takahashi, K. Tanaka, E. Horn, O. Kikuchi, N. Furukawa *Angew. Chem.* **1999**, *111, 1746–1748; Angew. Chem. Int. Ed.* **1999**, 38, 1638–1640; *Angew. Chem. Int. Ed.* **1999**, *38*, 1638–1640; b) K. Kobayashi, K. Tanaka, H. Izawa, Y. Arai, N. Furukawa, *Chem. Eur. J.* **2001**, *7*, 4272–4279.

[15] N. W. Alcock, W. D. Harrison, *J. Chem. Soc. Dalton Trans.* **1982**, 251–255.

[16] T. Steiner, *Angew. Chem.* **2002**, *114*, 50–80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76.

[17] J. Beckmann, J. Bolsinger, P. Finke, M. Hesse, *Angew. Chem.* **2010**, *122*, 8204–8206; *Angew. Chem. Int. Ed.* **2010**, *49*, 8030–8032.

[18] a) A. J. Canty, G. van Koten, *Acc. Chem. Res.* **1995**, *28*, 406–413; b) C. J. Carmalt, A. H. Cowley, *Main Group Chem. News* **1996**, *4*, 4–10.

[19] H. Fleischer, D. Schollmeyer, *Inorg. Chem.* **2001**, *40*, 324–328.
[20] A. P. Mirgorodsky, T. Merle-Méjean, J. C. Champarneaud, P. Thomas, B. Frit, *J. Phys. Chem. Solids* **2000**, *61*, 501–509.
[21] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[22] DIAMOND V2.1d, Crystal Impact, K. Brandenburg & M. Berndt GbR, **2002**.

Received: August 17, 2010

MANUSCRIPT X

13 The Photooxidation of Bis-(8-dimethylaminonaphthyl) Ditelluride

Jens Beckmann and Jens Bolsinger; *Z. Anorg. Allg. Chem.* **2011**, *637*, 29–30

13.1 SYNOPSIS

In organotellurium chemistry diorgano ditellurides $(RTe)_2$ (R = alkyl, aryl) are important starting materials[110], most of which are light-sensitive. Solutions of diorgano ditellurides decolorize rapidly upon radiation with ambient or UV light. Frequently amorphous, ill-defined solids precipitate then from the solutions, which were assigned to be polymeric tellurinic acids $[RTe(O)OH]_n$ or related anhydrides[132].

The interest of our work group was in the examination of molecular tellurinic acids[51], telluronic acids[122] and related telluroxane clusters and polymers[94]. Thus, the photooxidation of the diaryl ditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$[114,118] was examined.

A THF solution of the diaryl ditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ was saturated with air and radiated with a UV lamp. A small crop of the novel tetranuclear telluroxane cluster $(8\text{-}MeNC_{10}H_5TeO)_4$ was obtained, which can be classified as a tellurinic amide. Two 5,5'-binaphthyl moieties - formed upon oxidation of the activated C5–H bonds of two naphthyl groups - give rise to a C5–C5' cross-coupling, whereby the methyl group was cleaved and the coordinative Te···N bond turned into a covalent Te–N bond.

The four tellurium atoms give rise to two crystallographically related four-membered Te_2O_2 rings comparable to $[2,6\text{-}Mes_2C_6H_3)_2Te(O)OH]_2$[51] and $(Ph_2TeO)_2$[74]. The average Te–N bond is substantially shorter than the average coordinative Te···N bond lengths of $(8\text{-}Me_2NC_{10}H_6Te)_2$ and $(8\text{-}Me_2NC_{10}H_6Te)_2Te$[114,118]. Individual molecules are associated by intermolecular secondary Te···O interactions in the crystal lattice giving rise to the formation of a 1D coordination polymer

12.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann.

X-Ray Crystallography: Prof. Dr. Jens Beckman

DOI: 10.1002/zaac.201000343

The Photooxidation of Bis(8-dimethylaminonaphthyl) Ditelluride

Jens Beckmann*[a,b] and Jens Bolsinger[a]

Keywords: Binaphtyl; Organotellurides; Photooxidation; Supramolecular chemistry; Tellurium

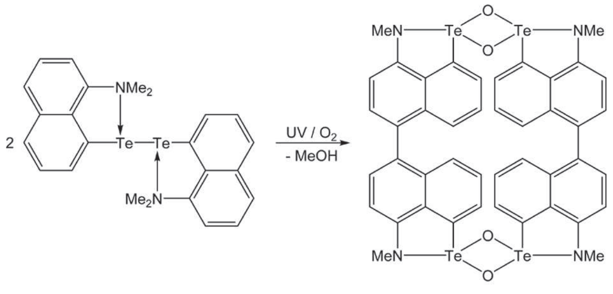
Abstract. The photooxidation of $(8\text{-}Me_2NC_{10}H_6Te)_2$ provided a complex reaction mixture from which the novel tetranuclear telluroxane cluster $(8\text{-}MeNC_{10}H_5TeO)_4$ (**1**) was isolated in 17 % yield. Compound **1** contains two 5,5'-binaphthyl moieties that presumably formed by oxidation of C5–H bonds of the naphthyl ring. Upon formation of **1**, one of the two methyl groups of the 8-dimethylamino group was cleaved and the remaining coordinative Te···N bond turned into a covalent Te–N bond. In the solid-state, individual molecules of **1** are associated through secondary Te···O interactions giving rise to a 1D coordination polymer.

Introduction

Diorgano ditellurides $(R\text{Te})_2$ (R = alkyl, aryl) are versatile starting materials in organotellurium chemistry [1]. Most of these diorgano ditellurides are light-sensitive, particularly in the presence of air. Upon radiation with ambient or UV light, solutions of the diorgano ditellurides decolorize rapidly and often amorphous ill-defined solids precipitate, which were assigned to be *polymeric* tellurinic acids $[R\text{Te(O)OH}]_n$ or related anhydrides [2]. Our interest in *molecular* tellurinic acids [3], telluronic acids [4] and related telluroxane clusters and polymers [5] that are stabilized by bulky or intramolecularly coordinating N-donor substituents prompted a study on the photooxidation of a diaryl ditelluride, namely $(8\text{-}Me_2NC_{10}H_6Te)_2$ [6].

Discussion

A THF solution containing the diaryl ditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ was saturated with air and radiated with a UV lamp. Within minutes, the deep orange color of the solution faded to light orange and a ^{1}H-NMR spectrum indicated that a complex reaction mixture had formed. Fractional crystallization afforded a small crop of the novel tetranuclear telluroxane cluster $(8\text{-}MeNC_{10}H_5TeO)_4$ (**1**) as orange crystalline solid (Scheme 1).



1

Scheme 1.

The structure of **1** was established by X-ray crystallography and is shown in Figure 1. Selected bond parameters are collected in the caption of the figure The key feature of **1** is the presence of two 5,5'-binaphthyl moieties, which apparently formed upon oxidation of the activated C5–H bonds of two naphthyl groups giving rise to a C5–C5' cross-coupling. At the same time one of the methyl groups was cleaved and the (formal) coordinative Te···N bond turned into a covalent Te–N bond. Most likely the cleaved methyl group was oxidized to methanol, however, no attempt was made to detect it in the crude reaction mixture. After the photolysis, the oxidation state of the tellurium atoms is 4. Thus, compound **1** can be classified as a tellurinic amide.

The spatial arrangement of the two crystallographically independent Te^{IV} atoms is distorted trigonal bipyramidal and defined by a CO_2N donor set and the stereochemically active lone pair. The four tellurium atoms give rise to two crystallographically related four-membered Te_2O_2 rings reminiscent to those of $[2,6\text{-}Mes_2C_6H_3)_2Te(O)OH]_2$ [3] and $(Ph_2TeO)_2$ [7]. The slight asymmetry of the four-membered Te_2O_2 ring is reflected in the Te–O bond lengths of 1.908(7) and 2.195(6) Å, which compare well with those of $[2,6\text{-}Mes_2C_6H_3)_2Te(O)OH]_2$ (1.897(5) and 2.143(5) Å) [3]. By contrast, the asymmetry of the four-membered Te_2O_2 ring is larger in $(Ph_2TeO)_2$ (av. 1.89(1) and av. 2.55(1) Å) [7]. The average Te–N bond of

---

* Prof. Dr. J. Beckmann
Fax: +49-421-218-9863160
E-Mail: j.beckmann@uni-bremen.de.
[a] Institut für Chemie und Biochemie
Freie Universität Berlin
Fabeckstraße 34–36
14195 Berlin, Germany
[b] Present address: Institut für Anorganische und Physikalische Chemie
Universität Bremen
Leobener Str. Gebäude NW2. Postfach 330440
28334 Bremen, Germany

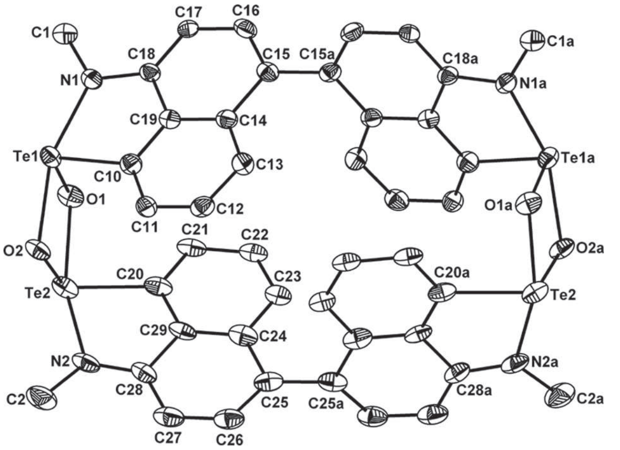


Figure 1. Molecular structure of **1** showing 30 % probability ellipsoids and the crystallographic numbering scheme. Symmetry code used to generate equivalent atoms: a = $-x$, y, $-0.5-z$). Selected bond parameters (Å, °): Te1–O1 1.908(7), Te1–O2 2.195(6), Te1–C10 2.122(9), Te1–N1 2.076(7), Te2–O1 2.155(6), Te2–O2 1.891(6), Te2–C20 2.112(8), Te2–N2 2.103(8), Te1–O2a 2.877(6), O1–Te1–O2 76.0(2), O1–Te1–C10 100.8(3), O2–Te1–C10 86.0(3), O1–Te1–N1 94.0(3), O2–Te1–N1 160.3(2), C10–Te1–N1 79.2(3), O1–Te2–O2 77.3(2), O1–Te2–C20 86.0(3), O1–Te2–N2 155.0(3), O2–Te2–C20 109.0(3), O2–Te2–N2 90.2(3), C20–Te2–N2 77.6(3).

2.090(8) Å is substantially shorter than the average coordinative Te···N bond lengths of the diaryl ditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ (2.721(5) Å) and diaryl tritelluride $(8\text{-}Me_2NC_{10}H_6Te)_2Te$ (2.67(1) Å) [6]. In the crystal lattice, individual molecules of **1** are associated by intermolecular secondary Te···O interactions of 2.877(6) Å giving rise to the formation of a 1D coordination polymer (Figure 2). Once isolated from the mother liqueur, the solubility of **1** in all solvents tested is very poor, presumably due to the high lattice energy associated with these secondary contacts. The ^1H NMR spectrum ($CDCl_3$) reveals a ratio of 20 aromatic to 12 aliphatic hydrogen atoms, which confirms the cleavage of one methyl group upon formation of **1**. The signal of the N–CH_3 group at $\delta = 3.40$ is significantly downfield shifted to that of the parent diaryl ditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ ($\delta = 2.87$) [6].

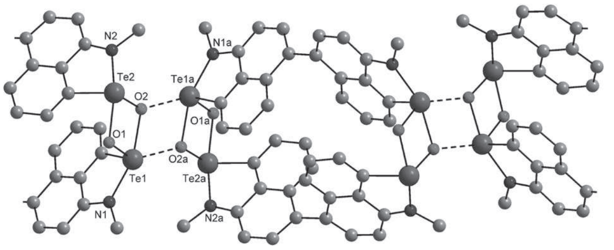


Figure 2. Supramolecular association of **1** through secondary Te···O interactions.

Experimental Section

Synthesis of $(8\text{-}MeNC_{10}H_5TeO)_4$ (1): A solution of $(8\text{-}Me_2NC_{10}H_6Te)_2$ (300 mg, 0.50 mmol) in THF (100 mL) was saturated with air and radiated with a UV lamp for 30 min. Fractional crystallization afforded orange prisms of **1** (58 mg, 0.043 mmol, 17 %; Mp. 293–295 °C.).

^{1}H NMR ($CDCl_3$): δ = 7.70 (d, 4 H, Ar), 7.38 (d, 4 H, Ar), 6.94 (t, 4 H, Ar), 6.80 (d, 4 H, Ar), 6.54 (d, 4 H, Ar), 3.40 (s, 12 H, NCH_3). $C_{52}H_{48}N_4O_6Te_4$ (1335.34): C 45.91, H 3.85; N 4.46. Found C 45.41, H 3.78; N 4.33 %.

Crystallography: Crystal data and structure solution of **1**·2 THF: $C_{52}H_{48}N_4O_6Te_4$, M_r = 1335.34, monoclinic, $C2/c$, a = 20.032(9), b = 12.041(4), c = 18.92(1) Å, β = 96.87(5)°, V = 4530(4) Å^3, Z = 4, D_x = 1.958 Mg·m^{-3}, $F(000)$ = 2576, μ = 2.608 mm^{-1}, T = 150 K. Intensity data were collected with a STOE IPDS 2T area diffractometer fitted with Mo-K_a radiation (graphite crystal monochromator, l = 0.71073 Å) to a maximum of q_{max} = 26.00° via w scans (completeness 98.7 % to q_{max}). Data were reduced and corrected for absorption and the structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX 2002 [8]. Full-matrix least-squares refinement on F^2, using all data, was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions using a riding model (including free rotation about C–C) and were refined isotropically. R_1 = 0.0521 for 2396 [$I > 2s(I)$] and wR_2 = 0.1170 for 4403 independent reflections. GooF = 0.909. The max. and min. residual electron densities were 1.159 and –1.060 e·Å^{-3}. Figures were prepared using DIAMOND [9]. Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 795555 (**1**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; E-Mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgement

The *Deutsche Forschungsgemeinschaft* (DFG) is gratefully acknowledged for financial support.

References

[1] I. D. Sadekov, V. I. Minkin, *Sulfur Rep.* **1997**, *19*, 285.
[2] a) P. Granger, S. Chapelle, M. McWhinnie, A. Al-Rubaie, *J. Organomet. Chem.* **1981**, *220*, 149; b) M. Sharma, K. K. Bhasin, S. K. Mehta, N. Singh, S. Kumar, *Radiat. Phys. Chem.* **2006**, *75*, 2029; c) H. Kunkely, A. Vogler, *Inorg. Chim. Acta* **2009**, *362*, 281.
[3] J. Beckmann, P. Finke, M. Hesse, B. Wettig, *Angew. Chem. Int. Ed.* **2008**, *47*, 9982.
[4] J. Beckmann, J. Bolsinger, P. Finke, M. Hesse, *Angew. Chem. Int. Ed.* **2010**, *49*, 8030.
[5] J. Beckmann, J. Bolsinger, A. Duthie, *Chem. Eur. J.* **2010**, published online, DOI: 10.1002/chem.201002391.
[6] a) S. C. Menon, H. B. Singh, J. M. Jasinksi, J. P. Jasinski, R. J. Butcher, *Organometallics* **1996**, *15*, 1707; b) J. Beckmann, J. Bolsinger, A. Duthie, *Organometallics* **2009**, *28*, 4610.
[7] N. W. Alcock, W. D. Harrison, *J. Chem. Soc., Dalton Trans.* **1982**, 251.
[8] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.
[9] *DIAMOND V2.1d*, Crystal Impact, K. Brandenburg & M. Berndt GbR, **2002**.

Received: September 16, 2010
Published Online: November 10, 2010

MANUSCRIPT XI

14 A Well-Defined Dinuclear Telluronic Acid [RTe(μ-O)(OH)$_3$]$_2$

Jens Beckmann, Jens Bolsinger, Pamela Finke and Malte Hesse; *Angew. Chem. Int. Ed.* **2010**, *49*, 8030 – 8032

14.1 SYNOPSIS

Sulfonic acids, RS(=O)$_2$(OH) (R = alkyl, aryl), are a well-established compound class that finds extensive utility in organic synthesis[52]. Concerning the related heavier congeners, little is known, which is probably due to their difficult preparation and handling[53,54,56,57].

Due to the progress concerning stable hexacoordinate organotellurium(VI) compounds, such as R_6Te, Ph_5TeF, and R_4TeF_2 (R=Me, Ph)[123] the preparation of the hitherto unknown telluronic acids was investigated.

The dinuclear *m*-terphenyltellurinic acid [2,6-$Mes_2C_6H_3Te(\mu\text{-}O)(OH)]_2$[51] was treated with sodium hydride to give the tetranuclear sodium *m*-terphenyltellurinate $Na_4(2,6\text{-}Mes_2C_6H_3Te)_4(\mu_3\text{-}O)_8$, which was oxidized by dry O_2 in the presence of [18]crown-6 to afford the dinuclear *m*-terphenyltelluronic acid [2,6-$Mes_2C_6H_3Te(m\text{-}O)(OH)_3]_2$.

In the absence of crown ether no reaction took place. Furthermore, all attempts to prepare the dinuclear *m*-terphenyltelluronic acid by the direct oxidation of the tellurinic acid using various strong oxidants, such as H_2O_2, $KMnO_4$, or $NaIO_4$, failed.

The molecular structure of the tetranuclear sodium *m*-terphenyltellurinate comprises an unprecedented $Na_4Te_4O_8$ cage structure that is completely shielded by four *m*-terphenyl groups. The Te-O bond lengths are significantly shorter than the average standard Te-O single bonds of $[(4\text{-}MeOC_6H_4)_2TeO]_n$[19] and indicate a formal bond order of 1.5. The coordination of the Te atoms is completed by a secondary Te···O contact that is substantially shorter than the sum of van der Waals radii[124].

The molecular structure of the telluronic acid comprises a dinuclear four membered Te_2O_2 ring structure that is completely shielded by two *m*-terphenyl groups, whereby the spatial arrangement of the Te atoms is octahedral. The average Te-O bond lengths of the telluronic acid are comparable with the bond length of the cubic orthotelluronic acid $Te(OH)_6$[125].

To estimate the relative stability of meta-, meso-, and orthophenylchalcogonic acids, DFT calculations were performed at the B3PW91/TZ level of theory.

These calculations confirm that for the lighter elements the tetracoordinated metaphenylchalcogonic acids PhE(=O)$_2$OH (E = S, Se) are more stable than the pentacoordinated or hexacoordinated compounds. The same applies to the paraphenylchalcogonic acid [PhE(μ_2-O)(OH)$_3$]$_2$ (E = S, Se). By contrast, the tetracoordinated and the pentacoordinated telluronic acids are less stable than the hexacoordinated acid and paraphenylchalcogonic acid [PhTe(μ_2-O)(OH)$_3$]$_2$, whereby the later have nearly the same stability.

The experimental and computational results uniformly show that a qualitative change in structures of arylchalcogonic acids occurs when going from 4th to the 5th period.

14.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed the experiments together with Dr. Malte Hesse. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann, Dr. Malte Hesse and Pamela Finke.

X-Ray Crystallography: Prof. Dr. Jens Beckmann
^{125}Te MAS-NMR spectra and analysis: Dr. Andrew Duthie
The DFT-calculations were carried out by Pamela Finke.

Telluronic Acids

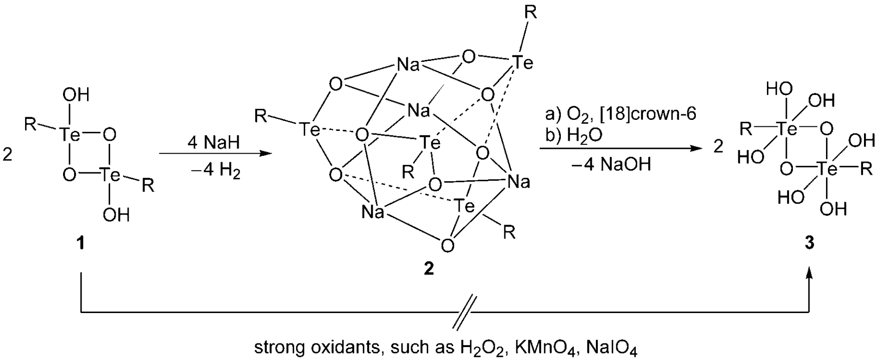
DOI: 10.1002/anie.201002545

A Well-Defined Dinuclear Telluronic Acid $[RTe(\mu\text{-}O)(OH)_3]_2$**

Jens Beckmann, Jens Bolsinger, Pamela Finke, and Malte Hesse*

In memory of Herbert Schumann

Compared to the well-established chemistry of sulfonic acids, RSO_3H, and their extensive utility in organic synthesis, the knowledge of the heavier congeners is rather modest. This discrepancy is arguably due to their tedious preparation and difficult handling.[1–4] Like sulfonic acids, selenonic acids, $RSeO_3H$,[1] are strong acids. However, unlike their sulfur analogues, selenonic acids are also strong oxidizing reagents; sufficiently strong to oxidize chloride ions to chlorine.[2] Although benzeneselenonic acid, $PhSeO_3H$, was obtained by selenonation of benzene,[3] a more general route for the preparation of selenonic acids, $RSeO_3H$, involves the oxidation of readily available seleninic acids, $RSeO_2H$, by $KMnO_4$ to give the potassium selenates $K[RSeO_3]$, which upon treatment with $HClO_4$ liberate the free acids.[4] Selenonic acids, $RSeO_3H$, are thermally unstable. Concentrated solutions of trifluoromethaneselenonic acid, F_3CSeO_3H, the selenium analogue of triflic acid, decompose violently at ambient temperature.



Scheme 1. Synthesis of **2** and **3** ($R = 2,6\text{-}Mes_2C_6H_3$).

Progress in the synthesis of stable hexacoordinate organotellurium(VI) compounds, such as R_6Te, Ph_5TeF, and R_4TeF_2 (R = Me, Ph)[5] prompted us to investigate the preparation of hitherto unknown telluronic acids, which was achieved for a kinetically stabilized prototype in two simple preparative steps (Scheme 1).

The dinuclear *m*-terphenyltellurinic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)]_2$[6] (**1**) was treated with sodium hydride to give the tetranuclear sodium *m*-terphenyltellurinate $Na_4(2,6\text{-}Mes_2C_6H_3Te)_4(\mu_3\text{-}O)_8$ (**2**), which was oxidized by dry O_2 in the presence of [18]crown-6 to afford the dinuclear *m*-terphenyltelluronic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$ (**3**). In the absence of crown ether no reaction took place. It should also be noted that all attempts to prepare **3** by the direct oxidation of **1** using various strong oxidants, such as H_2O_2, $KMnO_4$, or $NaIO_4$, failed.

The molecular structure of **2** comprises an unprecedented $Na_4Te_4O_8$ cage structure that is completely shielded by four *m*-terphenyl groups (Figure 1).[7] The spatial arrangement of the crystallographically equivalent Te atoms of **2** is distorted tetrahedral when taking into account the primary coordination sphere (O_2C donor set) and the stereochemically active lone pair. The Te–O bond lengths of 1.832(4) and 1.850(4) Å are significantly shorter than the average 'standard Te–O single bonds' of $[(4\text{-}MeOC_6H_4)_2TeO]_n$ (2.063(2) Å)[8] and indicate a formal bond order of 1.5. The coordination of the

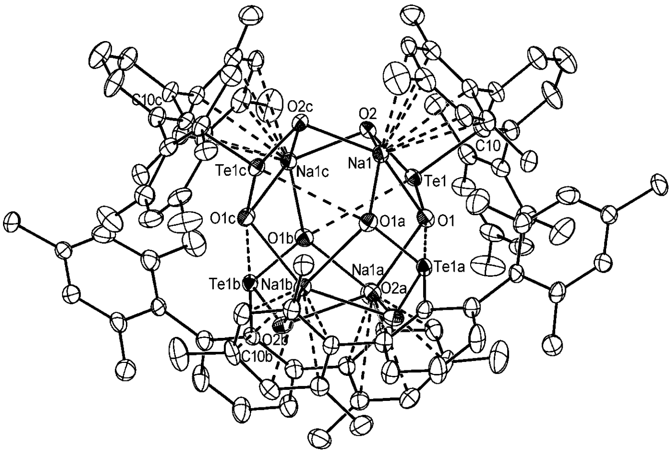


Figure 1. Molecular structure of **2**; thermal ellipsoids are set at 30% probability. Selected interatomic distances [Å]: Te1–O1 1.850(4), Te1···O1b 3.195(4), Te1–O2 1.832(4), Te1–C10 2.163(5), Na1–O1 2.568(5), Na1–O1a 2.357(4), Na1–O2 2.469(5), Na1–O2c 2.261(4).

---

[*] Prof. Dr. J. Beckmann,[+] Dipl.-Chem. J. Bolsinger,
Dipl.-Chem. P. Finke, Dr. M. Hesse
Institut für Chemie und Biochemie, Freie Universität Berlin
Fabeckstrasse 34/36, 14195 Berlin (Germany)

[+] Present address: Institut für Anorganische und Physikalische
Chemie, Universität Bremen
Leobener Strasse, 28359 Bremen (Germany)
E-mail: j.beckmann@uni-bremen.de

[**] $R = 2,6\text{-}Mes_2C_6H_3$. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201002545.

