Aluminum and Gallium Pentafluoroorthotellurates: Novel Superacids and Weakly Coordinating Anions

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Second Referee: Prof. Dr. Ingo Krossing
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Abstract

A one-pot synthesis of the Lewis acid Al(OTeF$_5$)$_3$ and the Brønsted acid [ArH][Al(OTeF$_5$)$_4$] (Ar = 1,2-difluorobenzene) is described and their properties in terms of acidity strength are analyzed. As a result, both compounds meet the requirements for the classification as superacids. Further work focuses on the utilization of [ArH][Al(OTeF$_5$)$_4$] and the corresponding weakly coordinating anion (WCA) [Al(OTeF$_5$)$_4$]$^-$. Due to the non-oxidizing behavior of [ArH][Al(OTeF$_5$)$_4$] the protonation of white phosphorus succeeded. For the first time, the structure of the [P$_4$H]$^+$ cation in solution is experimentally clarified, confirming the predicted insertion of the proton into an edge of the P$_4$ tetrahedron. Furthermore, the protonation of other arenes than 1,2-difluorobenzene with higher basicity than that is demonstrated and structurally proved by low-temperature single-crystal x-ray diffraction. The arenium ions are best described as cationic 1,4-cyclohexadienyl derivatives. The stabilization of these reactive cations is achieved by the simultaneous formation of the chemically robust and weakly coordinating anion [Al(OTeF$_5$)$_4$]$^-$. For a more universal utilization of this WCA useful starting materials such as the alkali metal, silver, trityl or nitrosonium salts are prepared. Inspired by the interesting results