Te atoms is completed by a secondary Te···O contact of 3.195(4) Å, that is substantially shorter than the sum of van der Waals radii (3.5 Å).[9]

The spatial arrangement of the sodium atoms is square pyramidal and defined by four Na−O bonds ranging from 2.261(4) to 2.568(5) Å as well as the η^6-coordination with one of the mesityl group of the organic substituent (shortest distance from the ideal plane 1.703(4) Å). Of note is that **2** is a potential model compound for amorphous sodium tellurite glasses $(Na_2O)_x(TeO_2)_{1-x}$ ($0.10 < x < 0.35$), for which little structural information is available.[10] In solution, **2** is characterized by a ^{125}Te NMR spectroscopic chemical shift of $\delta = 1698$ ppm, which is significantly different from that of the parent acid **1** ($\delta = 1403$ ppm).[6]

The molecular structure of **3** comprises a dinuclear four-membered Te_2O_2 ring structure that is completely shielded by two *m*-terphenyl groups (Figure 2). The spatial arrangement of the Te atoms of **3** is octahedral and defined by an O_5C donor set. The average Te−O bond lengths of 1.938(3) Å compare well with that of cubic orthotelluronic acid $Te(OH)_6$ (1.912(6) Å).[11] The IR spectrum of **3** shows two sharp intense signals at $\tilde{\nu} = 3665$ and 3616 cm^{-1}, which are assigned to OH stretching vibrations. The ^{125}Te NMR spectrum ($CDCl_3$) of **3** shows one signal at $\delta = 783$ ppm.

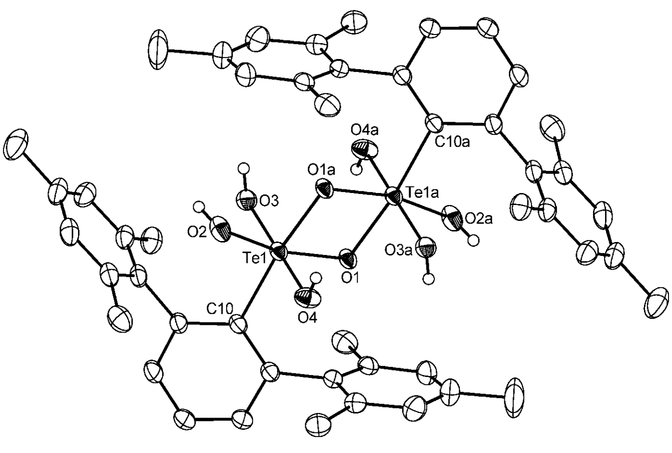


Figure 2. Molecular structure of **3**; thermal ellipsoids are set at 30% probability. Selected bond lengths [Å]: Te1–O1 1.943(2), Te1–O1a 1.971(2), Te1–O2 1.918(2), Te1–O3 1.938(3), Te1–O4 1.918(3), Te1–C10 2.154(3).

To estimate the relative stability of meta-, meso-, and orthophenylchalcogonic acids, DFT calculations were performed at the B3PW91/TZ level of theory (Figure 3).[12] These calculations confirm that for the lighter elements the tetracoordinated metaphenylchalcogonic acids $PhE(=O)_2OH$ (E = S,Se; (0 kJ mol^{-1})) are more stable than the pentacoordinated mesophenylchalcogonic acids $PhE(=O)(OH)_3$ (174 kJ mol^{-1} for E = S; 47 kJ mol^{-1} for E = Se) and the hexacoordinated orthophenylchalcogonic acids $PhE(OH)_5$ (263 kJ mol^{-1} for E = S; 46 kJ mol^{-1} for E = Se) and paraphenylchalcogonic acid $[PhE(\mu_2\text{-}O)(OH)_3]_2$ (241 kJ mol^{-1} for E = S; 33 kJ mol^{-1} for E = Se).

By contrast, the tetracoordinated metaphenyltelluronic acid $PhTe(=O)_2OH$ (173 kJ mol^{-1}) and the pentacoordinated mesophenyltelluronic acid $PhTe(=O)(OH)_3$ (101 kJ mol^{-1}) are less stable than the hexacoordinated orthophenyltelluronic acid $PhTe(OH)_5$ (3 kJ mol^{-1}) and paraphenylchalcogonic acid $[PhTe(\mu\text{-}O)(OH)_3]_2$ (0 kJ mol^{-1}), which have nearly the same stability. MP2 calculations performed at the same level of theory confirm the same trend; however, the energy differences are slightly more pronounced than for the DFT calculations (Figure 3).

Both the experimental and computational results uniformly show that a qualitative change in structures of arylchalcogonic acids occurs when going from 4th to the 5th period. We are currently investigating the reactivity of **3** and related compounds.

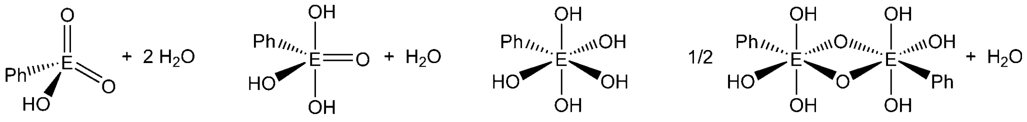
Experimental Section

2: A mixture of **1** (1.00 g, 1.10 mmol) and NaH (56 mg, 2.3 mmol) in toluene (40 mL) was stirred for 12 h at room temperature. The solution was filtered and the solvent removed in vacuum. The solid residue was recrystallized from MeCN/THF to give colorless crystals of **2** (890 mg, 0.45 mmol, 82%).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.39$ (t, 1H, Ar), 6.89 (d, 2H, Ar), 6.27 (s, 4H, Ar), 2.18 (s, 6H, CH_3), 1.96 (s, 12H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 147.5$, 144.6, 137.9, 137.6, 137.0, 130.0, 129.3, 108.0 (Ar), 21.2, 21.1 (CH_3) ppm. ^{125}Te NMR ($CDCl_3$, 126 MHz): $\delta = 1698$ ppm. IR (KBr): $\tilde{\nu}_{OH} = 3665$ and 3616 cm^{-1}. Elemental analysis calcd (%) for $C_{96}H_{100}Na_4O_8Te_4$ (1984.16): C 58.11, H 5.08; found: C 58.49, H 5.39.

3: Oxygen was bubbled through a hot solution of **2** (800 mg, 0.40 mmol) and [18]crown-6 (422 mg, 1.6 mmol) in THF (50 mL) for 2 h. Water (5 mL) was added and the layers separated. The organic layer was dried over Na_2SO_4 and the solvent removed in vacuum. The solid residue was recrystallized from THF/hexane and the solid dried in vacuum to give **3** as colorless solid (320 mg, 0.12 mmol, 50%).

^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.43$ (t, 1H; Ar), 6.92 (d, 2H; Ar), 6.29 (s, 4H; Ar), 2.22 (s, 6H; CH_3), 1.98 ppm (s, 12H; CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 146.9$, 144.1, 137.2, 136.8, 136.0,



E = S:	**0 kJ mol^{-1}**	174 kJ mol^{-1}	263 kJ mol^{-1}	241 kJ mol^{-1}
E = Se:	**0 kJ mol^{-1}**	47 kJ mol^{-1}	46 kJ mol^{-1}	33 kJ mol^{-1}
E = Te:	172 (221) kJ mol^{-1}	101 (139) kJ mol^{-1}	**3 (16) kJ mol^{-1}**	**0 (0) kJ mol^{-1}**

Figure 3. Relative stability of meta-, meso-, ortho-, and paraphenylchalcogonic acids (DFT/B3PW91 calculations for S, Se, and Te compounds; MP2 calculations for Te compounds in parenthesis).

129.9, 128.5, 126.9 (Ar), 20.8, 20.7 ppm (CH_3). ^{125}Te NMR ($CDCl_3$, 126 MHz): $\delta = 783$ ppm. Elemental analysis calcd (%) for $C_{48}H_{56}O_8Te_2$ (1016.23): C 56.73, H 5.55; found: C 56.49, H 5.43.

Received: April 28, 2010

Keywords: hypervalent compounds · oxides · tellurium

---

[1] T. W. Campbell, H. Walker, G. H. Coppinger, *Chem. Rev.* **1952**, *50*, 279–349.

[2] a) H. W. Doughty, *Am. Chem. J.* **1909**, *41*, 326–337; b) R. Lesser, R. Weiss, *Ber. Dtsch. Chem. Ges.* **1913**, *46*, 2640–2658.

[3] a) M. Schmidt, J. Wilhelm, *Chem. Ber.* **1964**, *97*, 872–875; b) K. Dostál, Z. Žak, M. Ĉernik, *Chem. Ber.* **1971**, *104*, 2044–2052.

[4] a) A. Haas, K.-U. Weiler, *Chem. Ber.* **1985**, *118*, 943–951; b) A. Haas, K. Schinkel, *Chem. Ber.* **1990**, *123*, 685–689; c) R. Boese, A. Haas, S. Herkt, M. Pryka, *Chem. Ber.* **1995**, *128*, 423–428.

[5] a) L. Ahmed, J. A. Morrison, *J. Am. Chem. Soc.* **1990**, *112*, 7411–7413; b) M. Minoura, T. Sagami, K. Akiba, C. Modrakowski, A. Sudau, K. Seppelt, S. Wallenhauer, *Angew. Chem.* **1996**, *108*, 2827–2829; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2660–2662; c) M. Minoura, T. Mukuda, T. Sagami, K. Akiba, *J. Am. Chem. Soc.* **1999**, *121*, 10852–10853; d) M. Miyasato, M. Minoura, K. Akiba, *Angew. Chem.* **2001**, *113*, 2746–2748; *Angew. Chem. Int. Ed.* **2001**, *40*, 2674–2676; e) M. Minoura, T. Sagami, K. Akiba, *Organometallics* **2001**, *20*, 2437–2439; f) M. Miyasato, T. Sagami, M. Minoura, Y. Yamamoto, K. Akiba, *Chem. Eur. J.* **2004**, *10*, 2590–2600; g) T. M. Klapötke, B. Krumm, K. Polborn, I. Schwab, *J. Am. Chem. Soc.* **2004**, *126*, 14166–14175.

[6] J. Beckmann, P. Finke, M. Hesse, B. Wettig, *Angew. Chem.* **2008**, *120*, 10130–10133; *Angew. Chem. Int. Ed.* **2008**, *47*, 9982–9984.

[7] a) Crystal data for **2**·4 THF ($C_{112}H_{132}Na_4O_{12}Te_4$): $M_r = 2272.54$, tetragonal space group $I\bar{4}$, $a = b = 19.238(6)$, $c = 14.276(5)$ Å, $V = 5283(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.428$ mg m^{-3}, crystal dimensions $0.25 \times 0.31 \times 0.42$ mm^3. 10780 collected and 6387 unique reflections. Final residuals $R_1 = 0.0419$, $wR_2 = 0.0838$ ($I > 2\sigma(I)$); $R_1 = 0.0708$, $wR_2 = 0.0912$ (all data). GooF = 0.877, 298 parameters. CCDC 782648 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif; b) Crystal data for **3**·4THF: ($C_{64}H_{88}O_{12}Te_2$): $M_r = 1304.54$, monoclinic space group $P2_1/n$, $a = 13.4434(9)$, $b = 15.9771(9)$, $c = 16.170(1)$ Å, $\beta = 113.191(5)°$, $V = 3192.5(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.357$ mg m^{-3}, crystal dimensions $0.5 \times 0.5 \times 0.5$ mm^3. 20749 collected and 8557 unique reflections. Final residuals $R_1 = 0.0401$, $wR_2 = 0.1113$ ($I > 2\sigma(I)$); $R_1 = 0.0572$, $wR_2 = 0.1280$ (all data). GooF = 1.055, 352 parameters. CCDC 782649 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] J. Beckmann, D. Dakternieks, A. Duthie, F. Ribot, M. Schürmann, N. A. Lewcenko, *Organometallics* **2003**, *22*, 3257–3261.

[9] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.

[10] Sodium tellurite glasses $(Na_2O)_x(TeO_2)_{1-x}$ ($0.10 < x < 0.35$) are promising optical materials characterized by a high refractive index, good and wide IR transmittance, and a large third order non-linear optical susceptibility. These remarkable properties arise from the free electron pair in the structural motifs of the Te^{IV} sites. While the network builder (TeO_2) itself is only a conditional glass former, the sodium oxide modifier (Na_2O) gives rise to stable and chemically durable glasses. The modifier changes the number of TeO_4 and TeO_3 structural units and thus, the glass transition temperature and non-linear optical response; a) R. El-Mallawany, *Mater. Chem. Phys.* **1998**, *53*, 93–120; b) R. El-Mallawany, *Mater. Chem. Phys.* **1999**, *60*, 103–131; c) R. El-Mallawany, *Mater. Chem. Phys.* **2000**, *63*, 109–115; d) J. C. McLaughlin, S. L. Tagg, J. W. Zwanziger, D. R. Haeffner, S. D. Shastri, *J. Non-Cryst. Solids* **2000**, *274*, 1–8; e) J. C. McLaughlin, S. L. Tagg, J. W. Zwanziger, *J. Phys. Chem. B* **2001**, *105*, 67–75.

[11] L. Falck, O. Lindqvist, *Acta Crystallogr. Sect. B* **1978**, *34*, 3145–3146.

[12] Calculations were performed both at the DFT/B3PW91 as well as at the MP2 level of theory. For tellurium an effective core potential with a cc-pVTZ basis set was applied, the split-valence 6-311 + G(2df,p) basis set for all other atoms was used. Stationary points were characterized as true minima by frequency calculations. See Supporting Information for details.

Supporting Information

Experimental

General. Air sensitive materials were handled under Argon using standard Schlenk and glove-box techniques. NMR spectra were collected using a Jeol JNM-LA 400 FT spectrometer and a Jeol Eclipse+ 500 FT spectrometer and are referenced against Me_4Si and Me_2Te. IR spectra were recorded with a Nicolet Nexus FT-IR spectrometer. Microanalyses were obtained from a Vario EL elemental analyser.

Crystallography. Intensity data were collected on a STOE IPDS 2T diffractometer with graphite-monochromated Mo-Kα (0.7107 Å) radiation. Data were reduced and corrected for absorption using the program X-Area (Stoe).[S1] The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[S2] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. Figures were created using DIAMOND.[S3]

Symmetry codes used to generate equivalent atoms are: a = –y, x, –z, b = y, –x, –z, c = –x, –y, z for **1** and a = –x, –y, –z for **2**. Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 782648 (**1**) and 782649 (**2**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Computational Methodology. Calculations were carried out using the Gaussian 03 suite of programs.[S4] All geometries were fully optimized independently at the DFT/B3PW91[S5] as well as at the MP2 level of theory using a large-core quasi-relativistic effective core potential[S6] with a cc-pVTZ basis set[S7] for tellurium and the split-valence 6-311+G(2df,p) basis set for all other atoms. Stationary points were characterized as true minima by frequency calculations. The energies have been corrected for zero point vibrational energies.

References

[S1] STOE X-Area and X-Red, **2004**, Stoe & Cie GmbH, Darmstadt, Germany.

[S2] L. J. Farrugia *J. Appl. Cryst.* **1999**, *32*, 837–838.

[S3] DIAMOND V2.1d, Crystal Impact, K. Brandenburg & M. Berndt GbR, **2002**.

[S4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian 03, revision D.01, Gaussian, Inc., Wallingford CT, **2004**.

[S5] a) J. P. Perdew in Electronic Structure of Solids ’91 (Hrsg. P. Ziesche, H. Eschring), Akademie-Verlag, Berlin, **1991**, S. 11–20; b) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M.R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B* **1992**, *46*, 6671–6687; c) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[S6] J. M. L. Martin, A. Sundermann, *J. Chem. Phys.* **2001**, *114*, 3408–3420.

[S7] A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, *80*, 1431–1441.

MANUSCRIPT XII

15 Synthesis, Structure and Reactivity of an Intramolecularly Coordinated Diarylditelluronic Acid [8-$Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$

Jens Beckmann, Jens Bolsinger, Andrew Duthie and Pamela Finke; *Organometallics,* **received**

15.1 SYNOPSIS

Using a bulky ligand, which was discussed in a previous paper, it was possible to synthesis the dinuclear telluronic acid [2,6-$Mes_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$, however, the reaction pathway is complex[122] and a more direct approach using strong oxidizing reagents, such as H_2O_2, CrO_3, $KMnO_4$ and $NaIO_4$, failed.

In contrast, an aqueous solution of the previously described intramolecularly coordinating telluroxane cluster (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$ or the polymer [(8-$Me_2NC_{10}H_6Te)_2O_3]_n$[94] can be easily oxidized using H_2O_2 to give the diarylditelluronic acid [(8-$Me_2NC_{10}H_6Te(=O)(OH)_2]_2(\mu\text{-}O)$ in high yield. Another route was established by a direct oxidation of an aqueous suspension of the parent diarylditelluride (8-$Me_2NC_{10}H_6Te)_2$ with H_2O_2.

It is worth mentioning that the photooxidation of the same diarylditelluride (8-$Me_2NC_{10}H_6Te)_2$ with molecular oxygen gave rise to a complex product mixture from which the tetranuclear telluroxane cluster (8-$MeNC_{10}H_5TeO)_4$ was isolated[126].

Each tellurium atom comprises one Te-O double bond and three Te-O single bonds, which compare reasonably well with the bond lengths of (2,4,6-*i*-$Pr_3C_6H_2)_2TeO_2$[127] and cubic $Te(OH)_6$[125]. The intramolecular Te···N coordination is significantly shorter than those of the parent compounds (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$[94] and (8-$Me_2NC_{10}H_6Te)_2$[114,118] pointing to strong attractive interactions. The intramolecular Te···N coordination possesses the shortest value observed for intramolecular Te···N bonds in 8-dimethylaminonaphthyltellurium compounds[94,114,128]. The molecular structure shows two asymmetric intramolecular hydrogen bonds of the type Te-O-H···O=Te, whereby the donor acceptor distance is consistent with medium strength hydrogen bonding[71].

Once isolated from the aqueous layer, the solubility of the diarylditelluronic acid in water is rather poor. The ^1H NMR spectrum (D_6-DMSO) reveals one set of signals for the 8-dimethylaminonaphthyl substituents with the two methyl groups being magnetically inequivalent, which suggests that the solid state structure is retained in this solvent. However, the ^{1}H NMR spectrum (D_2O) shows only one signal for the two methyl groups, which implies magnetic equivalence or an exchange process that is fast on the NMR time scale in water.

No evidence was found that the diarylditelluronic acid possesses any oxidizing power towards alcohols. Attempts at recrystallizing from methanol lead to the selective esterification of two hydroxyl groups and formation of the partial methyl ester $[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)(OMe)]_2(\mu\text{-}O)$. The molecular structure closely resembles the structure of the parent telluronic acid. The esterification occurred selectively at those hydroxyl groups that are not involved in intramolecular hydrogen binding and which are situated in *trans*-position of the oxygen bridge.

Interestingly, the minute structural change by the selective esterification of two hydroxyl groups significantly increased the solubility in common organic solvents, such as $CHCl_3$. The broad ^{1}H and ^{125}Te NMR spectra point to an equilibrium, which is fast on the NMR time scale and could be tentatively explained by a fast exchange between a monomeric and the dimeric structure.

DFT calculations:

The relative stabilities of the *meta*-, *meso*-, *ortho*- and *para*-telluronic acids counterbalanced with water were calculated. The energies of the most stable forms within the series, namely $[PhTe(O)(OH)_3]_2$ and $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$ were arbitrary set to 0 KJ mol^{-1}. These compounds comprise tellurium atoms with a coordination number of 6. All structure types that are characterized by lower coordination numbers, are significantly less stable, whereby telluronic acids comprising a coordination of 7 are only slightly less stable. Furthermore, the *meso*-telluronic acid and the *meta*-telluronic acid are considerably less stable.

Unlike the tetracoordinated sulfonic acids and selenonic acids, the related telluronic acids favor hexacoordinate dinuclear structures, whereby the structure type may be influenced by the choice of the organic substituent.

15.2 EXPERIMENTAL CONTRIBUTIONS

For this study, I performed 100% of the experiments and synthesized all compounds. Furthermore, I wrote the manuscript together with Prof. Dr. Jens Beckmann and Pamela Finke.

X-Ray Crystallography: Prof. Dr. Jens Beckmann
^{125}Te MAS-NMR spectra and analysis thereof: Dr. Andrew Duthie
The DFT-calculations were carried out by Pamela Finke

Organometallics - Note

Synthesis, Structure and Reactivity of an Intramolecularly Coordinated Diarylditelluronic Acid $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$

Jens Beckmann,[a,b] * Jens Bolsinger,[a] Andrew Duthie,[c] Pamela Finke[b]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstr. 34/36, 14195 Berlin, Germany*

[b] *Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Str., 28359 Bremen, Germany*

[c] *School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia*

Received

Summary: The oxidation of the telluroxane cluster $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**4**) or the diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ (**7**) using H_2O_2 provided the diarylditelluronic acid $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$ (**6**), which is the second member of this compound class and the first one to contain an intramolecularly coordinated substituent.

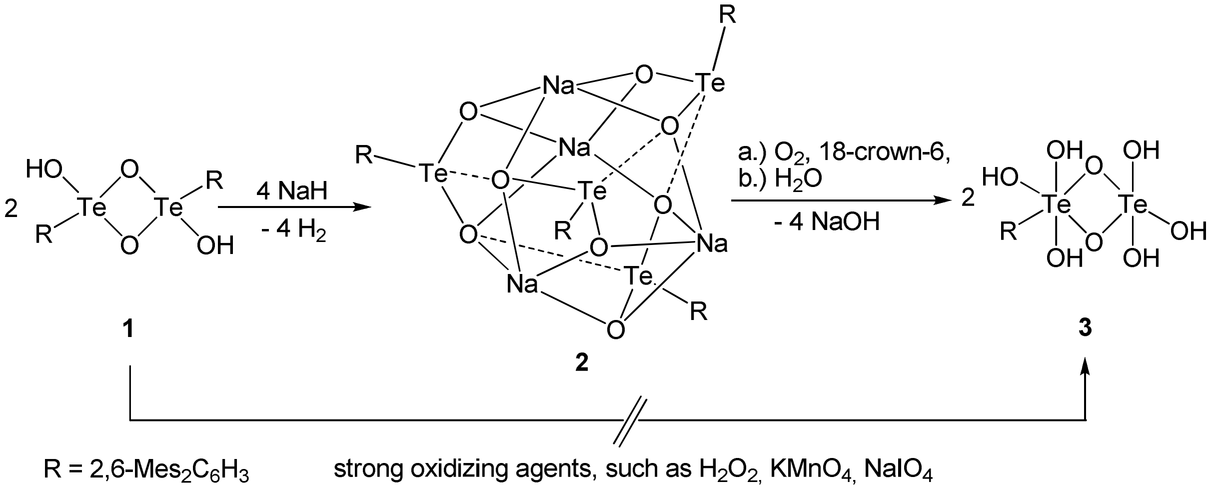
Sulfonic acids, $RS(O)_2(OH)$ (R = alkyl, aryl), are a well-established compound class, that finds extensive utility in organic synthesis.[1] By contrast, little is known about related selenonic acids, $RSe(O)_2(OH)$ (R = alkyl, aryl), which is arguably due to difficulties in their preparation and handling. Most known selenonic acids are characterized by a very high acidity, a strong oxidizing power and a low thermal stability.[2] Even less information is available on telluronic acids.

---

* Correspondence to Jens Beckmann: Fax ++49(0)421 218 9863160, E-mail: j.beckmann@uni-bremen.de

Only very recently, we reported, that the reaction of the dinuclear aryltellurinic acid [2,6-$Mes_2C_6H_3Te(O)(OH)]_2$ (**1**) with sodium hydride afforded the tetranuclear sodium aryltellurinate, [Na(2,6-$Mes_2C_6H_3Te(O)_2)]_4$ (**2**), which was oxidized by molecular oxygen in the presence of a crown ether to give the dinuclear telluronic acid [2,6-$Mes_2C_6H_3Te(O)(OH)_3]_2$ (**3**) (Scheme 1).[3]

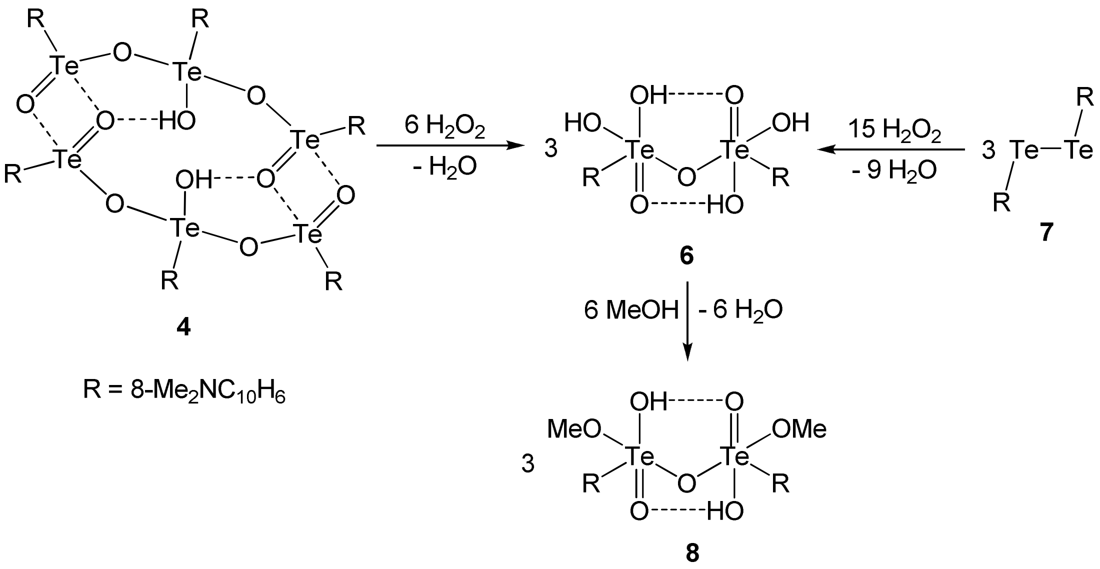
Scheme 1. Synthesis of the sodium aryltellurinate, [Na(2,6-$Mes_2C_6H_3Te(O)_2)]_4$ (**2**) and the diarylditelluronic acid [2,6-$Mes_2C_6H_3Te(O)(OH)_3]_2$ (**3**).



The kinetic stabilization of **1** - **3** was assured by applying bulky *m*-terphenyl substituents shielding the inorganic core structure. It is noted, that all attempts at directly converting **1** to **3** using strong oxidizing reagents, such as H_2O_2, $KMnO_4$ and $NaIO_4$, failed (Scheme 1).[3] Very recently, we also described the intramolecularly coordinating telluroxane cluster (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**4**) and the telluroxane polymer [(8-$Me_2NC_{10}H_6Te)_2O_3]_n$ (**5**), which both can be regarded as (partial) anhydrides of the same elusive aryltellurinic acid.[4] Compounds **4** and **5** dissolve in water to give the same solution of oligomeric telluroxane species having an average degree of aggregation of 2.5.

We have now found that an aqueous solution of **4** can be easily oxidized using H_2O_2 to give the diarylditelluronic acid $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$ (**6**) in 81% yield (Scheme 2). Alternatively, **6** can be prepared by the oxidation of an aqueous suspension of the parent diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ (**7**) with H_2O_2 in 70% yield (Scheme 2). Compound **6** was isolated by crystallization from the aqueous solution and obtained as colorless prisms when recrystallized from water.

Scheme 2 Synthesis and partial esterification of the diarylditelluronic acid $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$ (**6**).



It is worth mentioning, that the photooxidation of the same diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ (**7**) with molecular oxygen gave rise to a complex product mixture from which the tetranuclear telluroxane cluster $(8\text{-}MeNC_{10}H_5TeO)_4$ was isolated in 17% yield.[5] The molecular structure of **6**·4 H_2O is shown in Figure 1 and contains two crystallographically independent, albeit similar, aryltellurium(VI) sites, that are linked by an oxygen bridge (Te-O-Te 127.0(2)°).

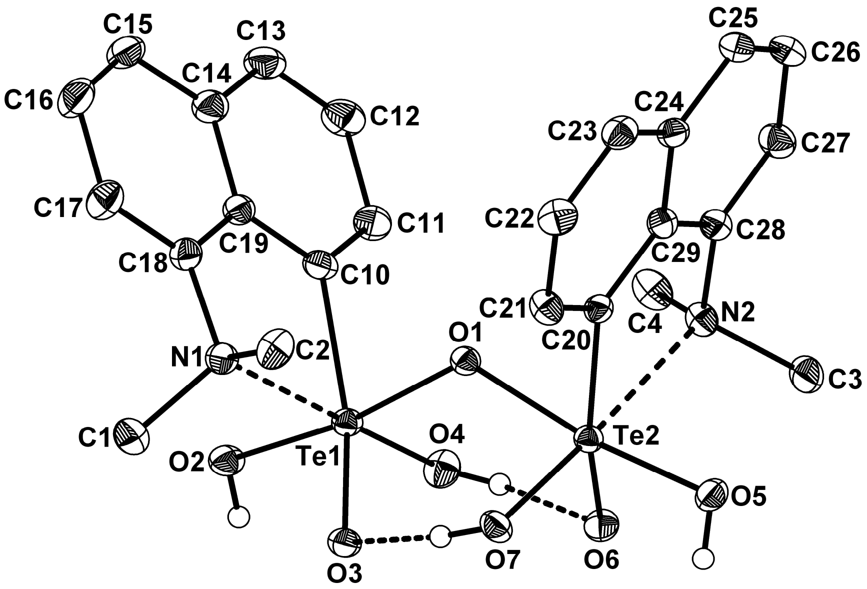


Figure 1. Molecular structure of **6** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-O1 1.969(3), Te1-O2 1.921(4), Te1-O3 1.836(3), Te1-O4 1.903(4), Te1···N1 2.376(4), Te1-C10 2.106(4), Te2-O1 1.983(3), Te2-O5 1.928(3), Te2-O6 1.834(3), Te2-O7 1.912(4), Te2···N2 2.366(4), Te2-C20 2.104(4), O3···O7 2.642(5), O4···O6 2.724(6), Te1-O1-Te2 127.0(2).

The spatial arrangement of tellurium atoms is distorted octahedral and defined by a CNO_4 donor set. The ^{125}Te MAS NMR spectrum of **6** shows one signal at δ_{iso} = 864.7 ppm. Each Te atom of **6** comprises one (formal) Te-O double bond (av. 1.835(3) Å) and three Te-O single bonds (av. 1.936(4) Å), which compare reasonably well with the bond lengths in $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2TeO_2$ (av. 1.802(3) Å)[6] and cubic $Te(OH)_6$ (1.913(6) Å).[7] The intramolecular Te···N coordination in**6** (av. 2.371(4) Å) is significantly shorter than those of the parent compounds $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**4**, av. 2.647(9) Å)[4] and $(8\text{-}Me_2NC_{10}H_6Te)_2$ (**7**, av. 2.721(5) Å)[8] pointing to strong attractive interactions. In fact, the intramolecular Te···N coordination in **6** is almost as short as that of the aryltellurenyl chloride $8\text{-}Me_2NC_{10}H_6TeCl$ (2.350(3) Å),[4] possessing the shortest value observed for intramolecular Te···N bonds in 8-dimethylaminonaphthyltellurium compounds.[4,8,9]

The molecular structure of **6** displays two asymmetric intramolecular hydrogen bonds of the type Te-O-H···O=Te. The donor acceptor distance (av. O···O 2.683(6) Å) is consistent with medium strength hydrogen bonding.[10] Most oxygen atoms of **6** are also involved in intermolecular hydrogen bonding with adjacent water molecules in the crystal lattice.

Once isolated from the aqueous layer, the solubility of **6** in water is rather poor. Compound **6** is most soluble in very polar organic solvents such as DMSO, but virtually insoluble in weakly or non-polar solvents. The ^{125}Te NMR spectrum (D$_6$-DMSO) of **6** exhibits a signal at $\delta = 867.0$ ppm, that resembles the ^{125}Te MAS NMR chemical shift. The ^{1}H NMR spectrum of **6** in D$_6$-DMSO reveals one set of signals for the 8-dimethylaminonaphthyl substituents with the two methyl groups being magnetically inequivalent, indicating that the solid-state structure is retained in this solvent. However, the ^{1}H NMR spectrum of **6** in D_2O shows only one signal for the two methyl groups, implying magnetic equivalence or an exchange process, that is fast on the NMR time scale in water. The ESI MS spectrum (MeCN, positive mode) of **6** shows six prominent mass clusters, that were assigned to the dinuclear cations $[(RTe)_2O_4(OH)]^+$ (m/z = 676.99), $[(RTe)_2O_3(OH)_3]^+$ (m/z = 695.00) and $[(RTe)_2O_2(OH)_5]^+$ (713.01), the trinuclear cation $[(RTe)_3O_4(OH)_6]^+$ (m/z = 1062.00) and the tetranuclear cations $[(RTe)_4O_6(OH)_7]^+$ (m/z = 1409.02) and $[(RTe)_4O_5(OH)_9]^+$ (m/z = 1427.00), respectively (R = 8-$Me_2NC_{10}H_6$). Apparently these cations are formed by autoionisation and condensation processes, that might be interpreted in terms of a rather high kinetic lability of the Te-O bonds. No evidence was found that **6** possesses any oxidizing power towards alcohols. Attempts at recrystallizing **6** from methanol led to the selective esterification of two hydroxyl groups and formation of the partial methyl ester [8-$Me_2NC_{10}H_6Te(O)(OH)(OMe)]_2(O)$ (**8**), which was obtained as colorless needles in 70% yield (Scheme 2). The molecular structure of **8** is shown in Figure 2 and closely resembles that of **6** with the essential bond parameters being practically identical.

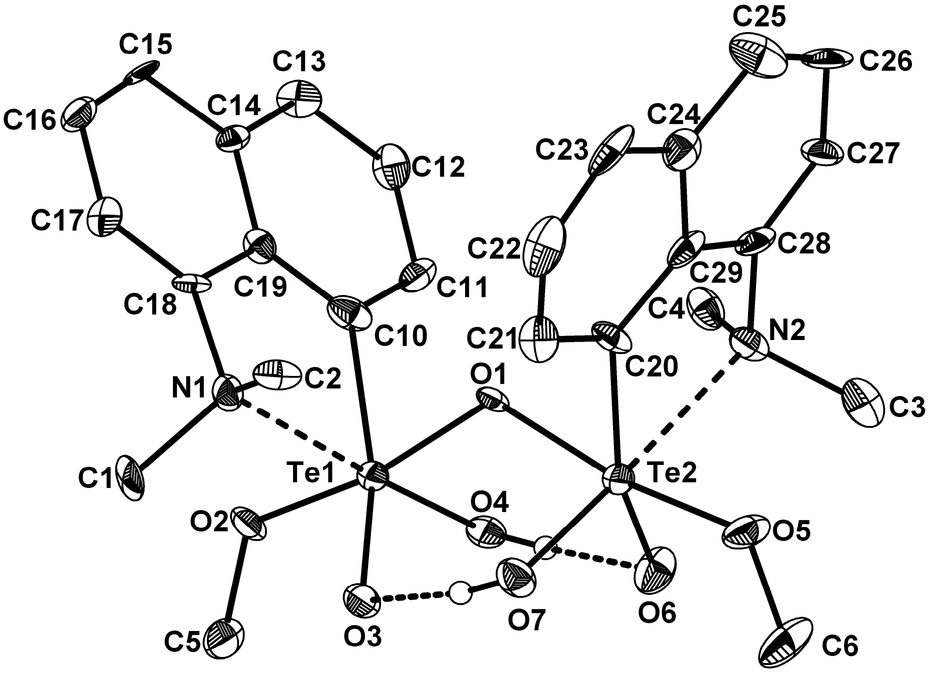


Figure 2. Molecular structure of **8** showing 30% probability ellipsoids and the crystallographic numbering scheme. Selected bond parameters [Å, °]: Te1-O1 1.981(5), Te1-O2 1.974(5), Te1-O3 1.830(6), Te1-O4 1.923(6), Te1···N1 2.406(8), Te1-C10 2.110(7), Te2-O2 1.976(5), Te2-O5 1.948(6), Te2-O6 1.837(7), Te2-O7 1.898(6), Te2···N2 2.384(7), Te2-C20 2.142(9), O3···O7 2.637(8), O4···O6 2.711(5), Te1-O1-Te2 125.3(3).

It is noted, that the esterification occurred selectively at those hydroxyl groups of **6** that are not involved in intramolecular hydrogen bonding and which are situated in the *trans*-position to the oxygen bridge. Interestingly, the minute structural change on going from **6** to **8** significantly increased the solubility in common organic solvents, such as CHCl$_3$. The ^{125}Te NMR spectrum (CDCl$_3$) of **8** shows one signal at δ = 885.5 ppm, that shifted only marginally from that of **6** (867.0 ppm). Like **6**, the ^{1}H NMR spectrum (CDCl$_3$) of **8** exhibits one set of signals for the 8-dimethylaminonaphthyl substituents with the two methyl groups being magnetically inequivalent.

The ESI MS spectrum (MeCN, positive mode) of **8** exhibits eight prominent mass clusters, that were assigned to the mononuclear cations $[(RTe)O(OMe)(OH)]^+$ (m/z = 364.02), $[(RTe)O(OMe)(ONa)]^+$ (m/z = 386.00) and $[(RTe)(OMe)_2(OH)_2]^+$ (m/z = 396.05), the dinuclear cations $[(RTe)_2O_3(OMe)_2(OH)]^+$ (m/z = 723.03), $[(RTe)_2O_3(OMe)_2(ONa)]^+$ (m/z = 745.01) and $[(RTe)_2O_2(OMe)_3(OH)_2]^+$ (m/z = 755.05) and the trinuclear cations $[(RTe)_3O_3(OMe)_2(OH)_6]^+$ (m/z = 1106.04) and $[(RTe)_3O_2(OMe)_3(OH)_7]^+$ (m/z = 1140.07), respectively (R = 8-$Me_2NC_{10}H_6$). Thus, the degree of aggregation is slightly reduced when compared to **6**.

DFT calculations

The observation of different structure types for the telluronic acids [2,6-$Mes_2C_6H_3Te(O)(OH)_3]_2$ (**3**) and [8-$Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$ (**6**) prompted us to calculate the relative stabilities of the *meta*-, *meso*-, *ortho*- and *para*-telluronic acids counterbalanced with water: 2 $RTe(O)_2OH$ + 4 H_2O, 2 $RTe(O)(OH)_3$ + 2 H_2O, 2 $RTe(OH)_5$, $[RTe(O)(OH)_3]_2$ + 2H_2O and $[RTe(O)(OH)_2]_2(O)$ + 3 H_2O (R = 8-$Me_2NC_{10}H_6$, Ph), which are collected in Figure 3. The energies of the most stable forms within the series, namely $[PhTe(O)(OH)_3]_2$ and [8-$Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$ (**6**) were arbitrary set to 0 KJ mol^{-1}. The tellurium atoms of these compounds are characterized by a coordination number of 6. Compared to the *para*-phenyltelluronic acid $[PhTe(O)(OH)_3]_2$, the *ortho*-phenyltelluronic acid $PhTe(OH)_5$, having the same coordination number, is only marginally less stable (6 kJ mol^{-1}), while all other structure types, that are characterized by lower coordination numbers, are significantly less stable (153, 203 and 345 KJ mol^{-1}).

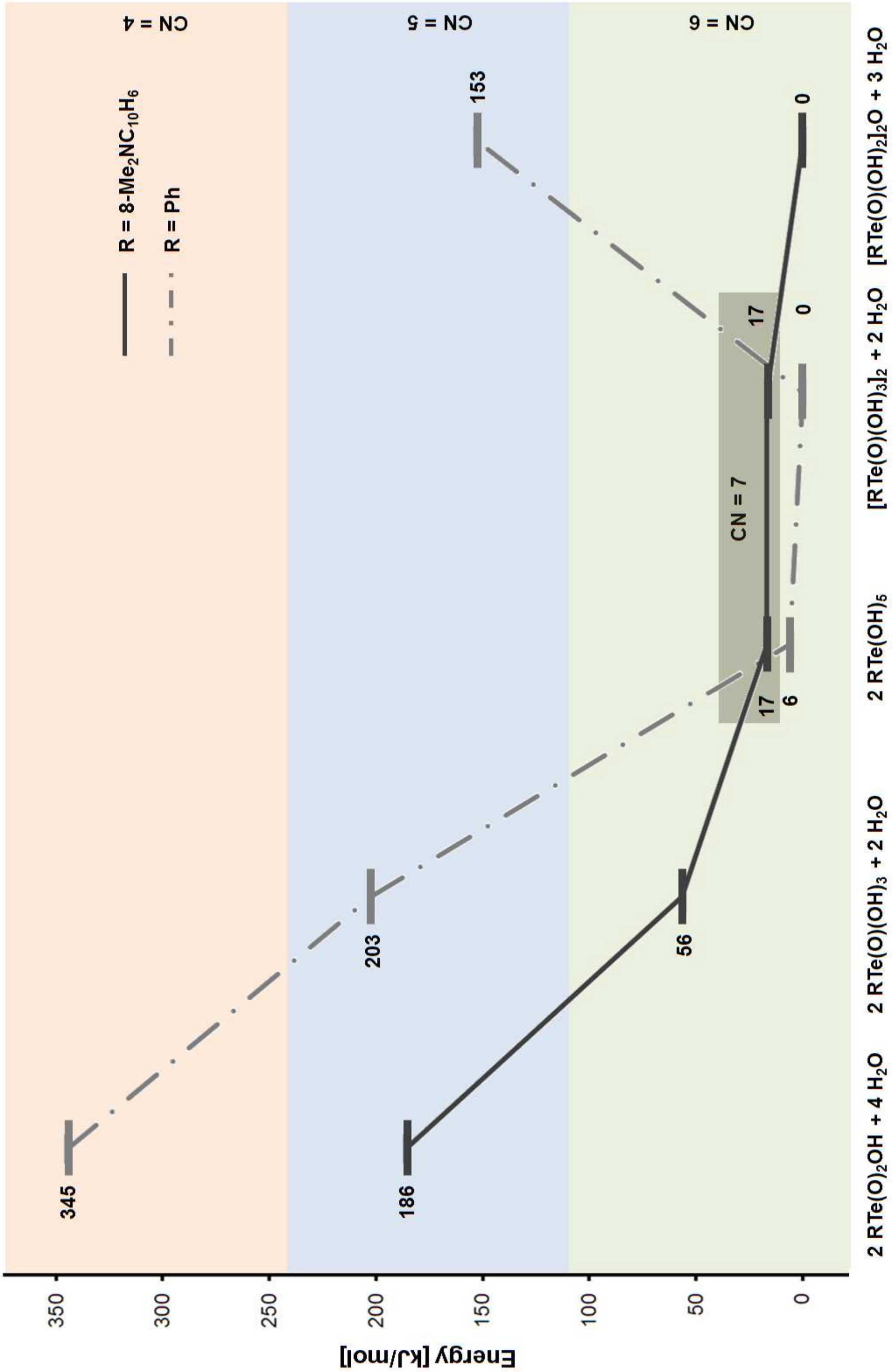


Figure 3. Relative stability of *meta*-, *meso*-, *ortho*-, and *para*-aryltelluronic acids.

In comparison to the *para*-telluronic acid $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$ (**6**), the *ortho*-telluronic acid $8\text{-}Me_2NC_{10}H_6Te(OH)_5$ and the *para*-telluronic acid $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_3]_2$ comprising coordination numbers of 7 are slightly less stable (both 17 KJ mol^{-1}), whereas the *meso*-telluronic acid $8\text{-}Me_2NC_{10}H_6Te(O)(OH)_3$ (56 KJ mol^{-1}) and the *meta*-telluronic acid $8\text{-}Me_2NC_{10}H_6Te\ (O)_2(OH)$ (186 KJ mol^{-1}) are considerably less stable.

Unlike the tetracoordinate sulfonic acids and selenonic acids, the related telluronic acids favor hexacoordinate dinuclear structures, whereby the structure type may be influenced by the choice of the organic substituent.

Experimental Section

General. The starting materials $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**4**)[4] and diarylditelluride $(8\text{-}Me_2NC_{10}H_6Te)_2$ (**7**)[8] were prepared according to literature procedures. The ^{1}H and ^{125}Te NMR spectra were recorded using Jeol GX 270 and Varian 300 Unity Plus spectrometers and are referenced to $SiMe_4$ (^{1}H, ^{13}C) and Me_2Te (^{125}Te). The ^{125}Te CP MAS NMR spectra were obtained using a JEOL Eclipse Plus 400 MHz NMR spectrometer equipped with a 6 mm rotor operating at spinning frequencies between 8 and 10 kHz. A 30 s recycle delay was used and typically 5000 to 10000 transitions were accumulated to obtain adequate signal-to-noise ratios. The isotropic chemical shifts δ_{iso} were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies and were referenced using solid $Te(OH)_6$ as the secondary reference (δ_{iso} 692.2 / 685.5 ppm). Infrared (IR) spectra were recorded using Nexus FT-IR spectrometer with a Smart DuraSamplIR. Microanalyses were obtained from a Vario EL elemental analyzer.

Synthesis of [8-$Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$ (6). Method A. To a solution of (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$ (**4**) (175 mg, 0.09 mmol) in water (20 mL), H_2O_2 (35%, 2 mL) was added and stirred for 1 h. Colorless prisms of **6**$\cdot$4 H_2O were obtained upon standing overnight (Yield 160 mg, 0.20 mmol, 74%; Mp. 225-227 °C). **Method B.** To a suspension of (8-$Me_2NC_{10}H_6Te)_2$ (**7**) (200 mg, 0.33 mmol) in water (10 mL), H_2O_2 (35%, 2 mL) was added and stirred for 1 d. A brownish solid precipitated that was collected by filtration, washed with water (20 mL) and dried in vacuum. Recrystallization of the crude product from water yielded colorless prisms of **6**$\cdot$4 H_2O (Yield 90 mg, 0.11 mmol, 34%; Mp. 225-227 °C).

^{1}H-NMR (D_2O): δ = 8.22 (d, 2H; Ar), 8.20 (d, 2H; Ar), 8.04 (d, 2H; Ar), 7.94 (d, 2H; Ar), 7.81 (t, 2H; Ar), 7.77 (t, 2H; Ar), 3.17 ppm (s, 12H; NMe). ^{1}H-NMR (D_6-DMSO): δ = 8.08 (d, 2H; Ar), 7.96 (d, 2H; Ar), 7.80 (d, 2H; Ar), 7.76 (d, 2H; Ar), 7.67 (t, 2H; Ar), 7.51 (t, 2H; Ar), 3.09 (s, 6H; NMe), 2.65 ppm (s, 6H; NMe). ^{125}Te-NMR (D_6-DMSO): δ = 867.0 ppm. ^{125}Te CP MAS NMR: δ_{iso} = 864.7 ppm. ESI MS (MeCN, positive mode): m/z = 1426.00 $[C_{48}H_{57}O_{14}N_4Te_4]^+$, 1409.02 $[C_{48}H_{55}O_{13}N_4Te_4]^+$, 1062.00 $[C_{36}H_{42}O_{10}N_3Te_3]^+$, 713.01 $[C_{24}H_{29}O_7N_2Te_2]^+$, 695.00 $[C_{24}H_{27}O_6N_2Te_2]^+$, 676.99 $[C_{24}H_{25}O_5N_2Te_2]^+$. IR: $\tilde{\nu}$ (OH) = 3156 cm^{-1} (broad). Anal. Calcd. for **6**$\cdot$4 H_2O: $C_{24}H_{36}N_2O_{11}Te_2$ (783.75): C, 36.78; H, 4.63; N, 3.57. Found: C, 37.01; H, 4.32; N, 3.59.

Synthesis of [8-$Me_2NC_{10}H_6Te(O)(OH)(OMe)]_2(O)$ (8). Recrystallization of **6**$\cdot$4 H_2O (78 mg, 0.10 mmol) from methanol (20 mL) gave a slightly pink solution from which off colorless needles of **8**$\cdot$MeOH crystallized. Drying in high vacuum afforded microcrystalline **8** (Yield 50 mg, 0.07 mmol, 68%; mp 212-214 °C).

^{1}H-NMR ($CDCl_3$): δ = 8.24, 7.81, 7.69-7.55, 7.42-7.34 (m, 12H; Ar), 3.83 (s, 6H; OMe), 3.16 (s, 6H; NMe), 2.81 ppm (s, 6H; NMe). ^{125}Te-NMR ($CDCl_3$): δ = 885.8 ppm. ESI MS (MeCN, positive mode): m/z = 1140.07 [$C_{39}H_{52}O_{12}N_3Te_3$]$^+$, 1106.04 [$C_{38}H_{48}O_{11}N_3Te_3$]$^+$, 755.05 [$C_{27}H_{35}O_7N_2Te_2$]$^+$, 745.01 [$C_{26}H_{30}O_6N_2NaTe_2$]$^+$, 723.03 [$C_{26}H_{31}O_6N_2Te_2$]$^+$, 396.05 [$C_{14}H_{20}O_4NTe$]$^+$, 386.00 [$C_{13}H_{15}O_3NNaTe$]$^+$, 364.02 [$C_{13}H_{16}O_3NTe$]$^+$. IR: $\tilde{\nu}$ (OH) = 3101 cm^{-1} (broad). Anal. Calcd. for **8**: $C_{26}H_{32}N_2O_7Te_2$ (739.74): C, 42.22; H, 4.36; N, 3.79. Found: C, 42.69; H, 4.04; N, 3.62.

Crystallography

Intensity data were collected on a STOE IPDS 2T diffractometer (**6**) at 150 K and a Bruker SMART 1000 CCD diffractometer (**8**) at 173 K with graphite-monochromated Mo-Kα (0.7107 Å) radiation. The structures were solved by direct methods and difference Fourier synthesis using SHELXS-97 implemented in the program WinGX 2002.[11] Full-matrix least-squares refinements on F^2, using all data, were carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms attached to carbon atoms were included in geometrically calculated positions for all structures using a riding model and were refined isotropically. Crystal and refinement data are collected in Table 1. Figures were created using DIAMOND.[12] Crystallographic data (excluding structure factors) for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Computational Methodology. Calculations were carried out using the Gaussian 03 suite of programs.[13] All geometries were fully optimized at the DFT/B3PW91[14] level of theory using a large-core quasi-relativistic effective core potential[15] with the appropriate cc-pVTZ basis set[16] for tellurium and the split-valence 6-311+G(2df,p) basis set for all other atoms. The geometries were optimized without any symmetry constraints except for [8-

$Me_2NC_{10}H_6Te(O)(OH)_3]_2$, $[PhTe(O)(OH)_3]_2$ and $[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2O$ (**6**), which were constrained to C_i and C_2 symmetries, respectively. Stationary points were characterized as true minima by frequency calculations. The energies have been corrected for zero point vibrational energies.

Acknowledgement

Irene Brüdgam (Freie Universität Berlin) and Dr. Malte Hesse (Universität Bremen) are thanked for the X-ray data collection. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

Supporting Information available. Cif files of **6**·4 H_2O and **8**·MeOH. The optimized geometries as well as the absolute energies. This material is available free of charge via the Internet at http://pubs.acs.org.

References

[1] Smith, M. B.; March, J. *March's Advanced Organic Chemistry*, 5th ed, Wiley-Interscience, 2001.

[2] (a) Campbell, T. W.; Walker, H.; Coppinger, G. H. *Chem. Rev*. **1952**, *50*, 279-349. (b) Doughty, H. W. *Am. Chem. J.* **1909**, *41*, 326-337. (c) Lesser, R.; Weiss, R. *Chem. Ber*. **1913**, *46*, 2640-2658. (d) Schmidt, M.; Wilhelm, I. *Chem. Ber*. **1964**, *97*, 872-875. (e) Dostál, K.; Žák, Z.; Černik, M. *Chem. Ber*. **1971**, *104*, 2044-2052. (f) Haas, A.; Weiler, H.-U. *Chem. Ber*. **1985**, *118*, 943-951. (g) Haas, A.; Schinkel, K. *Chem. Ber*. **1990**, *123*, 685-689. (h) Boese, R.; Haas, A.; Herkt, S.; Pryka, M. *Chem. Ber*. **1995**, *128*, 423-428.

[3] Beckmann, J.; Bolsinger, J.; Finke, P.; Hesse, M. *Angew. Chem.* **2010**, *122*, 8204-8206; *Angew. Chem. Int. Ed.* **2010**, *49*, 8030-8032.

[4] Beckmann, J.; Bolsinger, J.; Duthie, A. *Chem. Eur. J.* **2011**, *17*, 930-940.

[5] Beckmann, J.; Bolsinger, J. *Z. Anorg. Allg. Chem.* **2011**, *637*, 29-30.

[6] Oba, M.; Okada, Y.; Nishiyama, K.; Shimada, S.; Ando, W. *Chem. Commun.* **2008**, 5378-5380.

[7] Falck, L.; Lindqvist O. *Acta Cryst*. **1978**, *B34*, 3145-3146.

[8] Menon, S. C.; Singh, H. B.; Jasinksi, J. M.; Jasinski, J. P.; Butcher, R. J. *Organometallics* **1996**, *15*, 1707-1712.

[9] (a) Panda, A.; Mugesh, G.; Singh, H. B.; Butcher, R. J. *Organometallics* **1999**, *18*, 1986-1993. (b) Beckmann, J.; Bolsinger, J.; Hesse, M. Organometallics **2009**, *28*, 4225-4228. (c) Beckmann, J.; Bolsinger, J.; Duthie, A. *Organometallics* **2009**, *28*, 4610-4612. (d) Beckmann, J.; Bolsinger, J.; Duthie, A.; Finke, P. *Organometallics* **2011**, *30*, submitted (om-2011-008259).

[10] Steiner, T. *Angew. Chem.* **2002**, *114*, 50-80; *Angew. Chem. Int. Ed.* **2002**, *41*, 48-76.

[11] Farrugia, L. J. *J. Appl. Cryst.* **1999**, *32*, 837-838.

[12] DIAMOND V2.1d, Crystal Impact, K. Brandenburg & M. Berndt GbR, **2002**.

[13] Gaussian 03, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.;

Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, **2004**.

[14] a) Perdew, J. P.; Chevary, J. A.; Vosko, S. H.; Jackson, K. A.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671-6687. b) Becke, A. D. J. *Chem. Phys.* **1993**, *98*, 5648-5652.

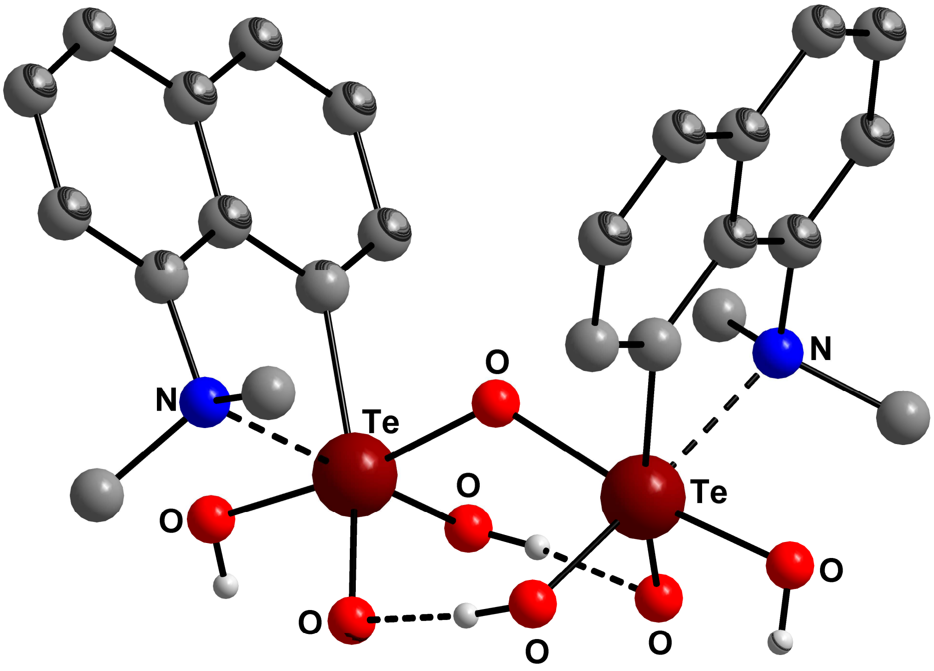
[15] Bergner, A.; Dolg, M.; Kuechle, W.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431-1441.

[16] Martin, J. M. L.; Sundermann, A. *J. Chem. Phys.* **2001**, *114*, 3408-3420.

Table 1. Crystal data and structure refinement of **6**·4 H_2O and **8**·MeOH.

	6·4 H_2O	**8**·MeOH
Formula	$C_{24}H_{36}N_2O_{11}Te_2$	$C_{27}H_{36}N_2O_8Te_2$
Formula weight, g mol^{-1}	783.75	771.78
Crystal system	Triclinic	Monoclinic
Crystal size, mm	0.32 × 0.25 × 0.16	0.35 × 0.18 × 0.10
Space group	P-1	$P2_1/n$
a, Å	10.81(1)	10.982(8)
b, Å	10.94(1)	23.84(2)
c, Å	12.70(1)	11.868(9)
α, °	108.88(8)	90.00
β, °	90.79(8)	111.15(6)
γ, °	95.28(9)	90.00
V, Å^3	1413(3)	2898(4)
Z	2	4
ρ_{calcd}, Mg m^{-3}	1.823	1.769
μ (Mo $K\alpha$), mm^{-1}	2.125	2.064
$F(000)$	756	1520
θ range, deg	1.70 to 29.23	2.76 to 29.22
Index ranges	$-13 \leq h \leq 14$	$-15 \leq h \leq 15$
	$-14 \leq k \leq 14$	$-32 \leq k \leq 28$
	$-17 \leq l \leq 17$	$-16 \leq l \leq 16$
No. of reflns collected	15933	17009
Completeness to θ_{max}	98.2%	96.6%
No. indep. Reflns	7526	7609
No. obsd reflns with ($I>2\sigma(I)$)	5611	4316
No. refined params	352	352
GooF (F^2)	0.932	0.879
R_1 (F) ($I > 2\sigma(I)$)	0.0334	0.0633
wR_2 (F^2) (all data)	0.0945	0.1474
$(\Delta/\sigma)_{max}$	< 0.001	< 0.001
Largest diff peak/hole, e Å^{-3}	1.259 / –1.639	2.039 / –1.177
CCDC number	000000	000000

For table of contents use only



Organometallics - Note

Synthesis, Structure and Reactivity of an Intramolecularly Coordinated Diarylditelluronic Acid [8-$Me_2NC_{10}H_6Te(O)(OH)_2]_2(O)$

Jens Beckmann,[a,b] * Jens Bolsinger,[a] Andrew Duthie,[c] Pamela Finke[b]

[a] *Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstr. 34/36, 14195 Berlin, Germany*

[b] *Institut für Anorganische und Physikalische Chemie, Universität Bremen, Leobener Str., 28359 Bremen, Germany*

[c] *School of Life and Environmental Sciences, Deakin University, Pigdons Road, Waurn Ponds 3217, Australia*

Supporting Information

Optimized geometries as well as absolute energies

---

* Correspondence to Jens Beckmann: Fax ++49(0)421 218 9863160, E-mail: j.beckmann@uni-bremen.de

Computational results:

All energies are given in Hartree/Particle

8-$Me_2NC_{10}H_6Te(O)_2OH$:

```
Te      -0.0000844148   0.0001162545  -0.0000044265
O        0.0000193852   0.0000273949   1.9458996816
H        0.9269324622  -0.0004105667   2.2173535295
O        1.7380131198  -0.3968517119  -0.2234518254
O       -0.6959360324   1.6008404649  -0.3895292423
C       -1.4966557152  -1.4867925994  -0.0444815275
C       -1.9922358005  -2.0233806988   1.1134177402
C       -2.0909213920  -1.7391932819  -1.2981197001
C       -3.1271508766  -2.8566582336   1.0548254017
H       -1.5321885055  -1.7828336598   2.0633413076
C       -3.2775014879  -2.5241120396  -1.3413320470
C       -3.7625461184  -3.0820675914  -0.1365481063
H       -3.5120355235  -3.2918417784   1.9700580098
H       -4.6592804174  -3.6921772904  -0.1710456084
C       -1.5567836916  -1.2232095953  -2.5045823831
C       -3.9280890737  -2.7099788414  -2.5806105923
C       -2.2251806478  -1.4085223645  -3.6865551686
C       -3.4242303953  -2.1447068733  -3.7202900766
H       -3.9352316985  -2.2791487608  -4.6668570929
H       -1.8242212952  -1.0065778457  -4.6095173403
H       -4.8360028647  -3.3027138425  -2.6140395004
N       -0.2699806614  -0.5838471634  -2.4129810741
C        0.7999966761  -1.5383269166  -2.7694337182
H        0.6927639288  -2.4455742180  -2.1750969269
H        0.7375547963  -1.7964718435  -3.8325815154
H        1.7622313876  -1.0883626955  -2.5328996335
C       -0.1443554275   0.6568103620  -3.1906461629
H       -0.1835290748   0.4587569098  -4.2673619268
H       -0.9303097888   1.3484624891  -2.8964790274
H        0.8181458468   1.1109796828  -2.9544515267

Full point group                 C1

Zero-point correction=                       0.230416
Thermal correction to Energy=                0.246754
Thermal correction to Enthalpy=              0.247699
Thermal correction to Gibbs Free Energy= 0.187104
Sum of electronic and
zero-point Energies=                      -753.267830
Sum of electronic and
thermal Energies=                         -753.251491
Sum of electronic and
thermal Enthalpies=                       -753.250547
Sum of electronic and
thermal Free Energies=                    -753.311142
```

8-$Me_2NC_{10}H_6Te(O)(OH)_3$:

```
Te      -0.0043296125  -0.0001207018  -0.0053050237
O        0.0027900582  -0.0004111237   1.9297488243
H        0.9271379132  -0.0008597057   2.2058163250
O       -0.1579203836   1.9595410508  -0.1091280928
H        0.7427231703   2.3072663861  -0.0933158259
O       -0.1585909509  -1.9597210457  -0.1096811928
H        0.7419435098  -2.3077400324  -0.0940920044
O        1.7691846088  -0.0003172243  -0.3498301363
C       -2.1058406278   0.0003141501  -0.1046096245
C       -2.8828090993   0.0005671344   1.0185699083
C       -2.6615766551   0.0003667323  -1.3955368722
C       -4.2863965960   0.0007518942   0.8838704761
H       -2.4265264999   0.0005537613   2.0003603493
C       -4.0803821217   0.0006703009  -1.5280811570
C       -4.8679072881   0.0008092870  -0.3547989421
H       -4.9028759934   0.0008758111   1.7758098602
H       -5.9484467568   0.0010441032  -0.4540154975
C       -1.8626594133   0.0003867344  -2.5658204059
C       -4.6471095740   0.0008620506  -2.8209010120
C       -2.4475409534   0.0006558427  -3.8045009498
C       -3.8486089124   0.0008606470  -3.9321877409
H       -4.2902448128   0.0010705221  -4.9222272217
H       -1.8337679904   0.0006900654  -4.6982575415
H       -5.7275876984   0.0010787130  -2.9199443426
N       -0.4246393737   0.0002419118  -2.3944455309
C        0.2103493910  -1.2063188899  -2.9629495914
H       -0.2846342746  -2.0927455486  -2.5746620269
H        0.1490396390  -1.1890470660  -4.0555452465
H        1.2561483496  -1.2097609774  -2.6531515490
C        0.2106639320   1.2068122085  -2.9625750366
H        0.1495725219   1.1898347780  -4.0551848007
H       -0.2842511626   2.0932252021  -2.5741607514
H        1.2564045558   1.2099942255  -2.6525729432

Full point group                 C1

Zero-point correction=                       0.256228
Thermal correction to Energy=                0.274477
Thermal correction to Enthalpy=              0.275421
Thermal correction to Gibbs Free Energy= 0.211483
Sum of electronic and
zero-point Energies=                      -829.701112
Sum of electronic and
thermal Energies=                         -829.682863
Sum of electronic and
thermal Enthalpies=                       -829.681919
Sum of electronic and
thermal Free Energies=                    -829.745856
```

8-$Me_2NC_{10}H_6Te(OH)_5$:

```
Te      -0.0026170826  -0.0018262656   0.0013466288
C        0.0013591570   0.0011104662   2.1828871933
C        1.1262222657   0.0019189346   3.0828874259
C       -1.2437754351  -0.3518692181   2.6475734553
C        0.9098046342  -0.6065912237   4.3675724754
C       -1.4601233945  -0.7881294272   3.9642842127
H       -2.0808205686  -0.3448402683   1.9633534348
C       -0.3891354634  -0.9753671592   4.7820949191
H       -2.4643761835  -1.0371907403   4.2877012180
H       -0.5095572549  -1.4030410191   5.7720682273
N        2.6631559445   1.4599811803   1.7851408293
C        2.4347873453   0.5631496528   2.8730720772
C        1.9862273281  -0.8429247287   5.2518407973
C        3.2496265387  -0.4494108609   4.9295949562
H        4.0829973103  -0.6462908522   5.5944431567
C        3.4543791775   0.2917436246   3.7581271531
H        1.7789406911  -1.3431766142   6.1917569300
H        4.4387975011   0.7017199490   3.5773992779
C        4.0557639489   1.6883108315   1.4168523564
H        4.6067824268   2.2738084538   2.1660978958
H        4.5672455849   0.7376483848   1.2608499313
H        4.0713584850   2.2482113448   0.4799706487
C        1.9794356057   2.7470623163   1.9784762320
H        0.9347619348   2.5892489974   2.2307498652
H        2.4665264932   3.3196520072   2.7802889490
H        2.0144153193   3.3157903305   1.0498985167
O       -0.0607421364   1.9368201345  -0.0206898919
H       -0.3262802690   2.2015201394  -0.9104351774
O       -0.0606167812   0.0466297967  -1.9464055808
H        0.8456183187  -0.0694478659  -2.2563259143
O       -1.9335571145  -0.0411045000  -0.1196985328
H       -2.1690115341  -0.8174594548  -0.6430872434
O       -0.0961582394  -1.9475962269  -0.0031368622
H        0.8019925949  -2.2906076298  -0.0800304278
O        1.9084020010  -0.1397257815  -0.1983721900
H        2.2740824757   0.5090270718   0.4680587333

Full point group                 C1

Zero-point correction=                           0.281735
Thermal correction to Energy=                    0.301840
Thermal correction to Enthalpy=                  0.302784
Thermal correction to Gibbs Free Energy=         0.235107
Sum of electronic and
zero-point Energies=                          -906.117249
Sum of electronic and
thermal Energies=                             -906.097145
Sum of electronic and
thermal Enthalpies=                           -906.096200
Sum of electronic and
thermal Free Energies=                        -906.163878
```

$[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_3]_2$:

```
Te       0.0229564396  -0.0112246293  -0.0155147064
O       -0.0108136200  -0.0022812657   1.9373366923
O        0.3798602060  -0.0212435056  -1.9156236248
H        0.8094021415  -0.8659712633  -2.1027725413
O        0.3723568232  -1.9320862788  -0.0909456421
H        0.9843129050  -2.1508351966   0.6325313938
O       -0.1259489356   1.9038757175  -0.0591721087
H       -0.7591975610   2.0791564577  -0.8032205135
C       -2.1250157399  -0.3385077356  -0.0231042450
C       -2.3920258791  -1.5300637403   0.6083018742
C       -3.1878367124   0.5995583823  -0.2744033212
C       -3.6742429629  -1.8627579253   1.0718395013
H       -1.5801483895  -2.2208204462   0.7890628688
C       -4.4532768014   0.2997914389   0.3380252269
C       -4.6678622650  -0.9375473535   0.9851780135
H       -3.8396741738  -2.8219903332   1.5487980818
H       -5.6479965279  -1.1300934400   1.4093234367
C       -3.1488406488   1.7914108663  -1.0780769520
C       -4.2030000859   2.6773319680  -1.0552028702
C       -5.5145190759   1.2319939300   0.3109553827
C       -5.3763548529   2.4244219121  -0.3327466058
N       -2.0422993921   2.0298805598  -1.9468312968
H       -4.1494986458   3.5808054650  -1.6478682209
H       -6.4381289293   0.9743104604   0.8181011921
H       -6.1794314358   3.1527072235  -0.3384150153
C       -2.0430497296   1.1152010177  -3.0969261523
C       -1.8634160566   3.4019197116  -2.4076803366
H       -1.0944206054   1.2008579224  -3.6243638846
H       -2.1488924039   0.0861679883  -2.7629057432
H       -2.8710800878   1.3609488219  -3.7773011206
H       -0.8940252538   3.4682804856  -2.9050249764
H       -1.8667607519   4.0901153311  -1.5611659817
H       -2.6327784465   3.7168060770  -3.1271833058
Te       1.8977279619   0.2575341883   2.3456670044
O        1.9314980216   0.2485908247   0.3928156056
O        1.5408241956   0.2675530646   4.2457759227
H        1.1112822601   1.1122808223   4.4329248392
O        1.5483275783   2.1783958378   2.4210979400
H        0.9363714966   2.3971447556   1.6976209041
O        2.0466333371  -1.6575661585   2.3893244067
H        2.6798819625  -1.8328468987   3.1333728115
C        4.0457001414   0.5848172947   2.3532565430
C        4.3127102807   1.7763732993   1.7218504237
C        5.1085211140  -0.3532488233   2.6045556192
C        5.5949273644   2.1090674843   1.2583127966
H        3.5008327911   2.4671300052   1.5410894291
C        6.3739612030  -0.0534818799   1.9921270710
C        6.5885466666   1.1838569125   1.3449742844
H        5.7603585754   3.0682998923   0.7813542161
H        7.5686809294   1.3764029990   0.9208288612
C        5.0695250503  -1.5451013072   3.4082292499
C        6.1236844874  -2.4310224090   3.3853551681
C        7.4352034775  -0.9856843710   2.0191969152
C        7.2970392545  -2.1781123531   2.6628989037
N        3.9629837936  -1.7835710008   4.2769835947
H        6.0701830474  -3.3344959060   3.9780205188
H        8.3588133309  -0.7280009013   1.5120511059
H        8.1001158374  -2.9063976645   2.6685673132
C        3.9637341312  -0.8688914586   5.4270784502
C        3.7841004582  -3.1556101526   4.7378326345
H        3.0151050069  -0.9545483633   5.9545161825
H        4.0695768054   0.1601415707   5.0930580411
H        4.7917644894  -1.1146392629   6.1074534185
H        2.8147096553  -3.2219709266   5.2351772743
H        3.7874451535  -3.8438057721   3.8913182796
H        4.5534628481  -3.4704965180   5.4573356037

Full point group                 CI

Zero-point correction=                           0.515904
Thermal correction to Energy=                    0.552088
Thermal correction to Enthalpy=                  0.553032
Thermal correction to Gibbs Free Energy=         0.449997
Sum of electronic and
zero-point Energies=                         -1659.417404
Sum of electronic and
thermal Energies=                            -1659.381220
Sum of electronic and
thermal Enthalpies=                          -1659.380276
Sum of electronic and
thermal Free Energies=                       -1659.483311
```

$[8\text{-}Me_2NC_{10}H_6Te(O)(OH)_2]_2O$ (**6**):

Te	-0.0001554865	-0.0000875652	0.0000308014
O	-0.0000336981	0.0000396086	1.9847811316
O	1.8175773538	-0.0002345618	-0.1042379243
O	-0.4731695482	-1.8343109114	-0.0992108114
H	-0.1134529282	-2.2804259852	0.7321394155
O	-0.2016140162	0.2234235143	-1.9290819607
H	0.6205153527	-0.0773197042	-2.3370160072
C	-1.9805386090	0.7327709197	0.1100841262
C	-3.0399683890	-0.1242103143	0.0092519455
C	-4.3506007661	0.3893245065	0.0960458665
C	-4.5642069252	1.7277946243	0.2886574606
C	-3.4808222457	2.6298969906	0.3872220947
C	-2.1562634141	2.1150518664	0.2811314981
C	-1.0607631795	3.0104671400	0.3448663608
C	-1.2743133016	4.3510588327	0.5307373502
C	-2.5821659827	4.8555788268	0.6524781189
C	-3.6612456089	4.0171134268	0.5775109007
H	-2.8687248151	-1.1838596535	-0.1390032207
H	-5.1917904779	-0.2896489248	0.0091519147
H	-5.5744394255	2.1173039349	0.3619275587
H	-0.4348261121	5.0354310549	0.5782774938
H	-2.7277288312	5.9199674806	0.7985840721
H	-4.6695782238	4.4092701787	0.6598069410
N	0.2602822925	2.4504362225	0.1848922482
C	0.9040322005	2.9053678293	-1.0638784153
H	1.8316208719	2.3455785140	-1.1842166954
H	1.1202133505	3.9778464113	-1.0120465344
H	0.2493426183	2.6992382016	-1.9074943613
C	1.1411367720	2.7329913331	1.3325755584
H	2.0517955144	2.1487562024	1.2060176804
H	0.6482366516	2.4301394366	2.2525181290
H	1.3904722167	3.7986236965	1.3745320909
Te	1.0691366637	-1.2563871100	3.0881852020
O	0.4952643218	-2.7182669938	2.1669890187
O	2.6951142280	-0.7773508085	2.2368993121
H	2.4652118461	-0.4838186857	1.2985274811
O	2.0063986697	-2.3447576029	4.4106860122
H	2.1720646683	-3.2050636994	4.0042606608
C	1.1336112503	0.2627029022	4.5576474056
C	2.2132875126	1.0958865307	4.6417879579
C	2.2265342411	2.1072917614	5.6245862120
C	1.1689948671	2.2629192058	6.4799338866
C	0.0475859580	1.4055103126	6.4127172318
C	0.0409112288	0.3713216138	5.4323162943
C	-1.0608024632	-0.5167903956	5.3737039373
C	-2.1163598346	-0.3656800267	6.2341120138
C	-2.1159771690	0.6665931408	7.1902771856
C	-1.0576391797	1.5294381481	7.2823442480
H	3.0475077884	0.9737191169	3.9611174557
H	3.0863499665	2.7643722775	5.6961244841
H	1.1806296000	3.0471562923	7.2299289134
H	-2.9585343864	-1.0468935380	6.1887873885
H	-2.9615819103	0.7672174935	7.8613107616
H	-1.0535576813	2.3176727094	8.0279740732
N	-1.0025370774	-1.5779939759	4.3965449993
C	-0.9024412409	-2.9072378345	5.0320734949
H	-0.7293119220	-3.6412264723	4.2449565778
H	-1.8288847801	-3.1448778583	5.5657969533
H	-0.0628001350	-2.9184992243	5.7232114920
C	-2.1430483743	-1.5553498723	3.4629282624
H	-1.9419274561	-2.2778945220	2.6729114683
H	-3.0704089260	-1.8240352039	3.9799499719
H	-2.2351104505	-0.5649365841	3.0252409016

```
Full point group                 C2

Zero-point correction=                           0.489792
Thermal correction to Energy=                    0.524136
Thermal correction to Enthalpy=                  0.525080
Thermal correction to Gibbs Free Energy=         0.426511
Sum of electronic and
zero-point Energies=                         -1583.015083
Sum of electronic and
thermal Energies=                            -1582.980739
Sum of electronic and
thermal Enthalpies=                          -1582.979795
Sum of electronic and
thermal Free Energies=                       -1583.078364
```

$PhTe(O)_2OH$:

Te	0.0006673270	0.0016800369	0.0081162853
C	0.0012472989	-0.0007038681	2.1007856709
C	1.2104914620	0.0021879268	2.7827177152
C	-1.2235783058	0.0177807616	2.7529850969
C	1.1836149032	0.0092198929	4.1698827232
H	2.1523079749	0.0105020422	2.2453133388
C	-1.2306002862	0.0239153351	4.1411829912
H	-2.1478043049	0.0360305499	2.1859204432
C	-0.0321619206	0.0175525536	4.8432533200
H	2.1146670411	0.0127329866	4.7250770766
H	-2.1750337011	0.0374260026	4.6730838918
H	-0.0448428265	0.0246480262	5.9274840387
O	-1.6390053321	0.4279239605	-0.5434324067
O	1.4941803898	0.7400750497	-0.6365170426
O	0.2314542494	-1.8824152455	-0.3187302287
H	0.9704527760	-2.0012036940	-0.9315632897

```
Full point group                 C1

Zero-point correction=                           0.109308
Thermal correction to Energy=                    0.119806
Thermal correction to Enthalpy=                  0.120750
Thermal correction to Gibbs Free Energy=         0.071305
Sum of electronic and
zero-point Energies=                          -465.792736
Sum of electronic and
thermal Energies=                             -465.782239
Sum of electronic and
thermal Enthalpies=                           -465.781294
Sum of electronic and
thermal Free Energies=                        -465.830739
```

$PhTe(O)(OH)_3$:

Te	-0.0048540657	-0.0056614869	-0.0004152755
O	-0.0002261576	-0.0033514777	1.9476684488
H	0.9299527733	-0.0059211399	2.2073025946
O	-0.2143453277	0.2714789573	-1.9527308591
H	0.6756956070	0.1838258140	-2.3180920165
O	-0.7401061045	1.7563597434	0.1456626079
H	-0.8601696167	2.0664048313	-0.7640421290
O	1.7534434795	-0.3186158644	-0.1446368995
C	-1.5671083650	-1.4203666516	-0.0138933316
C	-2.0314337642	-1.9247907721	1.1956108085
C	-2.0931343668	-1.8361481449	-1.2313166047
C	-3.0535985478	-2.8635758029	1.1758201868
H	-1.6017375229	-1.5858897650	2.1282185770
C	-3.1130146221	-2.7778637513	-1.2294473529
H	-1.7131394615	-1.4251370296	-2.1567269885
C	-3.5917736947	-3.2892313320	-0.0310556594
H	-3.4277075592	-3.2626399183	2.1118611693
H	-3.5325068134	-3.1108187327	-2.1720943192
H	-4.3885977075	-4.0248372053	-0.0375895335

```
 Full point group                 C1

Zero-point correction=                           0.136065
 Thermal correction to Energy=                   0.147992
 Thermal correction to Enthalpy=                 0.148936
 Thermal correction to Gibbs Free Energy=        0.097317
 Sum of electronic and
 zero-point Energies=                         -542.228413
 Sum of electronic and
 thermal Energies=                            -542.216487
 Sum of electronic and
 thermal Enthalpies=                          -542.215542
 Sum of electronic and
 thermal Free Energies=                       -542.267161
```

PhTe(OH)$_5$:

Te	0.0007870743	0.0065504314	-0.0012847327
O	0.0004154857	0.0046893996	1.9341541111
H	0.9126114324	-0.0232376437	2.2455766206
O	1.9362819250	0.1225722448	-0.0586567142
H	2.2983681896	-0.7599677442	-0.2008716017
O	-1.9330211850	-0.1321606122	0.0649479854
H	-2.1788163022	-0.9029481998	0.5903169177
O	0.1687185542	-1.9316344898	0.1044017344
H	0.0593552943	-2.2650617676	-0.7954514584
O	-0.0456613269	-0.2320307558	-1.9450172646
H	-0.9502401781	-0.0837849219	-2.2466256912
C	-0.1265516940	2.1055525710	-0.1464018999
C	-0.9493308520	2.7987410003	0.7301173544
C	0.6165180182	2.7659881731	-1.1148493141
C	-1.0288388735	4.1814815209	0.6297537161
H	-1.5196113665	2.2672296622	1.4815580459
C	0.5318728888	4.1494953435	-1.2029620566
H	1.2543344526	2.2087785215	-1.7896927078
C	-0.2896469009	4.8548238556	-0.3338195892
H	-1.6708530025	4.7324226788	1.3082292702
H	1.1112004792	4.6755784983	-1.9537457912
H	-0.3537326223	5.9350497571	-0.4072410090

```
Full point group                 C1

Zero-point correction=                           0.160794
Thermal correction to Energy=                    0.175155
Thermal correction to Enthalpy=                  0.176100
Thermal correction to Gibbs Free Energy=         0.119983
Sum of electronic and
zero-point Energies=                          -618.674463
Sum of electronic and
thermal Energies=                             -618.660102
Sum of electronic and
thermal Enthalpies=                           -618.659157
Sum of electronic and
thermal Free Energies=                        -618.715274
```

[PhTe(O)(OH)$_3$]$_2$:

Te	0.0051303987	-0.0456677985	-0.0040668390
O	0.0015828839	0.0697911950	1.9454149441
Te	1.9396996789	0.0456677986	2.3209923206
O	1.9432471938	-0.0697911950	0.3715105375
O	0.0426968592	-1.9814505363	-0.0460845871
H	0.7131295230	-2.2890474302	0.5867803241
O	0.0997970090	1.9052000508	-0.0891769632
H	0.6211515839	2.1579741318	-0.8611785548
O	0.3413194028	-0.0190006798	-1.9089066322
H	0.6205988508	-0.9042389343	-2.1744309831
O	1.9021332184	1.9814505363	2.3630100687
H	1.2317005547	2.2890474302	1.7301451576
O	1.8450330686	-1.9052000508	2.4061024449
H	1.3236784937	-2.1579741318	3.1781040364
O	1.6035106749	0.0190006799	4.2258321138
H	1.3242312268	0.9042389343	4.4913564648
C	-2.0964266957	-0.0255317551	-0.1365286607
C	-2.8486418866	-0.3143481996	0.9930930472
C	-2.6981653022	0.2689947734	-1.3516169359
C	-4.2340452472	-0.3087755819	0.8973410073
C	-4.0845074975	0.2705281632	-1.4331825747
C	-4.8504810700	-0.0178380966	-0.3119802404
H	-2.3611294495	-0.5350289716	1.9343021981
H	-2.0954971751	0.4886277119	-2.2243170681
H	-4.8315588532	-0.5327517450	1.7741491910
H	-4.5648354675	0.4976987314	-2.3785248045
H	-5.9328010495	-0.0156160921	-0.3809275584
C	4.0412567734	0.0255317552	2.4534541423
C	4.7934719643	0.3143481997	1.3238324345
C	4.6429953798	-0.2689947733	3.6685424176
C	6.1788753248	0.3087755819	1.4195844743
C	6.0293375752	-0.2705281631	3.7501080563
C	6.7953111477	0.0178380967	2.6289057220
H	4.0403272528	-0.4886277119	4.5412425497
H	4.3059595272	0.5350289716	0.3826232836
H	6.7763889309	0.5327517451	0.5427762906
H	6.5096655452	-0.4976987313	4.6954502862
H	7.8776311271	0.0156160922	2.6978530400

```
Full point group                 CI

Zero-point correction=                           0.274449
Thermal correction to Energy=                    0.299033
Thermal correction to Enthalpy=                  0.299978
Thermal correction to Gibbs Free Energy=         0.219087
Sum of electronic and
zero-point Energies=                         -1084.533970
Sum of electronic and
thermal Energies=                            -1084.509386
Sum of electronic and
thermal Enthalpies=                          -1084.508442
Sum of electronic and
thermal Free Energies=                       -1084.589332
```

$[PhTe(O)(OH)_2]_2O$:

```
Te       0.0026305819  -0.0104235291   0.0049555004
O        0.0103842534  -0.0063345609   1.8084474207
O        1.9784620752  -0.0053041786  -0.0984829913
O       -1.9228471966  -0.0267474260  -0.2458578058
H       -2.2872138674   0.8406115743  -0.0343621918
C        0.0579391928  -1.7865710568  -1.1284516854
C        1.1197366133  -2.6596956370  -0.9297529914
C       -0.9651876487  -2.0647995559  -2.0252929955
C        1.1478078991  -3.8473280300  -1.6468972242
H        1.9099317164  -2.4140085580  -0.2330123188
H       -1.7909105291  -1.3777117978  -2.1475794999
C       -0.9090899432  -3.2496597662  -2.7472966032
C        0.1398179717  -4.1383778868  -2.5566029717
H        1.9638096291  -4.5443746751  -1.4930657571
H       -1.6961774441  -3.4776024744  -3.4571496781
H        0.1710794149  -5.0650718319  -3.1190293053
O       -0.0210179087   1.6812654159  -0.8378971311
H        0.8583199442   2.1458256762  -0.6396369665
Te       3.1096092431   1.3621474846   0.7761550121
O        2.2570712065   2.7203336988  -0.0492101693
O        4.3840929721   2.4287337585   1.7805036532
H        3.9356508233   2.8731201774   2.5093524852
C        4.7671230865   0.3754547178  -0.0732429078
C        4.6119173141  -0.2139165117  -1.3213587858
C        5.9779681478   0.3509275320   0.6063049991
C        5.7064471890  -0.8371901482  -1.9036746063
H        3.6547232606  -0.1902624229  -1.8247821087
H        6.0782882084   0.8340393941   1.5682818148
C        7.0562749165  -0.2941706341   0.0151796655
C        6.9226711834  -0.8820101822  -1.2350153866
H        5.6036370849  -1.2906639411  -2.8830562134
H        8.0061730992  -0.3288364029   0.5365697744
H        7.7724791836  -1.3766095965  -1.6924648898
O        2.4145679353   0.8298191290   2.4513599742
H        1.4950704128   0.4300710015   2.2997736083

Full point group                 C1

Zero-point correction=                     0.247736
Thermal correction to Energy=              0.270335
Thermal correction to Enthalpy=            0.271279
Thermal correction to Gibbs Free Energy=   0.193736
Sum of electronic and
zero-point Energies=                   -1008.067140
Sum of electronic and
thermal Energies=                      -1008.044542
Sum of electronic and
thermal Enthalpies=                    -1008.043598
Sum of electronic and
thermal Free Energies=                 -1008.121140
```

H_2O:

```
O       -0.0157750784   0.0000000000  -0.0111487231
H        0.0200177246   0.0000000000   0.9484105462
H        0.9006931849   0.0000000000  -0.2977164089

Full point group                 C2V

Zero-point correction=                     0.021437
Thermal correction to Energy=              0.024273
Thermal correction to Enthalpy=            0.025217
Thermal correction to Gibbs Free Energy=   0.003801
Sum of electronic and
zero-point Energies=                     -76.408607
Sum of electronic and
thermal Energies=                        -76.405771
Sum of electronic and
thermal Enthalpies=                      -76.404827
Sum of electronic and
thermal Free Energies=                   -76.426243
```

16 CONCLUSION

During the course of this work it was possible to gain a deeper insight into the reactivity and structural diversity of organotellurium compounds comprising secondary interactions. Especially the use of the intramolecularly coordinating 8-dimethylaminonaphthyl ligand yielded a diversity of interesting new organotelluroxanes clusters and polymers, several ionic diaryltelluronium compounds as well as highly oxidized mono- and diorganotellurium(VI) compounds.

The reactivity of diorganotellurium oxides, R_2TeO ($R=Ph$, p-$MeOC_6H_4$, p-$Me_2NC_6H_4$), towards phenol and *o*-nitrophenol is surprisingly diverse and afforded diorganotellurium phenolates and oranotelluroxanes. This stands in contrast to the other main group element oxides (e.g., Ph_3PO, Ph_3AsO, Ph_2SO, Ph_2SeO)[61], which form hydrogen-bonded complexes with phenol and related compounds. Only few diorganotellurium dialcolates have been prepared recently[58],[129].

The reaction of the diorganotelluriumoxides R_2TeO with phenol yielded exclusively the monomolecular compounds $R_2Te(OH)OPh$ and $R_2Te(OPh)_2$, which show no secondary $Te\cdots O$ interactions, whereby the reaction with *o*-nitrophenol ($R' = o$-$NO_2C_6H_4$) proceeds with condensation and produces organotelluroxanes, which comprise secondary $Te\cdots O$ interactions, namely $(R'O)R_2TeOTeR_2(OR')$ ($R=p$-$MeOC_6H_4$; p-$Me_2NC_6H_4$) and $(R'O)Ph_2TeOTePh_2OTePh_2(OR')$. Especially the formation of dinuclear diorganotellurium compounds in the form of $XR_2TeOTeR_2X$ appears to be a common motif concerning the synthesized compounds

This structural motif was observed in several synthesized compounds like the telluroxanes $ClR_2TeOTeR_2Cl$ ($R= Ph$, p-$MeOC_6H_4$, p-$Me_2NC_6H_4$), $IR_2TeOTeR_2I$ ($R=p$-$MeOC_6H_4$) or the alkyltellurium compounds $(Me_2Te)_2OI_2$ and the cluster 2 $(Me_2Te)_2O(I)OH \cdot H_2O$. The latter features two polymer strings, whereby the first polymer string is comparable to a $(Me_2TeO)_n$ polymer. Notably, the structures of $Me_2Te(OH)_2$ and potential condensation products, such as $(Me_2TeO)_n$, are still unknown. The second polymer string, however, comprises $R_2Te(OH)TeR_2(OH)$

units – comparable to the motif $XR_2TeOTeR_2X$ – that are associated by short secondary Te···O(H) interactions.

The iodide ions are not involved in a primary bonding to the Te atoms. However, apparently they play an integral role for the supramolecular association as they form secondary bonds to all Te atoms building 2D-polymer strings. This structural directing effect is comparable to the structurally directing bromide ion in the dodecanuclear isopropyltelluriumoxo cluster $[Li(THF)_4][\{(i\text{-}PrTe)_{12}O_{16}Br_4\{Li\text{-}(THF)Br\}_4\}Br] \cdot 2\ THF$[130].

Since it was demonstrated by our work group that diorganotellurium oxides, such as (p-$MeOC_6H_4$)TeO, showed potential for applications in the fixation of carbon dioxide[48] the ability of carbon fixation of simple dialkyltellurium dioles was examined. The obtained dialkyltelluroxane carbonates $(Me_2TeOTeMe_2CO_3)_n$ and $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH \cdot 2H_2O$ can be described as 1D and 2D coordination polymers, respectively. Each structure comprises secondary Te···O contacts and features the repeating structural motif $OR_2TeOTeR_2O$.

It appears that the possibility of secondary interactions (e.g. through *o*-nitrophenol or halides) leads to stabile tetraorganotellurium or hexaorganotellurium compounds rather than mononuclear compounds, whereas compounds comprising ligands with a lesser ability to such interactions (e.g. phenole) seem to prefer a mononuclear state.

However, the possibility of providing secondary interactions does not exclusively lead to di- or trinuclear diorganotellurium compounds. Surprisingly, attempts to form a complex – analogous to $(Ph_3Sb)_2OI_2 \cdot \frac{1}{4}\ I_2$[65] – of $[(p\text{-}MeOC_6H_4)_2Te]_2OI_2$ and iodine failed and co-crystals of the mononuclear $(p\text{-}MeOC_6H_4)_2TeI_2 \cdot \frac{1}{2}\ I_2$ were obtained, which could be rationalized by the kinetic lability of the Te-X (X= O, Cl, Br, I) bonds. A similar observation was made concerning the formation of the previously described tetraorganotelluroxanes $ClR_2TeOTeR_2Cl$ via a redistribution reaction. The crystal structure consists of a centrosymmetric tetramer made of $(p\text{-}MeOC_6H_4)_2TeI_2$ molecules, which are associated via secondary Te···I interactions, whereas the iodine molecule links adjacent tetramers in the crystal lattice via I···I contacts, thus, indicating an important contribution of the secondary intermolecular interactions to the supramolecular association of diorganotellurium compounds.

These results indicate that secondary tellurium interactions play a significant role in stabilizing dimeric or higher aggregated diorganotellurium compounds or in the supramolecular assembly of such compounds, whereby the motif $XR_2TeOTeR_2X$ appears to be a favored form in the solid state. This is supported by the findings that the equimolar reaction of diorganotellurium dichlorides R_2TeCl_2 and their corresponding bis(phenolates) $R_2Te(OPh)_2$ yielded only in solution the mononuclear compound $R_2Te(Cl)(OPh)$, which furnished upon standing the dinuclear compound $ClR_2TeOTeR_2Cl$. A similar observation was made by the attempt to isolate a diorganohydroxytelluronium ion $[R_2TeOH]^+$ by the reaction of $(p\text{-}MeOC_6H_4)_2TeO$ with HO_3SCF_3. However, all attempts at isolating this product resulted in a condensation reaction yielding the tetraarylditelluroxane $[(p\text{-}MeOC_6H_4)_2Te]_2O(O_3SCF_3)_2$[22], which comprises the same already observed structural motif $XR_2TeOTeR_2X$.

The possible stabilization of the ionic state of diorganotellurium compounds $[R_2TeX]^+$ (X= OH, Cl, Br, I) by compensating the charge of the tellurium atom via an intramolecularly coordinating ligand – in order to avoid condensation reactions to e.g. dinuclear compounds – was another aspect of this work. Therefore, the reactivity of diorganotellurium compounds comprising the 8-dimethylaminonaphthyl ligand was investigated.

In order to achieve the isolation of the respective diorganohydroxytelluronium ion $[R_2TeOH]^+$ the diaryltellurium oxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$ was prepared, however, during the course of this preparation quite unexpected results were achieved.

The reaction of the diaryltelluride $(8\text{-}Me_2NC_{10}H_6)_2Te$ with H_2O_2 did not afford the expected diaryltellurium(IV) oxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$, but the diaryltellurium(VI) dioxide $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$. This facile formation is unusual as the oxidation of other known diaryltellurides with most oxidizing agents either stops at the stage of diaryltellurium(IV) oxides or produces ill-defined product mixtures[23]. This is presumably due to the intramolecular coordination by the N donor ligands, which probably stabilize an intermediate state R_2Te^+-O^- and enhance the reactivity for a nucleophilic attack on the tellurium. The diaryltellurium dioxide is, aside from the recently described kinetically stabilized (2,4,6-*i*-$Pr_3C_6H_2)_2TeO_2$[27], only the second example of this compound class.

The synthesis of the diaryltellurium oxide (8-$Me_2NC_{10}H_6)_2TeO$ was achieved by the comproportionation reaction of (8-$Me_2NC_{10}H_6)_2Te$ and (8-$Me_2NC_{10}H_6)_2TeO_2$. In solution and in the solid state the diaryltellurium oxide is sensitive to air oxidation, which stands in contrast to the previously described difficult oxidation of such compounds. All attempts at obtaining single crystals suitable for X-ray crystallography failed, however, based on the obtained data a polymeric structure, similar to that of (*p*-$MeOC_6H_4)_2TeO$[19], is proposed. Such intramolecularly coordinated diaryltellurium(IV) oxides are very rare. There are only a few examples like the (2-$Me_2NCH_2C_6H_4)_2TeO$[25] and the very recently reported (2-$PhNNC_6H_4)_2TeO$[26].

The protonation of the diaryltellurium oxide using HO_3SCF_3 provided the compound [(8-$Me_2NC_{10}H_6)_2Te(OH)](O_3SCF_3)$ featuring the [(8-$Me_2NC_{10}H_6)_2Te(OH)]^+$ ion. The stabilization of this compound is attributed to the charge compensation by the intramolecularly coordinating N donor substituents. A similar observation was recently made for the related arylhydroxystibonium triflate [2,6-$(Me_2NCH_2)_2C_6H_3Sb(OH)](O_3SCF_3)$ containing a NCN pincer type ligand[134]. No condensation reactions to the respective dinuclear tetraorganotelluroxane, like in the comparable synthesis of [(*p*-$MeOC_6H_4)_2Te]_2O(O_3SCF_3)_2$[22] was observed.

It is noteworthy that another unusual reaction took place. The diorganotellurium oxide (8-$Me_2NC_{10}H_6)_2TeO$ reacts – in absence of triflic acid – with acetonitrile. The reaction proceeds with reversible oxygen transfer providing the diaryltellurium(IV) acetimidate (8-$Me_2NC_{10}H_8)_2TeNC(O)CH_3$ in the solid state. While the catalyzed hydrolysis of acetonitrile to acetamide in the coordination sphere of transitions metals, such as platinum and rhodium,[86] is well documented such a facile formation of the acetimidate moiety is unprecedented. The question why such an exceptional reaction takes place is still unsolved at the moment. Given this unprecedented reaction and the fact that only very few diorganotellurium oxides comprising an intramolecularly ligand are known, it is reasonable to assume that a charge compensation of the tellurium atom by the N donor ligand plays an integral role, however, calculations concerning electron density (AIM and ELI-D) and the energies of the educt and product are conducted by our work group, in order to shed some light on this unexpected reaction.

The same ligand system was examined concerning the respective diaryltellurium dihalides, which lead to a new series of diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl, Br, I) comprising different counteranions, depending on the reaction conditions.

The reaction of bis(8-dimethylaminonaphthyl) telluride $(8\text{-}Me_2NC_{10}H_6)_2Te$[73] with one equivalent of SO_2Cl_2, Br_2 and I_2 afforded the mononuclear diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = Cl, Br, I). A hydrolysis of this compounds yielded the diarylhydroxytelluronium cation $(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+$, whereby no condensation reactions to dinuclear compounds were observed either. Using an excess of SO_2Cl_2 or three equivalents of Br_2 proceeds with an electrophilic substitution at the 8-dimethylaminonaphthyl residues and provided the diaryltellurium halides $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$ and $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$, respectively, whereby an excess of Br_2 gave the diarylbromotelluronium cation $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+\cdot Br_3^-$. Two or three equivalents of iodine provided $[(8\text{-}Me_2NC_{10}H_6)_2TeI]^+\cdot I_3^-$ and $[(8\text{-}Me_2NC_{10}H_6)_2TeI]^+\cdot I_3^-\cdot I_2$, respectively.

The structural analysis of the diaryltellurium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = OH, Cl, Br, I) shows that the Te···N bond lengths in axial coordination are significantly shorter than the Te···N bond lengths of the equatorial coordination. A similar observation was made concerning the compound $(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+ \cdot O_3SCF_3^-$. The tellurium-halides bond lengths are significantly shorter than those of the related diaryltellurium dihalides Ph_2TeX_2[74-76] and $(4\text{-}Me_2NC_6H_4)_2TeX_2$ (X = Cl, Br, I)[77]. These short bond lengths could be due to the compensation of the formal positive charge situated at the Te atoms by strong attractive interactions. The diarylhalotellurium cations, however, are weakly associated with the halogen atoms of the anions (weak ion pairing) via secondary Te···Y interactions (Y = Cl, Br, I).

The ^{1}H and ^{13}C NMR spectra of the diaryltelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = OH, Cl, Br, I) suggest that the cationic structures are retained in solution. The ^{125}Te NMR spectra exhibit signals for the diarylhalotelluronium cations regardless of the counter ions, however, in $CDCl_3$, the chemical shifts for the chloride and bromide of the diarylhydroxytelluronium cations differ, which apparently suggests some degree of association between the diarylhydroxytelluronium cation and counteranion. The molar conductivity measurements confirm the presence of significant concentration of electrolytes in solution.

However, within the diaryltellurium dihalides $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$ and $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ the tellurium-halogen bond lengths compare well with those of the related diaryltellurium dihalides Ph_2TeX_2 (X = Cl, Br)[74,76] and $(4\text{-}Me_2NC_6H_4)_2TeX_2$ (X = Cl, Br)[77] and the Te···N bond lengths compare well with the weaker equatorial N coordination found in the above mentioned diarylhalotellurium cations. The NMR analysis of the diaryltellurium dichloride $(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_4)_2TeCl_2$ indicates that in solid state as well as in solution no ionic structure could be obtained. The molar conductivity was below the detection limit. In contrast, the structure of the diaryltellurium dibromide $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ depends in solution on the solvent. In acetonitrile, electrolytic dissociation to $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+$ Br^- takes place, while in chloroform, the solid state structure of $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ is retained.

It appears that the electrophilic substitution at the ligand system reduces the ability of charge compensation by the intramolecularly coordinating N donor substituents, which leads to mainly covalent tellurium halide bonding. However, in case of the monosubstituted bromide compound $(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr_2$ it is still possible to stabilize the ionic state under certain conditions, which was observed in the cation $[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_5)_2TeBr]^+\cdot Br_3^-$ or in the above described dissociation in solution.

These results indicate that only one of the intramolecularly coordinating N donor substituents plays an integral role in the compensation of the charge on the tellurium atom and therefore in the stabilization of the ionic state. Nevertheless, by using this rather stiff intramolecularly coordinating group a new series of diarylhalotelluronium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = OH, Cl, Br, I) could be isolated. Very few organotellurium halides stabilized by intermolecular coordination are known. Only two, namely $[(2\text{-}Me_2NCH_2C_6H_4)PhTeX]^+X^-$ (X = Br, I), were isolated and characterized by X-ray crystallography[38], whereby recently the diarylhalotelluronium cation $[(2\text{-}PhNNC_6H_4)_2TeI]^+I_3^-$ was reported[26].

All the bis(8-dimethylaminonaphthyl)tellurium compounds could be isolated as mononuclear diorganotellurium species. This stands in contrast to the isolation of the di- or trinuclear compounds of the previously described organotelluroxanes lacking an intramolecularly coordinating ligand, which were essentially stabilized by intermolecular secondary interactions in the solid state. It appears that the stabilization by the charge compensation of the tellurium atom via the intramolecularly coordinating donor ligand is more effective than the stabilization of the condensated products via intermolecular secondary interactions.

The use of the 8-dimethylaminonaphthyl ligand was further investigated concerning monorganotellurium compounds. While synthesizing the starting material, namely (8-dimethylaminonaphthyl) ditelluride, by a procedure similar to that of *Singh et al.*[114], two interesting observations could be made. Using fractioned crystallization the respective tritelluride RTeTeTeR was additionally isolated, which is only moderately stable in solution, however, indefinitely stable in solid state and can be handled in air for a short time. By conducting a ^{125}Te NMR spectrum in CD_2Cl_2 at -90 ℃ it was further possible to find the first spectroscopic evidence for the existence of tetratellurides RTeTeTeTeR.

The base hydrolysis of the aryltellurium trichloride comprising the 8-dimethylaminonaphthyl substituent turned out to be a rational approach for the synthesis of a series of well-defined telluroxane clusters and polymers. All of the synthesized compounds comprises intramolecular coordinating Te···N interactions but only several comprise additional secondary Te···O interactions, whereby two dominating structural motifs could be observed.

Surprisingly, the structural motif $XR_2TeOTeR_2X$ could be observed for the dinuclear telluroxane $(8\text{-}Me_2NC_{10}H_6Te)_2OCl_4$ and $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3\cdot 7/3\ H_2O]_n$, the latter is the first structurally characterized aryltellurinic anhydride which features two crystallographically independent, albeit similar 1D Te-O double strings. Both structures are comparable to the supramolecular association of $[(2\text{-}Me_2NC_6H_4)_2Te]_2OCl_2$. Furthermore, the proposed structure of the telluroxane $(8\text{-}Me_2NC_{10}H_6Te)_6O_5Cl_8$ is consistent with the established structures of the synthesized telluroxanes.

The second structural motif for the synthesized telluroxane clusters appears to be a ring structure, which was observed in the clusters $(8\text{-}Me_2NC_{10}H_6Te)_6O_8Cl_2\cdot 8CHCl_3$, $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ and $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2\cdot 4THF\cdot 6H_2O$. The average bond length of the Te···Cl bond of the first two compounds suggest a rather ionic Te···Cl bond, which could be attributed to the charge compensation of the tellurium atom – comparable to the previously described diorganotellurium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = OH, Cl, Br, I) – by the intramolecularly coordinating N donor ligand. No secondary Te···O interactions were observed for this compounds, whereby the last compound comprises only one secondary Te···O interaction.

It has to be noted that the structural motif of inorganic Te atoms of the octanuclear telluroxane cluster $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ is unusual. They assemble in a four-membered Te_2O_2 ring, whereby the spatial arrangement of the symmetry-related inorganic Te sites is distorted square pyramidal or distorted octahedral when taking into account the stereochemically active lone pair. In comparison, the crystal structures of α- and β-TeO_2 comprise distorted trigonal bipyramidal arrangements[131].

It appears that the possibility of secondary Te···Cl bonds favors the structural motif $XR_2TeOTeR_2X$ or a comparable open chain structure analogue to the observations made for the organotelluroxanes. By a successive hydrolysis of the respective trichloride – thus reducing the possibility of Te···Cl interactions – the structural motif changes during the process to an organotelluroxane ring structure comprising few or no intermolecular directing secondary Te···O bonds and a rather ionic Te···Cl bond. However, it appears that secondary Te···O interactions are also suited to stabilize a comparable structural motif to the observed motif $XR_2TeOTeR_2X$, as observed in the polymer $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$. However, the energy difference between the polymer $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$ and the ring structure $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ seems to be rather small, since the compounds are interconvertible by crystallization from H_2O and THF/hexane, respectively.

Aside from the other secondary interactions the intramolecularly coordination of the N donor group deserves a closer look. Usually, the 8-dimethylaminonaphthyl group ('stiff-arm ligand') is considered to be quite rigid[120], however, the Te···N bond lengths vary substantially in the synthesized compounds. They increase with an increasing degree of hydrolysis, which suggest a successive reduction of the Lewis acidity of the Te atoms with an increasing degree of hydrolysis and aggregation. The higher Lewis acidity leads to a stronger interaction of the N donor system to which the stabilization of products with a low degree of hydrolysis by intramolecularly coordinating Te···N and the secondary Te···Cl interactions could be attributed. However, this effect is successively reduced during the ongoing process leading to polymer or ring structures in which the secondary interactions between tellurium and oxygen or covalent tellurium oxygen bonds dominate the structural motif.

It has to be noted that the new series of well-defined telluroxanes, telluroxane clusters and polymers stands in contrast to the described kinetically stabilized compounds $[2,6\text{-}Mes_2C_6H_3Te(O)Cl]_2$ and $[2,6\text{-}Mes_2C_6H_3Te(O)(OH)]_2$ prepared under similar conditions[51], which seem to stabilize only near completed hydrolysis products.

Interestingly, the examinations of organometalatelluroxane lead to compounds with comparable structures. On the one hand, yielded the reaction of a diorganotellurium oxide with a diorganosilan diole not the expected open chain compounds but the tellurasiloxane ring *cyclo*-$[(p\text{-}MeOC_6H_4)_2TeOSi\textit{t}\text{-}Bu_2O]_3$, comprising no secondary Te···O contacts. Therefore, the coordination sphere of the tellurasiloxane ring differs substantially from the structures of related tetraorganoditelluroxanes[20-22] and tellurastannoxanes[48,49], which comprise a number of secondary Te···O intra- and intermolecular contacts. However, the structure is comparable in some degree to the formation of the previously described telluroxane ring structures.

On the other hand, the reaction of (t-Bu_2SnO)$_3$ with 8-$Me_2NC_{10}H_6TeCl_3$ provided the dinuclear stannatelluroxane 8-$Me_2NC_{10}H_6TeO_2Sn$-t-Bu_2Cl, which is a rare example of a molecular oxide incorporating two heavy main group elements. The dinuclear stannatelluroxane comprises a dimeric structure, whereby two adjacent molecules are linked by secondary Te···O interactions. The structural motif is comparable to the motif $XR_2TeOTeR_2X$ of the previously products. For example, the primary Te-O bond lengths and the distance of the intramolecularly coordinating Te···N interactions of the stannatelluroxane are reasonable comparable with the respective bond length observed in the polymer [(8-$Me_2NC_{10}H_6Te)_2O_3]_n$.

Since some stannatelluroxanes have the ability to absorb gaseous carbon dioxide by forming tetranuclear stannatelluroxane carbonate clusters[48,49] the same ability was examined. However, no reaction was observed by means of IR- and NMR-spectroscopy after the treatment of a respective solution with gaseous CO_2. This could be explained by the fact that the Lewis acidity of the tellurium atom is too strongly reduced by the intramolecularly coordinated N donor ligands. A comparable observation was made concerning aryltin and arylantimony carbonates[46,46], whereby due to the N donor ligands the least involvement in the carbonate coordination on the metal was observed. It is probable that the intramolecular coordination of the 8-dimethylaminonaphthyl ligand prevents the absorption of gaseous carbon dioxide.

Due to the progress concerning stable hexacoordinate organotellurium(VI) compounds, such as R_6Te, Ph_5TeF, and R_4TeF_2 (R=Me, Ph)[123] the preparation of the hitherto unknown organotelluronic acids was also investigated and it was possible to obtain the first two completely characterized examples of this elementary compound class, using a kinetically stabilization and a stabilization via an intramolecularly coordinating ligand.

The tetranuclear sodium *m*-terphenyltellurinate $Na_4(2,6\text{-}Mes_2C_6H_3Te)_4(\mu_3\text{-}O)_8$, synthesized from the dinuclear *m*-terphenyltellurinic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{–}O)(OH)]_2$[51], was oxidized by dry O_2 in the presence of [18]crown-6 to afford the first dinuclear *m*-terphenyltelluronic acid $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$. The molecular structure of the tetranuclear sodium *m*-terphenyltellurinate comprises an unprecedented $Na_4Te_4O_8$ cage structure that is completely shielded by four *m*-terphenyl groups. The molecular structure of the diarylditelluronic acid comprises a dinuclear four membered Te_2O_2 ring also completely shielded by two *m*-terphenyl groups, whereby spatial arrangement of the Te atoms is octahedral. The average Te-O bond lengths are comparable with the bond length of cubic $Te(OH)_6$[125].

Given the synthetic difficult approach to this kinetically stabilized diarylditelluronic acid and bearing in mind the easy oxidation of the diaryltelluride $(8\text{-}Me_2NC_{10}H_6)_2Te$ to the tellurone $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$, it was attempted to oxidize an aqueous solution of the corresponding analogues of the intramolecularly coordinated aryltellurinic acid, namely $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ and $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$, using H_2O_2, which yielded the diarylditelluronic acid $[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)_2]_2(\mu\text{-}O)$.

Each Te atom of this diarylditelluronic acid comprises one Te-O double bond and three Te-O single bonds, which compare reasonably well with the bond lengths of $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2TeO_2$[127] and $Te(OH)_6$[125]. The intramolecular Te···N coordination is significantly shorter – it is the shortest value observed concerning the synthesized 8-dimethylaminonaphthyltellurium compounds – pointing to strong attractive interactions. The easy oxidation could be attributed, as already discussed concerning the tellurone $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$, to the intramolecular Te···N coordination.

Interestingly, no evidence was found that the diarylditelluronic acid possesses any oxidizing power towards alcohols, in contrary, attempts at recrystallizing from methanol lead to the selective esterification of two hydroxyl groups and formation of the partial methyl ester $[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)(OMe)]_2(\mu\text{-}O)$. Another noteworthy observation is that the slight structural change by this esterification significantly increased the solubility in common organic solvents, such as $CHCl_3$. The same effect was observed when the compound was dissolved in other alcohols like ethanol or isopropanol. The solubility of the residue in $CDCl_3$ was increased and the respective ^{125}Te NMR spectra of the crude residues imply that an esterification took place. However, the ^{1}H NMR spectrum indicates an equilibrium in solution of the partial methyl ester $[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)(OMe)]_2(\mu\text{-}O)$. It has to be noted that by using bulkier alcohols, the NMR spectroscopy data indicates that only one structure is retained in solution. It is probable that the use of a steric effect concerning the respective alcohols will favor a mononuclear ester compound. However, a full characterization of these other esterification products remained unfinished at the time and therefore, the structure of these compounds in solution remains mere speculation at this moment.

As the above mentioned results show, the influence of secondary interactions on the structure and reactivity of tellurium compounds is substantial, whereby the structural motif $XR_2TeOTeR_2X$ appears to be favored in structures dominated by mainly secondary intermolecular interactions. Aside the intermolecular interactions especially the influence of the intramolecularly coordinating ligand systems on the formation of organotellurium cations or organotelluroxane clusters respectively polymers is significant. Particularly the easy formation of the tellurone respectively the telluronic acid or the formation of the acetimidate are unusual, which points to a significant influence of the intramolecularly coordinating ligand on the reactivity of the tellurium atom.

The effective stabilization of the cationic state by the N donor substituent concerning organotellurium compounds, whereby the cationic state is retained in solution and the counteranion plays only a secondary role, could make these compounds promising reagents for catalyst applications. It appears that the effectifity of the stabilization by the N donor substituent is effected by small changes on the ligand system, like the described electrophilic substitution. Therefore, it could be possible to tune an eventual catalyst by applying small changes on the ligand system. Additionally, the crystallographic data implies that only one N donor is effectively involved in the charge compensation, however, a stiff ligand system in relative close proximity to the tellurium atom was already used. Nevertheless, it was possible to isolate reasonable stable cationic compounds. Therefore, it could be possible to isolate a dicationic species $[R_2Te]^{2+}$ by using a more rigid ligand system, in which both N donor substituents or a donor with a higher electron density like an O donor system are forced into a very close proximity to the tellurium atom and therefore, both donor substituents could be forced into intramolecular interactions.

Furthermore, the simple esterification of the diarylditelluronic acid $[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)_2]_2(\mu\text{-}O)$ in combination with the enhanced solubility in contrast to the virtual non solubility of the parent telluronic acid in most of the polar solvents make these compounds interesting candidates for mild esterification reagents. Additionally, the combination of the electronic stabilization by an intramolecularly coordination ligand could be combined with a kinetic stabilization of a reasonable bulky ligand, in order to obtain a better insight into the structures and the reactivity of organotellurinic and -telluronic acids.

17 REFERENCES

[1] Einführung in die Technische Chemie, Behr A., Agar D.W., Jörissen J., **2010**, *VII*, 278.

[2] Elmar Steingruber "Indigo and Indigo Colorants" Ullmann's Encyclopedia of Industrial Chemistry 2004, Wiley-VCH, Weinheim.

[3] Reinhard Brückner "Reaktionsmechanismen – Organische Reaktionen, Stereochemie, moderne Synthesemethoden", 2. Auflage, **2003**, Spektrum Akademischer Verlag GmbH, Heidelberg, p. 384, 480f.

[4] Löwig, C. *J. Pogg. Ann*. **1836**, *37*, 552.

[5] K. B. Sharpless, R. F. Lauer; *J. Am. Chem. Soc.*, **1973**, *95*, 2697.

[6] K. B. Sharpless, R. F. Lauer und A. Y. Teranishi; *J. Am. Chem. Soc.*,**1973**, *95*, 6137.

[7] K. B. Sharpless, M. W. Young und R. F. Lauer; *Tetrahedron Lett.*, **1973**, *22,* 1979

[8] D. L. J. Clive; *J. Chem. Soc. Chem. Commun.*,**1973**, 695.

[9] H. J. Reich, I. L. Reich und J. M. Renga; *J. Am. Chem. Soc.*,**1973**, *95*, 5813.

[10] F. Wöhler, *Liebigs Ann. Chem.,* **1840***, 35***,** 111.

[11] (a) K. Lederer, *Ann. Chem.* **1912**, *391*, 326;
(b) K. Lederer, *Chem. Ber.* **1916**, *49*, 1076;
(c) K. J. Irgolic, *The Organic Chemistry of Tellurium* **1974** (Gordon and Breach: New York, NY), and references cited therein.

[12] Hollemann-Wiberg, “Lehrbuch der Anorganischen Chemie”, 101. Auflage, **1995**, Walter de Gruyter & Co., p. 614.

[13] (a) Barton, D. H. R.; Ley, S. V.; Meerholz, C. A. *J. Chem. Soc., Chem. Commun.* **1979**, 755;
(b) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron Lett.* **1980**, *21*, 1785;
(c) Engman, L.; Cava, M. P. *Tetrahedron Lett.* **1981**, *22*, 5251;
(d) Ley, S. V.; Meerholz, C. A.; Barton, D. H. R. *Tetrahedron, Suppl.* **1981**, 213;
(e) Akiba, M.; Lakshimikantham, M. V.; Jen, K.-Y.; Cava, M. P. *J. Org. Chem*. **1984**, *49*, 4819;
(f) Oba, M.; Endo, M.; Nishiyama, K.; Ouchi, A.; Ando, W. *Chem. Commun*. **2004**, 1672;
(g) Oba, M.; Okada, Y.; Nishiyama, K.; Ando, W. *Org. Lett*. **2009**, *11*, 1879.

[14] (a) Shen, J. K.; Gao, Y.; Shi, Q.; Rheingold, A. L.; Basolo, F. *Inorg. Chem.* **1991**, *30*, 1868;
(b) Xue, M.; Gao, Y. C.; Shen, J. K.; Shi, Q. Z.; Basolo, F. *Inorg. Chim. Acta* **1993**, *207*, 207;
(c) Liu, X.; Gao, Y. C.; Su, Z. X.; Wang, Y. Y.; Shi, Q. Z. *Trans. Met. Chem.* **1999**, *24*, 666;
(d) Song, L. C.; Li, Q. S.; Hu, Q. M.; Dong, Y. B. *J. Organomet. Chem.* **2001**, *619*, 194;
(e) Okada, Y.; Oba, M.; Arai, A.; Tanaka, K.; Nishiyama, K.; Ando, W. *Inorg. Chem*. **2010**, *49*, 383.

[15] (a) Kanda, T.; Engman, L.; Cotgreave, I. A.; Powis, G. *J. Org. Chem*. **1999**, *64*, 8161;
(b) You, Y.; Ahsan, K.; Detty, M. R. *J. Am. Chem. Soc*. **2003**, *125*, 4918.

[16] (a) J. Zuckerman-Schpector, I. Haiduc, *Phosphorus, Sulfur, Silicon,* **2001**, *171*, 73;
(b) I. Haiduc, J. Zuckerman-Schpector*, Phosphorus, Sulfur, Silicon*, **2001**, *171*, 171;
(c) W.-W. du Mont, C.G. Hrib, *Handbook of Chalcogen Chemistry*, **2007**, 833;
(d) M.C. Aragoni, M. Arca, F.A. Devillanova, A. Garau, F. Isaia, V. Lippolis, A. Mancini, *Bioinorg. Chem. Appl*. **2007**, 1.

[17] N.W. Alcock, W. D. Harrison, *J. Chem. Soc., DaltonTrans.* **1982**, 709.

[18] (a) Naumann, D.; Tyrra, W.; Hermann, R.; Pantenburg, I.; Wickleder, M. S. *Z. Anorg. Allg. Chem.* **2002**, *628*, 833;
(b) Klapötke, T. M.; Krumm, B.; Mayer P.; Piotrowski, H.; Ruscitti, O. P. *Z. Naturforsch*. **2002**, *B57*,145.

[19] J. Beckmann, D. Dakternieks, A. Duthie, F. Ribot, M. Schürmann, N. A. Lewcenko, *Organometallics* **2003**, *22*, 3257.

[20] (a) Kobayashi, K.; Izawa, H.; Yamaguchi, K.; Horn, E.; Furukawa, N. *Chem. Commun*. **2001**, 1428.
(b) Alcock, N. W.; Culver, J.; Roe, S. M. *J. Chem. Soc., Dalton Trans*. **1992**, 1477.

[21] Alcock, N. W.; Harrison, W. D. *J. Chem. Soc., Dalton Trans*. **1982**, 1421.

[22] Beckmann, J.; Dakternieks, D.; Duthie, A.; Lewcenko, N. A.; Mitchell, C.; Schürmann, M. *Z. Anorg. Allg. Chem*. **2005**, *631*, 1856.

[23] Engman, L.; Lind, J.; Merényi, G. *J. Phys. Chem*. **1994**, *98*, 3174.

[24] Klapötke, T. M.; Krumm, B.; Scherr, M. *Acta Cryst*. **2007**, *E63*, 4189.

[25] Klapötke, T. M.; Krumm, B.; Scherr, M. *Phosphorous Sulfur Silicon* **2009**, *184*, 1347.

[26] Srivastava, K.; Shah, P.; Singh, H.; Butcher, R. J. *Organometallics* **2011**, *30*, 534.

[27] (a) Oba, M.; Okada, Y.; Nishiyama, K.; Shimada, S.; Ando, W. *Chem. Commun*. **2008**, 5378.
(b) Oba, M.; Okada, Y.; Endo, M.; Tanaka, K.; Nishiyama, K.; Shimada, S.; Ando, W. *Inorg. Chem*. **2010**, *49*, 10680.

[28] Engman, L.; Cava, M. P*. J. Chem. Soc. Chem. Commun*. **1982**, 164.

[29] (a) Knobler C, McCullough JD, *Inorg. Chem.* **1972**, *11*, 3026
(b) Zukerman-Schpector J, Haiduc I, *Phosphorus Sulfur Silicon*, **2001**, *171*,73;
(b) Haiduc I, Zukerman-Schpector J, *Phosphorus Sulfur Silicon*, **2001**, *71*,171.

[30] a) J. Zukerman-Schpector, I. Haiduc, *Phosphorous, Sulfur, Silicon* **2001**,*171*, 73.
b) J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, M. Schürmann, *Aust. J. Chem.,* **2005***,* 58, 119;

[31] (a) P. H. Laur, S. M. Saberi-Niaki, M. Scheiter, C. Hu, U. Englert, Y. Wang, J. Fleischhauer *Phosphorous, Sulfur, Silicon* **2005**, *180*, 1035.
(b) E. Faoro, G. Manzoni den Oliveira, E. Schulz Lang, C. B. Pereira *J. Organomet. Chem*. **2010**, *695*, 1480.

[32] a) L. Reichel, E. Kirschbaum, *Justus Liebigs Ann. Chem.*, **1936**, *523*, 211;
b) P. Thavornyutikarn, W. R. McWhinnie, *J. Organomet. Chem.,* **1973***, 50,* 135;
c) J. Bergman, J. Siden, K. Maartmann-Moe, *Tetrahedron,* **1984***, 40,* 1607;
d) D. H. R. Barton, J.-P. Finet, M. Thomas, *Tetrahedron,* **1986***, 42*, 2319.

[33] (a) W.-W. du Mont, H.U. Meyer, S. Kubinoik, S. Pohl, W. Saak, *Chem. Ber.* **1992**, *125*, 761;
(b) A.C. Hillier, S.-Y. Liu, A. Sella, M.R.J. Elsegood, *Angew. Chem., Int. Ed.,* **1999** *38,* 2745;
(c) D. Witthaut, K. Kirschbaum, O. Conrad, D.M. Giolando, *Organometallics,* **2000** *19,* 5238;
(d) H.T.M. Fischer, D. Naumann, W. Tyrra, *Chem. Eur. J.*, **2006** *12,* 2515;
(e) J. Beckmann, S. Heitz, M. Hesse, *Inorg. Chem*. **2007**,*46*, 3275;
(f) J. Beckmann, M. Hesse, H. Poleschner, K. Seppelt*, Angew. Chem., Int. Ed.,* **2007** *46,* 8277.

[34] (a) E.S. Lang, R.M. Fernandes Jr., E.T. Silveira, U. Abram, E.M. Vázquez-López*, Z. Anorg. Chem.,* **1999**, *625*, 1401;
(b) P.D. Bolye, W.I. Cross, S.M. Godfrey, C.A. McAuliffe, R.G. Pritchard, S. Sarward, J.M. Sheffield, *Angew. Chem., Int. Ed.,* **2000***, 39,* 1796;
(c) E.S. Lang, G. Manzoni de Oliveira, R.M. Fernandes Jr., E.M. Vázquez-López, *Inorg. Chem. Comm.,* **2003***, 6,* 869;
(d) D.B. Werz, R. Gleiter, F. Rominger, *J. Organomet. Chem.,* **2004***, 689,* 627;
(e) G.N. Ledesma, E.S. Lang, U. Abram, *J. Organomet. Chem.,* **2004***, 689,* 2092;

(f) E.S. Lang, G. Manzoni de Oliveira, G.N. Ledesma, *Z. Anorg. Allg. Chem.,* **2005**, *631,* 1524;
(g) J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, M. Schürmann, *Aust. J. Chem.,* **2005**, 58, 119;
(h) J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, *Acta Crystallogr., Sect.,* **2005**, *E61,* 986;
(i) G. Manzoni de Oliveira, E. Faoro, E.S. Lang, G.A. Casagrande, *Z. Anorg. Allg. Chem.,* **2006**, *632*, 659;
(j) E.S. Lang, G. Manzoni de Oliveira, G.A. Casagrande, *J. Organomet. Chem.,* **2006**, *691,* 59;
(k) E. Faoro, G. Manzoni de Oliveira, E.S. Lang, *J. Organomet. Chem*.,**2006**, *691*, 5867;
(l) E.S. Lang, G.A. Casagrande, G. Manzoni de Oliveira, G.N. Ledesma, S.S. Lemos, E.E. Castellano, U. Abram, *Eur. J. Inorg. Chem.*, **2006**, 958.

[35] (a) J. Zuckerman-Schpector, I. Haiduc, *Phosphorus, Sulfur, Silicon,* **2001**, *171*, 73;
(b) W.-W. du Mont, C.G. Hrib, *Handbook of Chalcogen Chemistry*, **2007**, 833;
(c) M.C. Aragoni, M. Arca, F.A. Devillanova, A. Garau, F. Isaia, V. Lippolis, A. Mancini, *Bioinorg. Chem. Appl*. **2007**, 1.

[36] P. D. Boyle, S. M. Godfrey *Coord. Chem. Rev*. **2001**, *223*, 265.

[37] (a) M. R. Detty, A. E. Friedman, M. McMillian, *Organometallics* **1994**, *13*, 3338.
(b) M. R. Detty, A. J. Williams, J. M. Hewitt, M. McMillan *Organometallics* **1995**, *14*, 5258.

[38] A. V. Zakharov, I. D. Sadekov, V. I. Minkin, *Russ. Chem.*,**2006**, *75,* 207.

[39] (a)Schmidbaur, H. *Angew. Chem*. **1965**, *77*, 206;
(b)Schindler, F.; Schmidbaur H. *Angew. Chem*. **1967**, *79*, 697;
(c)Voronkov, M.G.; Lavrentyev, V. I. *Top. Curr. Chem*. **1982**, *102*, 199;
(d)Murugavel, R.;Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Re*V. **1996**, *96*, 2205.

[40] (a) Roesky, H. W.; Mazzah, A.; Hesse, D.; Noltemeyer, M. *Chem. Ber*. **1991**, *124*, 519;
(b) Driess, M.; Von Hänisch, C.; Merz, K. *Z. Anorg. Allg. Chem*. **1999**, *625*, 493;

[41] (a) Holmes, R. R. *Acc. Chem. Res.,* **1989**, 22, 190;
(b) Jain, V. K. *Coord. Chem. Rev.,* **1994**, *135-136*, 809;
(c) Beckmann, J.; Jurkschat, K. *Coord. Chem. Rev.* **2001**, *215*, 267.
(d) Chandrasekhar, V.; Nagendran, S.; Baskar, V. *Coord. Chem. Rev.,* **2002**, *235*, 1.
(e) Chandrasekhar, V.; Gopal, K.; Thilagar, P. *Acc. Chem. Res.,* **2007**, *40*, 420.

[42] a) A.-A. G. Shaikh, S. Sivaram, *Chem. Rev.* **1996**, *96*, 951;
b) M. Shi, Y.-M. Shen, *Curr. Org. Chem.* **2003**, *7*, 737;

c) G. W. Coates, D. R. Moore, *Angew. Chem. Int. Ed.* **2004**, *43*, 6618;
d) I. Omae, *Catal. Today* **2006**, *115*, 33;
e) T. Sakakura, J.-C. Choi, H. Yasuda, *Chem. Rev.* **2007**, *107*, 2365;
f) D. J. Darensbourg, *Chem. Rev.* **2007**, *107*, 2388;
g) T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312.

[43] a) D. H. Gibson, *Chem. Rev.* **1996**, *96*, 2063;
b) X. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27.

[44] J. Kümmerlen, A. Sebald, H. Reuter, *J. Organomet. Chem.* **1992**, *427*, 309.

[45] Z. Padělkova, H. Vaňkatova, I. Cisařova, M. S. Nechaev, T. A. Zevaco, O. Walter, A. Růžička, *Organometallics* **2009**, *28*, 2629

[46] a) H. Reuter, Ph. D. Thesis, University of Bonn, Germany **1986**;
b) D. Ballivet-Tkatchenko, R. Burgat, S. Chambrey, L. Plasseraud, P. Richard, *J. Organomet. Chem.* **2006**, *691*, 1498.

[47] G.-L. Zheng, J.-F. Ma, J. Yang, Y.-Y. Li, X.-R. Hao, *Chem. Eur. J.* **2004**, *10*, 3761.

[48] Beckmann, J.; Dakternieks, D.; Duthie, A.; Lewcenko, N. A.; Mitchell, C. *Angew. Chem., Int. Ed.,* **2004**, *43*, 6683.

[49] Beckmann, J.; Dakternieks, D.; Duthie, A.; Mitchell, C. *Dalton Trans.,* **2005**, 1563.

[50] K. Lederer, *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 1345.

[51] J. Beckmann, P. Finke, M. Hesse, B. Wettig, *Angew. Chem.* **2008**,*120*, 10130; *Angew. Chem. Int. Ed.* **2008***, 47*, 9982.

[52] M. B. Smith, J. March: March's Advanced Organic Chemistry, 5th edition, Wiley-Interscience, **2001**.

[53] T.W. Campbell, H. Walker, G. H. Coppinger, *Chem. Rev.* **1952***, 50,* 279.

[54] a) H.W. Doughty, *Am. Chem. J.* **1909***, 41,* 326;
b) R. Lesser, R. Weiss*, Ber. Dtsch. Chem. Ges.* **1913***, 46,* 2640.

[55] (a) T. W. Campbell, H. Walker, G. H. Coppinger, *Chem. Rev*. **1952**, *50*, 279.
(b) H. W. Doughty, *Am. Chem. J.* **1909**, *41*, 326;
(c) R. Lesser, R. Weiss, *Chem. Ber*. **1913**, *46*, 2640;
(d) M. Schmidt, J. Wilhelm, *Chem. Ber*. **1964**, *97*, 872;
(e) K. Dostál, Z. Žak, M. Ĉernik, *Chem. Ber*. **1971**, *104*, 2044;
(f) A. Haas, K.-U. Weiler, *Chem. Ber*. **1985**, *118*, 943;
(g) A. Haas, K. Schinkel, *Chem. Ber*. **1990**, *123*, 685;
(h) R. Boese, A. Haas, S. Herkt, M. Pryka, *Chem. Ber*. **1995**, *128*, 423.

[56] a) M. Schmidt, J. Wilhelm, *Chem. Ber.* **1964***, 97,* 872;
b) K. Dostál, Z. Žak, M. Ĉernik, *Chem. Ber.* **1971***, 104*, 2044.

[57] a) A. Haas, K.-U. Weiler, *Chem. Ber.* **1985***, 118,* 943;
b) A. Haas, K. Schinkel, *Chem. Ber.* **1990***, 123,* 685;
c) R. Boese, A. Haas, S. Herkt, M. Pryka, *Chem. Ber.* **1995***, 128,* 423.

[58] P. C. Srivastava, S. Bajpai, C. Ram, R. Kumar, R. J. Butcher, *J. Organomet. Chem.* **2007**, *692*, 2482.

[59] N.W. Alcock, W. D. Harrison, C. Howes, *J. Chem. Soc., Dalton Trans.***1984**, 1709.

[60] A. A. Maksimenko, I. D. Sadekov, V. I. Minkin, *Zh. Obshch. Khim.* **1986**, *56*, 2605.

[61] $Ph_2SO \cdot HOR$ and $Ph_2SeO \cdot HOR$ complexes:
(a) R. H. Figueroa, E. Roig, H. H. Szmant, *Spectrochim. Acta* **1966**, *22*, 1107;
(b) W. Saffioti, G. Nazario, I. M. L. Gullo, *Eclectica Quimica* **1976**, *1*, 59.

$Ph_3PO \cdot HOR$ and $Ph_3AsO \cdot HOR$ complexes:
(c) C. Lariucci, R. H. A. Santos, J. R. Lechat, *Acta Crystallogr.* **1986**,*C42*, 731.
(d) K. Tomita, W. Saffioti, C. R. Leite, *Eclectica Quimica* **1979**, *4*, 55.
(e) B. Birknes, *Acta Chem. Scan.* **1976**, *B30*, 450;
(f) H. Schindlbauer, H. Stenzenberger, *Monatsh. Chem.* **1986**, *99*, 2468;
(g) T. Gramstad, *Acta Chem. Scan.* **1992**, *46*, 1087;
(h) R. M. Fuquen, J. R. Lechat, *Acta Crystallogr.* **1992**, *C48*, 1690.

[62] (a) J. Beckmann, D. Dakternieks, A. Duthie, N.A. Lewcenko, C. Mitchell, *Angew. Chem., Int. Ed.,* ***2004****, 43,* 6683;
(b) J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, Dalton Trans.,**2005**, 1563;
(c) J. Beckmann, J. Bolsinger, *Organometallics,* **2007***, 26,* 3601;
(d) J. Beckmann, J. Bolsinger, A. Duthie, *Austr. J. Chem*, **2008**, *61*, 172

[63] M.J. Taylor, L.-J. Baker, C.E.F. Rickard, P.W.J. Surman, *J. Organomet. Chem.,* **1995***, C14,* 498.

[64] Beckmann, J.; Bolsinger, J.; Duthie, A. *Aust. J. Chem.* **2008**, *61*, 172.

[65] M.J. Almond, M.G.B. Drew, D.A. Rice, G. Salisbury, M.J. Taylor, *J. Organomet. Chem.,* **1996***, 522,* 265.

[66] H. Pritzkow, *Inorg. Chem.,* **1979***, 18,* 311.

[67] (a) P.C. Srivastava, S. Bajpai, S. Bajpai, C. Ram, R. Kumar, J.P. Jasinski, R.J. Butcher, *J. Organomet. Chem.,* **2004***, 689,* 194;
(b) P.C. Srivastava, S. Bajpai, R. Lath, R.J. Butcher, *J. Organomet. Chem.,* **2000***, 608*, 96.

[68] (a) R.H. Vernon, *J. Chem. Soc.,* **1920***, 117,* 889;
(b) R.H. Vernon, *J. Chem. Soc.,* **1921***, 119,* 687.

[69] G.T. Morgan, F.H. Burstall, *J. Chem. Soc.*, **1931**, 180.

[70] Panda, A.; Mugesh, G.; Singh, H. B.; Butcher, R. J. *Organometallics* **1999**, *18*, 1986.

[71] T. Steiner, *Angew. Chem.* **2002**, *114*, 50, *Angew. Chem., Int. Ed.,* **2002***, 41,* 48.

[72] This work was presented in part at the Tenth International Conference on the Chemistry of Selenium and Tellurium (ICCST-10), Lodz, Poland, 22-27 June **2007**, Book of Abstracts and Program, Poster P4.

[73] J. Beckmann, J. Bolsinger, A. Duthie, P. Finke, *Organometallics* **2011;** submitted.

[74] N. W. Alcock, W. D. Harrison, *J. Chem. Soc., Dalton Trans.* **1982**, 251.

[75] N. W. Alcock, W. D. Harrison, *J. Chem. Soc., Dalton Trans.* **1984**, 869.

[76] (a) G. D. Christofferson, J. D. McCullough, *Acta Crystallogr*. **1959**, *11*, 249.
(b) For redetermination of the X-ray structure of Ph_2TeBr_2 see: J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, *Acta Crystallogr*. **2004**, *E60*, 2511.

[77] J. Beckmann, D. Dakternieks, A. Duthie, C. Mitchell, M. Schürmann, *Aust. J. Chem.* **2005**, *58*, 119.

[78] M. Oba, M. Endo, K. Nishiyama, A. Ouchi, W. Ando, *Chem. Commun*. **2004**, 1672.

[79] D. H. R. Barton, S. V. Ley, C. A. Meerholz, *J. Chem. Soc. Chem. Commun*. **1979**, 755.

[80] S. V. Ley, C. A. Meerholz, D. H. Barton, *Tetrahedron Suppl*. **1981**, *37*, 213.

[81] (a) J. K. Shen, Y. Gao, Q. Shi, A. L. Rheingold, F. Basolo, *Inorg. Chem.* **1991**, *30*, 1868.
(b) M. Xue, Y. C. Gao, J. K. Shen, Q. Z. Shi, F. Basolo, *Inorg. Chim. Acta* **1993**, *207*, 207.
(c) X. Liu, Y. C. Gao, Z. X. Su, Y. Y. Wang, Q. Z. Shi, *Trans. Met. Chem.* **1999**, *24*, 666.
(d) L. C. Song, Q. S. Li, Q. M. Hu, Y. B. Dong, *J. Organomet. Chem.* **2001**, *619*, 194.

[82] (a) L. Engman, M. P. Cava, *Tetrahedron Lett*. **1981**, *22*, 5251.
(b) M. Akiba, M. V. Lakshmikantham, K-Y. Jen, M. P. Cava, *J. Org. Chem*. **1984**, *49*, 4819.

[83] M. Oba, Y. Okada, K. Nishiyama, W. Ando, *Org. Lett*. **2009**, *11*, 1879.

[84] Y. Okada, M. Oba, A. Arai, K. Tanaka, K. Nishiyama, W. Ando, *Inorg. Chem.* **2010**, *49*, 383.

[85] (a) M. R. Detty, S. L. Gibson, Scott, *Organometallics* **1992**, *11*, 2147;
(b) L. Engman, S. Stern, M. Pelcman, C. M. Andersson, *J. Org. Chem*. **1994**, *59*, 1973;
(c) M. R. Detty, A. E. Friedman, A. R. Oseroff, *J. Org. Chem*. **1994**, *59*, 8245;
(d) K .Vessman, M. Ekstroem, M. Berglund, C.-M. Andersson, L. Engman, *J. Org. Chem*. **1995**, *60*, 4461;
(e) K. A. Leonard, F. Zhou, M. R. Detty, *Organometallics* **1996**, *15*, 4285;
(f) M. R. Detty, F. Zhou, A. E. Friedman, *J. Amer. Chem. Soc.* **1996**, *118*, 313;
(g) T. Kanda, L. Engman, I. A. Cotgreave, G. Powis, *J. Org. Chem*. **1999**, *64*, 8161;
(h) D. E. Higgs, M. I. Nelen, M. R. Detty, *Org. Lett*. **2001**, *3*, 349;
(i) C. Francavilla, M .D. Drake, F. V. Bright, M. R. Detty, *J. Amer. Chem. Soc*. **2001**, *123*, 57;
(j) Y. You, K. Ahsan, M. R. Detty, *J. Amer. Chem. Soc*. **2003**, *125*, 4918;
(k) K. Ahsan, M. D. Drake, D. E. Higgs, A. L. Wojciechowski, B. N. Tse, M. A. Bateman, Y. You, Youngjae; M. R. Detty, *Organometallics* **2003**, *22*, 2883.

[86] (a) V. Y. Kukushkin, A. J. L. Pombeiro *Inorg. Chim. Acta* **2005**, *358*, 1;
(b) N. A. Bokach, V. Y. Kukushkin *Russ. Chem. Rev*. **2005**, *72*, 153 and ref. cited therein.

[87] S. Geetha, Maochun Ye, J. G. Verkade, *Inorg. Chem.*, **1995**, *34,* 6158.

[88] Weidenbruch, M.; Pesel, H.; Van Hieu, D. *Z. Naturforsch.* **1980**, *35b*, 31.

[89] Gosink, H.-J.; Roesky, H. W.; Noltemeyer, M.; Schmidt, H.-G.; Freire-Erdbrügger, C.; Sheldrick, G. M. *Chem. Ber*. **1993**, *126*, 279.

[90] (a) Schmidbaur, H. *Angew. Chem*. **1965**, *77*, 206.
(b) Schindler, F.; Schmidbaur H. *Angew. Chem*. **1967**, *79*, 697.
(c) Voronkov, M.G.; Lavrentyev, V. I. *Top. Curr. Chem*. **1982**, *102*, 199.
(d) Murugavel, R.; Voigt, A.; Walawalkar, M. G.; Roesky, H. W. *Chem. Re*V. **1996**, *96*, 2205.

[91] J. Beckmann; J. Bolsinger, *Organometallics* **2007**, *26*. 3601.

[92] Foucher, D. A.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1996**, *108*, 1712.

[93] Dakternieks, D.; Jurkschat, K.; Tiekink, E. R. T. Main Group Met. Chem. **1994**, 17, 471.

[94] Beckmann, J.; Bolsinger, J. Duthie, A. *Chem. Eur. J*. **2011**, *17*, 930.

[95] Jens Beckmann, Jens Bolsinger and Johan Spandl; *J. Organomet. Chem.,* **2008**, *693*, 957.

[96] R. H. Vernon, *J. Chem. Soc.* **1920**, *117*, 86.

[97] M. M. Mangion, M. R. Smith, E. A. Meyers, *J. Heterocycl. Chem.* **1973**, *10*, 543.

[98] K. Kobayashi, N. Deguchi, E. Horn, N. Furukawa, *Angew. Chem.* **1998**, *110*, *Angew. Chem. Int. Ed.* **1998**, *37*, 984.

[99] H. W. Roesky, R. J. Butcher, S. Bajpai, P. C. Srivastava, *Phosphorus Sulfur Silicon Relat. Elem.* **2000**, *161*, 135.

[100] K. Kobayashi, K. Tanaka, H. Izawa, Y. Arai, N. Furukawa, *Chem. Eur. J.* **2001**, *7*, 4272.

[101] K. Kobayashi, H. Izawa, N. Furukawa, K. Yamaguchi, E. Horn, *Chem. Commun.* **2001**, 1428.

[102] R. Oilunkaniemi, R. S. Laitinen, M. Ahlgren, *Z. Naturforsch.* **2001**, *56b*, 215.

[103] T. M. Klapötke, B. Krumm, P. Mayer, K. Polborn, I. Schwab, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2677.

[104] T. M. Klapötke, B. Krumm, P. Mayer, M. Scherr, *Z. Naturforsch.* **2006**, *61b*, 528.

[105] S.-F. Yin, J. Maruyama, T. Yamashita, S. Shimada, *Angew. Chem.* **2008**, *120*, *Angew. Chem. Int. Ed.* **2008**, *47*, 6590.

[106] H. J. Breunig, L. Konigsmann, E. Lork, M. Nema, N. Philipp, C. Silvestru, A. Soran, R. A. Varga, R. Wagner, *Dalton Trans.* **2008**, 1831.

[107] L. Dostál, R. Jambor, A. Růžiĉka, M. Erben, R. Jirasko, E. Cernoškova, J. Holeĉek, *Organometallics* **2009**, *28*, 2633.

[108] G. Lang, K. W. Klinkhammer, C. Recker, A. Schmidt, *Z. Anorg. Allg. Chem.* **1998**, *624*, 689.

[109] a) G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227;
b) G. B. Deacon, F. Huber, R. J. Phillips, *Inorg. Chim. Acta* **1985**, *104*, 41.

[110] Sadekov, I. D.; Minkin, V. I. *Sulfur Rep*. **1997**, *19*, 285.

[111] Sladky, F.; Bildstein, B.; Rieker, C.; Gieren, A.; Betz, H.; Hübner, T. *J. Chem. Soc., Chem. Commun*. **1985**, 1800.

[112] (a) Hamor, T. A.; Al-Salim, N.; West, A. A.; McWhinnie, W. R. *J. Organomet. Chem.* **1986**, *310*, C5;
(b) Al-Salim, N.;West, A. A.; McWhinnie, W. R.; Hamor, T. A. *J. Chem. Soc., Dalton Trans.* **1988**, 2363.

[113] Klapötke, T. M.; Krumm, B.; Nöth, H.; Gálvez-Ruiz, J. C.; Polborn, K.; Schwab, I.; Suter, M. *Inorg. Chem.* **2005***, 44,* 5254.

[114] Menon, S. C.; Singh, H. B.; Jasinksi, J. M. Jasinski, J. P.; Butcher, R. J. *Organometallics* **1996**, *15*, 1707.

[115] Maslakov, A. G.; Greaves, M. R.; McWhinnie, W. R.; McWhinnie, S. L. W. *J. Organomet. Chem.* **1994***, 468,* 125.

[116] Granger, P.; Chapelle, S.; McWhinnie, W. R.; Al-Rubaie, A. *J. Organomet. Chem.* **1981***, 220*, 149.

[117] Beckmann, J.; Hesse, M.; Poleschner, H.; Seppelt, K. *Angew. Chem., Int. Ed.* **2007***, 46,* 8277

[118] Beckmann, J.; Bolsinger, J.; Duthie, A. *Organometallics* **2009**, *28*, 4610.

[119] J. Beckmann, S. Heitz, M. Hesse, *Inorg. Chem.* **2007***, 46,* 3275.

[120] a) A. J. Canty, G. van Koten, *Acc. Chem. Res.* **1995***, 28,* 406;
b) C. J. Carmalt, A. H. Cowley, *Main Group Chem. News* **1996***, 4,* 4.

[121] K. Srivastava, S. Sharma, H. B. Singh, U. P. Singh, R. J. Butcher, *Chem. Commun.* **2010***, 46,* 1130.

[122] J. Beckmann, J. Bolsinger, P. Finke, M. Hesse*, Angew. Chem.* **2010***, 122,* 8204; *Angew. Chem. Int. Ed.* **2010***, 49,* 8030.

[123] a) L. Ahmed, J. A. Morrison, *J. Am. Chem. Soc.* **1990***, 112,* 7411;
b) M. Minoura, T. Sagami, K. Akiba, C. Modrakowski, A. Sudau, K. Seppelt, S. Wallenhauer, *Angew. Chem.* **1996***, 108,* 2827*; Angew. Chem. Int. Ed. Engl.* **1996***, 35,* 2660;
c) M. Minoura, T. Mukuda, T. Sagami, K. Akiba, *J. Am. Chem. Soc.* ***1999****, 121*, 10852;
d) M. Miyasato, M. Minoura, K. Akiba, *Angew. Chem.* ***2001****, 113, 2746*; *Angew. Chem. Int. Ed.* **2001***, 40*, 2674;
e) M. Minoura, T. Sagami, K. Akiba, *Organometallics* **2001***, 20,* 2437;
f) M. Miyasato, T. Sagami, M. Minoura, Y. Yamamoto, K. Akiba, *Chem. Eur. J.* **2004***, 10*, 2590;
g) T. M. Klapötke, B. Krumm, K. Polborn, I. Schwab, *J. Am. Chem. Soc.* **2004***, 126,* 14166.

[124] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441.

[125] L. Falck, O. Lindqvist, *Acta Crystallogr. Sect. B* **1978***, 34,* 3145.

[126] J. Beckmann, J. Bolsinger *Z. Anorg. Allgem. Chem.* **2011**, 637, 29.

[127] M. Oba, Y. Okada, K. Nishiyama, S. Shimada, W. Ando *Chem. Commun*. **2008**, 5378.

[128] (a) A. Panda, G. Mugesh, H. B. Singh, R. J. Butcher, *Organometallics* **1999**, *18*, 1986.
(b) J. Beckmann, J. Bolsinger, M. Hesse, Organometallics **2009**, *28*, 4225.
(c) J. Beckmann, J. Bolsinger, A. Duthie, *Organometallics* **2009**, *28*, 4610.
(d) J. Beckmann, J. Bolsinger, A. Duthie, P. Finke *Organometallics* **2011**, *30*, *received*.

[129] M. Wieber, E. Kaunzinger, *J. Organomet. Chem.* **1977**, *129*, 339.

[130] H. Citeau, K. Kirschbaum, O. Conrad, d.M. Giolando, *Chem. Commun.,* **2001***,* 2006.

[131] A. P. Mirgorodsky, T. Merle-Méjean, J. C. Champarneaud, P. Thomas, B. Frit, *J. Phys. Chem. Solids* **2000***, 61*, 501.

[132] a) P. Granger, S. Chapelle, M. McWhinnie, A. Al-Rubaie, *J. Organomet. Chem.* **1981**, *220*, 149;
b) M. Sharma, K. K. Bhasin, S. K. Mehta, N. Singh, S. Kumar, *Radiat. Phys. Chem.* **2006**, *75*, 2029;
c) H. Kunkely, A. Vogler, *Inorg. Chim. Acta* **2009**, *362*, 281.

[133] H. Fleischer, D. Schollmeyer*, Inorg. Chem.* **2001***, 40,* 324 .

[134] Fridrichová, A.; Svoboda, T.; Jambor, R.; Padělková, Z.; Růžička A.; Erben, M.; Jirásko, R.; Dostál, L. *Organometallics* **2009**, *28*, 5522.

18 APPENDIX

18.1 SUMMARY

The reactivity and structural diversity of organotellurium compounds comprising inter- and intramolecularly interactions was examined.

Concerning the reactivity of diorganotellurium compounds R_2TeO and R_2TeX_2 (R= aryl, alkyl; X= OH, Cl, I) a number of completely characterized new compounds could be isolated. Only a few mononuclear compounds were observed, however, the formation of dinuclear or higher aggregated compounds comprising secondary intermolecular Te···X (X= O, Cl, I) interactions sæms to be favored, whereby the structural motif $XR_2TeOTeR_2X$ appears to be a common motif.

This structural motif was observed in several synthesized compounds like the telluroxanes $(R'O)R_2TeOTeR_2(OR')$ (R=*p*-$MeOC_6H_4$; *p*-$Me_2NC_6H_4$), $ClR_2TeOTeR_2Cl$ (R= Ph, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$), $IR_2TeOTeR_2I$ (R=*p*-$MeOC_6H_4$) or the alkyltellurium compounds $(Me_2Te)_2OI_2$ and 2 $(Me_2Te)_2O(I)OH \cdot H_2O$. The latter features two polymer strings, whereby the first polymer string is comparable to a $(Me_2TeO)_n$ polymer and the second polymer string comprises $R_2Te(OH)TeR_2(OH)$ units. Further examples are the dialkyltelluroxane carbonates $(Me_2TeOTeMe_2CO_3)_n$ and $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH$. The structures can be described as 1D and 2D coordination polymers, respectively, whereby each structure features repeating $OR_2TeOTeR_2O$ units associated via secondary Te···O contacts.

Thus, the stabilizing effect of secondary interactions with the tellurium atom seems to play a significant role in stabilizing dinuclear or higher aggregated diorganotellurium compounds or in their supramolecular assembly, whereby the motif $XR_2TeOTeR_2X$ seems to be favored in the solid state of diorganotellurium compounds.

However, by using the intramolecularly coordinating 8-dimethylaminonaphthyl ligand, which compensates the charge of the tellurium atom and thus, avoiding condensation reactions to dinuclear or higher aggregated compounds, it was possible to isolate a new series of mononuclear diorganotellurium cations $[R_2TeX]^+$ (X= OH, Cl, Br, I).

The stabilization by the charge compensation of the tellurium atom via the intramolecularly coordinating N donor ligand seems to be more effective than the stabilization of the condensated products via intermolecular secondary interactions and thus leading to exclusively mononuclear compounds.

Further investigations of organotellurium compounds featuring this N donor ligand yielded interesting results. The reaction of the diaryltelluride $(8\text{-}Me_2NC_{10}H_6)_2Te$ with H_2O_2 afforded the diaryltellurium(VI) dioxide $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$, which is only the second example of this compound class, the diaryltellurium(VI) dioxide $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2TeO_2$ was isolated using kinetic stabilization[27]. The reaction is unusual since the oxidation of other diaryltellurides only yields diaryltellurium(IV) oxides or ill-defined product mixtures[23]. The diaryltellurium(IV) oxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$ is – in contrast – sensitive to air oxidation in solution and solid state yielding the diaryltellurium(VI) dioxide. Furthermore, the diaryltellurium(IV) oxide $(8\text{-}Me_2NC_{10}H_6)_2TeO$ reacts with acetonitrile, which proceeds with reversible oxygen transfer providing the diaryltellurium(IV) acetimidate $(8\text{-}Me_2NC_{10}H_8)_2TeNC(O)CH_3$ in the solid state. Such a facile formation of the acetimidate moiety is unprecedented.

The use of the intramolecularly coordinating 8-dimethylaminonaphthyl ligand seems to have – aside from the stabilization of the respective diorganotellurium cations – a significant effect on the reactivity of diorganotellurium oxides. This could be tentatively explained by the intramolecular coordination stabilizing an intermediate state $R_2Te^+\text{-}O^-$ which enhances the reactivity.

Other interesting results were obtained by the examination of the same ligand concerning monorganyltellurium compounds. A series of well-defined telluroxane clusters and polymers – with two dominating structural motifs – could be obtained by the base hydrolysis of the aryltellurium trichloride $8\text{-}Me_2NC_{10}H_6TeCl_3$.

Surprisingly, the structural motif $XR_2TeOTeR_2X$ could be observed for the telluroxane $(8\text{-}Me_2NC_{10}H_6Te)_2OCl_4$ and $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$. Furthermore, the proposed structure of the telluroxane $(8\text{-}Me_2NC_{10}H_6Te)_6O_5Cl_8$ is consistent with the established structures of the synthesized telluroxanes. A comparable structural motif was also observed in the new dinuclear stannatelluroxanes $8\text{-}Me_2NC_{10}H_6TeO_2Sn\text{-}t\text{-}Bu_2Cl$. This compound is rare example of a molecular oxide incorporating two heavy main group elements, which comprises a dimeric structure, comparable to the motif $XR_2TeOTeR_2X$. The primary Te-O bond lengths and the distance of the Te···N interactions are reasonable comparable with the respective bond length observed in the polymer $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$.

The second structural motif for the synthesized telluroxane clusters appears to be a ring structure, which was observed in the clusters $(8\text{-}Me_2NC_{10}H_6Te)_6O_8Cl_2$, $(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ and $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$. The average bond length of the Te···Cl bond of the first two compounds suggest a rather ionic Te···Cl bond and no secondary Te···O interactions could be observed, however the last compound comprises one secondary Te···O interaction. A comparable structure was observed in the tellurasiloxane ring *cyclo*-$[(p\text{-}MeOC_6H_4)_2TeOSi\text{-}t\text{-}Bu_2O]_3$ comprising also no secondary Te···O contacts.

Given the possibility of secondary Te···Cl and Te··O bonds the already observed structural motif $XR_2TeOTeR_2X$ is favored. By successively hydrolyzing the respective trichloride the structural motif changes to a telluroxane ring structure comprising few or no intermolecular secondary Te···O bonds and rather ionic Te···Cl bond, the latter are due to a stabilizing effect of the N donor ligand, which was also observed in the diorganotellurium cations $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = OH, Cl, Br, I).

However, in absence of possible secondary Te···Cl interactions it appears that the energy difference between the polymer structure $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$, featuring the motif $XR_2TeOTeR_2X$ associated via secondary Te···O interactions, and the ring structure $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ seems to be rather small, since the compounds are interconvertible by crystallization from H_2O and THF/hexane, respectively.

In contrast to the previously described kinetically stabilized compounds $[2,6\text{-Mes}_2C_6H_3Te(O)X]_2$ (X= Cl, OH)[51], which seem to stabilize only near completed hydrolysis products, a new series of well-defined telluroxanes, telluroxane clusters and polymers in a low degree of hydrolysis respectively in a high degree of aggregation could be isolated. This is tentatively explained by the higher Lewis acidity of compounds with a low degree of hydrolysis, which leads to a stronger interaction of the N donor system, which is becoming less important during the ongoing process. Thus, polymer and ring structures are favored in which secondary Te···O interactions or covalent Te-O bonds dominate the structural motif.

During the course of this work, it was also possible to isolate the first two completely characterized organotelluronic acids. The first dinuclear *m*-terphenyltelluronic acid $[2,6\text{-Mes}_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$ was synthesized – featuring a kinetic stabilization – via the oxidation of the intermediate $Na_4(2,6\text{-Mes}_2C_6H_3Te)_4(\mu_3\text{-}O)_8$ by dry O_2 in the presence of [18]crown-6, however, a direct oxidation of the respective tellurinic acid failed. Contrary to this, the intramolecularly coordinated diarylditelluronic acid $[(8\text{-Me}_2NC_{10}H_6Te(=O)(OH)_2]_2(\mu\text{-}O)$ was readily synthesized by oxidation of an aqueous solution of the analogues to the respective tellurinic acid using H_2O_2, which is comparable to the easy synthesis of the diaryltellurone $(8\text{-Me}_2NC_{10}H_6)_2TeO_2$. The diarylditelluronic acid possesses no oxidizing power towards alcohols, in contrary, recrystallizing from methanol lead to the selective esterification of two hydroxyl groups yielding the partial methyl ester $[(8\text{-Me}_2NC_{10}H_6Te(=O)(OH)(OMe)]_2(\mu\text{-}O)$.

As the above mentioned results show, the influence of secondary interactions on the structure and reactivity of organotellurium compounds is substantial. It is noteworthy that structures dominated by mainly secondary intermolecular interactions appear to favor the structural motif $XR_2TeOTeR_2X$ in the solid state. Furthermore, the influence of intramolecularly coordinating N donor ligand on the formation of organotellurium cations or organotelluroxane clusters respectively polymers is significant. Particularly the easy formation of the diaryltellurone respectively the diarylditelluronic acid or the formation of the acetimidate are unusual, which could be attributed to a significant influence of the intramolecularly coordinating ligand on the reactivity of the tellurium atom.

18.2 ZUSAMMENFASSUNG

Die Reaktivität und strukturelle Vielfalt von Organotellurverbindungen, die inter- und intramolekulare Wechselwirkungen aufweisen, wurde untersucht.

In Bezug auf die Reaktivität der Diorganotellurverbindungen R_2TeO and R_2TeX_2 (R= aryl, alkyl; X= OH, Cl, I) konnte eine Vielzahl von komplett charakterisierten neuen Verbindungen isoliert werden. Nur eine geringe Anzahl an mononuklearen Verbindungen konnte beobachtet werden, wohingegen die Bildung dinuklearer oder höher aggregierter Verbindungen, welche sekundäre Wechselwirkungen $Te\cdots X$ (X= O, Cl, I) aufweisen, offensichtlich bevorzugt sind, wobei das Strukturmotiv $XR_2TeOTeR_2X$ ein häufiges Motiv zu sein scheint.

Diese Strukturmotiv wurde in verschiedenen synthetisierten Verbindungen beobachtet, wie in den Telluroxanen $(R'O)R_2TeOTeR_2(OR')$ (R=*p*-$MeOC_6H_4$; *p*-$Me_2NC_6H_4$), $ClR_2TeOTeR_2Cl$ (R= Ph, *p*-$MeOC_6H_4$, *p*-$Me_2NC_6H_4$), $IR_2TeOTeR_2I$ (R=*p*-$MeOC_6H_4$) oder den Alkytellurverbindungen $(Me_2Te)_2OI_2$ and 2 $(Me_2Te)_2O(I)OH \cdot H_2O$. Letztere verfügt über zwei Polymerstränge, wobei der erste Polymerstrang vergleichbar zu dem $(Me_2TeO)_n$ Polymer ist und der zweite Polymerstrang $R_2Te(OH)TeR_2(OH)$ Einheiten aufweist. Weitere Beispiele sind die Dialkyltelluroxan-carbonate $(Me_2TeOTeMe_2CO_3)_n$ und $HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH$. Die Strukturen können als 1D bzw. 2D Koordinationspolymere beschrieben werden, wobei jede Struktur eine sich wiederholende $OR_2TeOTeR_2O$ Einheit mit sekundären Wechselwirkungen ausweist.

Der stabilisierende Effekt der sekundären Wechselwirkungen mit dem Telluratom scheint eine signifikante Rolle in der Stabilisierung dinuklearer oder höher aggregierter Diorganotellurverbindungen oder in Ihrer supramolekularen Anordnung zu spielen, wobei das Motiv $XR_2TeOTeR_2X$ in der Festkörperstruktur der Diorganotellurverbindungen bevorzugt erscheint.

Allerdings war es möglich bei Verwendung eines intramolekular koordinierenden 8-Dimethylaminonaphthylliganden, der die Ladung am Telluratom kompensiert und somit Kondensationsreaktionen zu dinuklearen oder höher aggregierter Diorganotellurverbindungen verhindert, eine neue Serie von mononuklearen Diorganotellurverbindungen $[R_2TeX]^+$ (X= OH, Cl, Br, I) zu isolieren.

Die Stabilisierung der Ladung am Telluratom über einen intramolekular koordinierenden N-Donor-Ligand erscheint effektiver als die Stabilisierung der kondensierten Produkte über intermolekulare sekundäre Wechselwirkungen wobei dadurch ausschließlich mononukleare Verbindungen isoliert wurden.

Weitere Untersuchungen von Organotellurverbindungen die den N-Donor-Liganden aufweisen führte zu interessanten Ergebnissen. Die Reaktion des Diaryltellurids $(8\text{-}Me_2NC_{10}H_6)_2Te$ mit H_2O_2 ergab das Diaryltellur(VI)dioxid $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$, welches erst das zweite Beispiel dieser Verbindungsklasse ist, das Diaryltellur(VI) dioxid $(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2TeO_2$ wurde unter Verwendung einer kinetischen Stabilisierung[23] isoliert. Diese Reaktion ist ungewöhnlich, da Oxidationen anderer Diaryltelluride nur zu den Diaryltellur(IV)oxiden oder zu undefinierbaren Produktmischungen[27] führen. Das Diaryltellur(IV)oxid $(8\text{-}Me_2NC_{10}H_6)_2TeO$ ist - im Gegensatz dazu - leicht durch Luft sowohl in Lösung als auch im Festkörper zu dem Diaryltellur(VI)oxid oxidierbar. Weiterhin reagiert das Diaryltellur(IV)oxid $(8\text{-}Me_2NC_{10}H_6)_2TeO$ mit Acetonitril, wobei über eine reversible Sauerstoff-übertragung das Diaryltellur(IV)acetimidat $(8\text{-}Me_2NC_{10}H_8)_2TeNC(O)CH_3$ im Festkörper gebildet wird. Eine derartig leichte Bildung der Acetimidatgruppe im Festkörper ist beispiellos.

Die Verwendung der intramolekular koordinierenden 8-Dimethylaminonaphthyl-liganden scheint – neben dem stabilisierenden Effekt des entsprechenden Diorganotellurkations – einen signifikanten Einfluss auf die Reaktivität von Diorganotelluroxiden zu haben. Dies könnte eventuell durch einen stabilisierten Zwischenzustand $R_2Te^+\text{-}O^-$ mittels der intramolekularen Koordination erklärt werden, welche die Reaktivität erhöht.

Weitere interessante Resultate wurden bei der Untersuchung desselben Liganden in Bezug auf Monorganotellurverbindungen erzielt. Eine Serie definierter Telluroxane, Telluroxancluster und Polymere – die zwei dominierende Strukturmotive aufweisen – konnte durch die basische Hydrolyse des Aryltellurtrichlorids 8-$Me_2NC_{10}H_6TeCl_3$ isoliert werden.

Überraschenderweise konnte das Strukturmotiv $XR_2TeOTeR_2X$ bei den Telluroxanen (8-$Me_2NC_{10}H_6Te)_2OCl_4$ und [(8-$Me_2NC_{10}H_6Te)_2O_3]_n$ beobachtet werden. Weiterhin ist die vorgeschlagene Struktur des Telluroxans (8-$Me_2NC_{10}H_6Te)_6O_5Cl_8$ übereinstimmend mit den erhaltenen Strukturen der synthetisierten Telluroxane. Ein vergleichbares Strukturmotiv wurde auch in dem neuen dinuklearen Stannatelluroxane 8-$Me_2NC_{10}H_6TeO_2Sn$-*t*-Bu_2Cl beobachtet. Diese Verbindung ist ein seltenes Beispiel eines molekularen Oxids welches zwei schwere Hauptgruppenelemente aufweist und eine dimere Struktur besitzt, vergleichbar zu dem Motiv $XR_2TeOTeR_2X$. Die primären Te-O Bindungslängen und die Abstände der Te···N Wechselwirkungen sind relativ gut vergleichbar mit den entsprechenden Bindungslängen des Polymers [(8-$Me_2NC_{10}H_6Te)_2O_3]_n$.

Das zweite Strukturmotiv der synthetisierten Telluroxancluster scheint eine Ringstruktur zu sein, welche in den Cluster (8-$Me_2NC_{10}H_6Te)_6O_8Cl_2$, (8-$Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_2$ und (8-$Me_2NC_{10}H_6Te)_6O_8(OH)_2$ beobachtet wurde. Die durchschnittliche Bildungslänge der Te···Cl Bindungen der ersten beiden Verbindungen deutet auf eine eher ionische Te···Cl Bindung hin und keine sekundären Te···O Wechselwirkungen konnten beobachtet werden, wobei jedoch die letzte Verbindung eine sekundäre Te···O Wechselwirkung aufweist. Eine vergleichbare Struktur wurde in dem 12-gliedrigen Tellursiloxanring *cyclo*-[(*p*-$MeOC_6H_4)_2TeOSi$*t*-$Bu_2O]_3$ beobachte, der ebenfalls keine sekundären Te···O Wechselwirkungen aufweist.

Durch die Möglichkeit sekundäre Te···Cl und Te···OBindungen auszubilden ist das bereits beobachtete Strukturmotiv $XR_2TeOTeR_2X$ bevorzugt. Durch eine stetige Hydrolysierung des entsprechenden Trichlorids wechselt das Strukturmotiv zu Telluroxanringstrukturen mit wenigen oder keinen intermolekularen sekundären Te···O Bindungen und eher ionischen Te···Cl Bindungen, wobei letztere dem stabilisierenden Effekt der N-Donor-Liganden zugeordnet werden, welcher auch bei den Diorganotellurkationen $[(8\text{-}Me_2NC_{10}H_6)_2TeX]^+$ (X = OH, Cl, Br, I) beobachtet wurden.

In Abwesenheit von mögliche sekundären Te···Cl Wechselwirkungen erscheint jedoch die Energiedifferenz zwischen der Polymerstruktur $[(8\text{-}Me_2NC_{10}H_6Te)_2O_3]_n$, die das Strukturmotiv $XR_2TeOTeR_2X$ aufweist, welches durch sekundäre Te···O Wechselwirkungen untereinander verbunden ist, und der Ringstruktur $(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2$ verhältnismäßig klein, da die beiden Verbindungen durch entsprechende Umkristallisierung aus H_2O bzw. THF/Hexan ineinander umwandelbar sind.

Im Gegensatz zu den bereits beschriebenen kinetisch stabilisierten Verbindungen $[2,6\text{-}Mes_2C_6H_3Te(O)X]_2$ (X= Cl, OH)[51], welche offensichtlich nur fast komplett hydrolysierte Produkte stabilisieren, konnte eine neue Serie von definierten Telluroxanen, Telluroxancluster und Polymere mit einem geringen Grad an Hydrolyse bzw. einem hohen Grad an Aggregation isoliert werden. Dies ist eventuell durch die höhere Lewissäurestärke der Verbindungen mit geringem Hydrolysegrad erklärbar, welche zu einer stärkeren Wechselwirkung des N-Donor-Systems führt, die während des vorgehenden Prozesses weniger wichtig wird. Dadurch werden Polymer- und Ringstrukturen bevorzugt in welchen sekundäre Te···O Wechselwirkungen und kovalente Te-O Bindungen das Strukturmotiv dominieren.

Im Laufe dieser Arbeit war es weiterhin möglich die ersten beiden komplett charakterisierten Organotelluronsäuren zu isolieren. Die erste dinukleare *m*-Terphenyltelluronsäure $[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$ – welche eine kinetische Stabilisierung aufweist – wurde durch die Oxidation des Zwischenproduktes $Na_4(2,6\text{-}Mes_2C_6H_3Te)_4(\mu_3\text{-}O)_8$ mittels trockenem O_2 in Gegenwart von [18]crown-6 synthetisiert, allerdings ist eine direkte Oxidation dieser Tellurinsäure fehlgeschlagen. Im Gegensatz dazu gelang Synthese der intramolekular koordinierten Diaryltelluronsäure $[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)_2]_2(\mu\text{-}O)$ auf einfach Weise durch die Oxidation eine wässrigen Lösung der Analogen der entsprechenden Tellurinsäure mittels H_2O_2, die vergleichbar ist mit der einfachen Synthese des Diaryltellurids $(8\text{-}Me_2NC_{10}H_6)_2TeO_2$. Die Diaryltelluronsäure besitzt keine Oxidationskraft gegenüber

Alkoholen, im Gegenteil, Umkristallisation aus Methanol führte zu der selektiven Veresterung zweier Hydroxylgruppen und der partielle Ester $[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)(OMe)]_2(\mu\text{-}O)$ konnte isoliert werden.

Wie die oben genannten Ergebnisse zeigen, ist der Einfluss der sekundären Wechselwirkungen auf die Struktur und Reaktivität von Organotellurverbindungen substantiell. Es ist bemerkenswert, dass die Strukturen die durch hauptsächlich sekundäre Wechselwirkungen dominiert werden offensichtlich das Strukturmotiv $XR_2TeOTeR_2X$ im Festkörper bevorzugen. Weiterhin ist der Einfluss des intramolekular koordinierenden Liganden auf die Bildung von Organotellurkationen oder Organotelluroxanen bzw., Polymeren signifikant. Insbesondere weist die einfache Bildung der Organotellurone bzw. Organotelluronsäuren und die einfache Bildung des Acetimidats auf einen signifikanten Einfluss des intramolekular koordinierenden Liganden auf die Reaktivität des Telluratoms hin.

18.3 INDEX

Index of the compounds

Nr.	Name	Abrevation	X-Ray
1	Diphenyltellurium hydroxy phenolates	$Ph_2Te(OH)OPh$	-
2	Dianisoltellurium hydroxy phenolates	$(p\text{-}MeOC_6H_4)_2Te(OH)OPh$	Manuscript I
3	Diannilintellurium hydroxy phenolates	$(p\text{-}Me_2NC_6H_4)_2Te(OH)OPh$	-
4	Diphenyltellurium bis(phenolates)	$Ph_2Te(OPh)_2$	Manuscript I
5	Dianisoltellurium bis(phenolates)	$(p\text{-}MeOC_6H_4)_2Te(OPh)_2$	-
6	Diannilintellurium bis(phenolates)	$(p\text{-}Me_2NC_6H_4)_2Te(OPh)_2$	Manuscript I
7	Tetraanisolditelluroxane bis(*o*-nitrophenolates)	$R_2(R'O)TeOTe(OR')R_2$ $R = p\text{-}MeOC_6H_4;$ $R' = o\text{-}NO_2C_6H_4)$	Manuscript I
8	Tetraannilinditelluroxane bis(*o*-nitrophenolates)	$R_2(R'O)TeOTe(OR')R_2$ $R = p\text{-}Me_2NC_6H_4;$ $R' = o\text{-}NO_2C_6H_4)$	-
9	Hexaphenyltritelluroxane bis(*o*-nitrophenolate)	$(RO)Ph_2TeOTePh_2OTePh_2(OR)$ $R = o\text{-}NO_2C_6H_4$	Manuscript I
10	Tetraphenylditelluroxanes	$Ph_2(PhO)TeOTe(OPh)Ph_2$	-
11	Tetranisolditelluroxanes	$R_2(PhO)TeOTe(OPh)R_2$ $R = p\text{-}MeOC_6H_4$	-
12	Tetrannilinditelluroxanes	$R_2(PhO)TeOTe(OPh)R_2$ $R = p\text{-}Me_2NC_6H_4$	-
13	Diphenyltellurium chloro phenolates	$Ph_2Te(Cl)OPh$	-
14	Dianisoltellurium chloro phenolates	$(p\text{-}MeOC_6H_4)_2Te(Cl)OPh$	-
15	Diannilintellurium chloro phenolates	$(p\text{-}Me_2NC_6H_4)_2Te(Cl)OPh$	-
16	Tetraphenyltelluroxane dichlorides	$Ph_2(Cl)TeOTe(Cl)Ph_2$	-
17	Tetraanisoltelluroxane dichlorides	$R_2(Cl)TeOTe(Cl)R_2$ $R = p\text{-}MeOC_6H_4$	Manuscript I
18	Tetraannilintelluroxane dichlorides	$R_2(Cl)TeOTe(Cl)R_2$ $R = p\text{-}Me_2NC_6H_4$	Manuscript I
19	Tetraanisolditelluroxane diiodide	$[(p\text{-}MeOC_6H_4)_2Te]_2OI_2$	Manuscript II
20	Dianisoltelluriumdiiodide iodine adduct	$(p\text{-}MeOC_6H_4)_2TeI_2 \cdot ½ I_2$	Manuscript II

21	Tetramethylditelluroxane	$(Me_2Te)_2OI_2$	Manuscript II
22	Dimethyltellurium-Polymer	$2\ (Me_2Te)_2O(I)OH \cdot H_2O$	Manuscript II
23	Tritelluroxane diiodide	$(C_4H_8Te)_3O_2I_2$	Manuscript II
24	Bis(8-dimethylaminonaphthyl) telluride	$(8\text{-}Me_2NC_{10}H_6)_2Te$	Manuscript III
25	Bis(8-dimethylaminonaphthyl) tellurium(VI) dioxide hydrate perhydrate	$(8\text{-}Me_2NC_{10}H_6)_2TeO_2 \cdot H_2O \cdot H_2O_2$	Manuscript III
26	Bis(8-dimethylaminonaphthyl) tellurium(VI) dioxide dihydrate	$(8\text{-}Me_2NC_{10}H_6)_2TeO_2 \cdot 2\ H_2O$	Manuscript III
27	Bis(8-dimethylaminonaphthyl) tellurium(IV) oxide	$(8\text{-}Me_2NC_{10}H_6)_2TeO$	-
28	Bis(8-dimethylaminonaphthyl) hydroxytelluronium triflate	$[(8\text{-}Me_2NC_{10}H_6)_2TeOH](O_3SCF_3)$	Manuscript III
29	Bis(8-dimethylaminonaphthyl) chlorotelluronium chloride	$[(8\text{-}Me_2NC_{10}H_6)_2TeCl]^+ \cdot Cl^- \cdot H_2O \cdot 1/2THF$	Manuscript IV
30	Bis(8-dimethylaminonaphthyl) bromotelluronium bromide	$[(8\text{-}Me_2NC_{10}H_6)_2TeBr]^+ \cdot Br^-$	Manuscript IV
31	Bis(8-dimethylaminonaphthyl) bromotelluronium bromide hydrate	$[(8\text{-}Me_2NC_{10}H_6)_2TeBr]^+ \cdot Br^- \cdot H_2O$	-
32	Bis(8-dimethylaminonaphthyl) iodotelluronium iodide	$[(8\text{-}Me_2NC_{10}H_6)_2TeI]^+ \cdot I^-$	
33	Bis(8-dimethylaminonaphthyl) iodotelluronium triiodide	$[(8\text{-}Me_2NC_{10}H_6)_2TeI]^+ \cdot I_3^-$	Manuscript IV
34	Bis(8-dimethylaminonaphthyl) iodotelluronium triiodide iodine	$[(8\text{-}Me_2NC_{10}H_6)_2TeI]^+ \cdot I_3^- \cdot I_2$	Manuscript IV
35	Bis(8-dimethylaminonaphthyl) chlorotelluronium hexafluorophosphate	$[(8\text{-}Me_2NC_{10}H_6)_2TeCl]^+\ PF_6^-$	Manuscript IV
36	Bis(8-dimethylaminonaphthyl) bromotelluronium bromide hexafluorophosphate	$[(8\text{-}Me_2NC_{10}H_6)_2TeBr]^+_2\ Br^-\ PF_6^-$	Manuscript IV
37	Bis(5,7-dichloro-8-dimethyl-aminonaphthyl) tellurium dichloride	$(5,7\text{-}Cl_2\text{-}8\text{-}Me_2NC_{10}H_6)_2TeCl_2$	Manuscript IV
38	Bis(5-bromo-8-dimethyl-aminonaphthyl)tellurium dibromide	$(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_6)_2TeBr_2$	Manuscript IV
39	Bis(5-bromo-8-dimethyl-aminonaphthyl)bromo telluronium tribromide	$[(5\text{-}Br\text{-}8\text{-}Me_2NC_{10}H_6)_2TeBr]^+\ Br_3^-$	Manuscript IV
40	Bis(8-dimethylaminonaphthyl) hydroxytelluronium chloride	$[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+\ Cl^-$	Manuscript IV
41	Bis(8-dimethylaminonaphthyl) hydroxytelluronium bromide	$[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+ \cdot Br^- \cdot H_2O \cdot THF$	Manuscript IV
42	Bis(8-dimethylaminonaphthyl) hydroxytelluronium iodide	$[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+\ I^-$	Manuscript IV

43	Bis(8-dimethylaminonaphthyl) hydroxytelluronium triiodide	$[(8\text{-}Me_2NC_{10}H_6)_2TeOH]^+ I_3^- \cdot H_2O$	Manuscript IV
44	Bis(8-dimethylaminonaphthyl) tellurium(IV) acetimidate	$(8\text{-}Me_2NC_{10}H_8)_2TeNC(O)CH_3$	Chapter 7
45	12-membered tellurasiloxane ring	*cyclo*-$[(p\text{-}MeOC_6H_4)_2TeOSi\text{-}t\text{-}Bu_2O]_3$	Manuscript V
46	Dinuclear stannatelluroxanes	$8\text{-}Me_2NC_{10}H_6TeO_2Sn\text{-}t\text{-}Bu_2Cl$	Manuscript VI
47	Dimethyltelluroxane carbonate	$(Me_2TeOTeMe_2CO_3)_n$	Manuscript VII
48	Dialkyltelluroxane carbonate cluster	$HO(CH_2)_4TeOTe(CH_2)_4CO_3Te(CH_2)_4OH \cdot 2H_2O$	Manuscript VII
49	Bis(8-dimethylaminonaphthyl) tritelluride	$(8\text{-}Me_2NC_{10}H_8)_2Te_3$	Manuscript VIII
50	(8-dimethylaminonaphthyl) tellurenyl chloride	$8\text{-}Me_2NC_{10}H_6TeCl$	Manuscript IX
51	(8-dimethylaminonaphthyl) tellurenyl trichloride	$8\text{-}Me_2NC_{10}H_6TeCl_3$,	Manuscript IX
52	Tetra(8-dimethylaminon-aphthyl) telluroxane	$(8\text{-}Me_2NC_{10}H_6Te)_2OCl_4$	Manuscript IX
53	Hexa(8-dimethylamino-naphthyl)telluroxane oktachloride	$(8\text{-}Me_2NC_{10}H_6Te)_6O_5Cl_8$	-
54	Hexa(8-dimethylaminon-aphthyl)telluroxane dichloride	$(8\text{-}Me_2NC_{10}H_6Te)_6O_8Cl_2 \cdot 8CHCl_3$	Manuscript IX
55	12-membered telluroxane ring	$(8\text{-}Me_2NC_{10}H_6Te)_6O_8(OH)_2 \cdot 4THF \cdot 6H_2O$	Manuscript IX
56	Bis(8-dimethylaminonaphthyl) telluroxane polymer	$[(8\text{-}Me_2NC_{10}H_6Te)_2O_3 \cdot 7/3\ H_2O]_n$,	Manuscript IX
57	Hexa(8-dimethylamino-naphthyl) telluroxane Cluster	$(8\text{-}Me_2NC_{10}H_6Te)_6Te_2O_{12}Cl_{12}$	Manuscript IX
58	Bis(5,5'-binaphthyl) telluroxane	$(8\text{-}MeNC_{10}H_5TeO)_4$	Manuscript X
59	Sodium *m*-terphenyltellurinate	$Na_4(2,6\text{-}Mes_2C_6H_3Te)_4(\mu_3\text{-}O)_8$	Manuscript XI
60	m-terphenyltelluronic acid	$[2,6\text{-}Mes_2C_6H_3Te(\mu\text{-}O)(OH)_3]_2$	Manuscript XI
61	Di(8-dimethylaminonaphthyl) ditelluronic acid	$[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)_2]_2(\mu\text{-}O)$	Manuscript XII
62	Di(8-dimethylaminonaphthyl) ditelluronyl dimethanolate	$[(8\text{-}Me_2NC_{10}H_6Te(=O)(OH)(OMe)]_2(\mu\text{-}O)$	Manuscript XII

List of abrevations

t-Bu	*tert*-butylgroup
THF	tetrahydrofurane
DMSO	dimethylsulfoxide
EA	elemental analysis
i-Pr	*iso*-propylgroup
M	molar mass
Me	methylgroup
Mes	mesitylgroup (2,4,6- trimethylphenyl)
n-BuLi	*n*-buthyllithium
Ph	phenylgroup
R	organic ligand
r.t.	room temperature
mp.	melting point
μ_2	ligand with two binding partners
μ_3	ligand with three binding partners
MS	mass spectroscopy
MAS	magic angel spinning
NMR	nuclear magnetic resonance
d, m, s, t	dublett, multiplett, singulett, triplett
ppm	parts per million
IR	infrared
UV	ultraviolet
ESI	electrospray ionisation

List of Schemes/Figures/Tables

18.4 CURRICULUM VITAE

The CURRICULUM VITAE is omitted in the online version due to privacy reasons.

18.5 ACKNOWLEDGEMENT

I want to express my gratitude to Prof. Dr. Jens Beckmann for mentoring and providing such a creative and open environment to work in, for all the ideas and support

Furthermore, I want to thank Prof. Dr. Konrad Seppelt for being the reviewer of this thesis.

In particular I would like to thank all the staff members of the service department of the FU Berlin for their engagement and their support, for providing analytical data, technical support and a good work environment.

Especially I want to thank all the former and actual members of our work group for providing the best environment to work in and for accepting, since more or less everybody had to share a lab with me at some point, that my research needed sometimes “some” space in the lab. In particular I wanted to thank Marian Grassmann, Malte und Maxi Hesse, Alexandra Schütrumpf, Usman Ahmad, Nelly Rivas and Pamela Finke for the great time inside and outside the lab and for their help.

Furthermore, I want to express my gratitude to Prof Dr. Danis Dakternieks for providing the opportunity to continue my research down under at the Deakin University. Especially I want to thank Andrew Duthie and his family for the warm welcome in Australia and for all the support. You made our stay so much easier and worthwhile. I would like to take this opportunity to greet all my mates in Australia, especially my roommate Brad and my fellow scientist Adam. It was the best time. „The Germans“ are missing Australia and especially our mates. We hope we can come back someday.

Thanks “Chef” for this opportunity and for all your support - chemistry related and beyond.

18.6 SELBSTSTÄNDIGKEITSERKLÄRUNG

Hiermit erkläre ich, dass ich diese Arbeit selbst verfasst habe sowie keine anderen als die angegebenen Quellen und Hilfsmittel in Anspruch genommen habe. Ich versichere, dass diese Arbeit in dieser oder anderer Form keiner anderen Prüfungsbehörde vorgelegt wurde.

Jens Bolsinger

Berlin, Oktober 2011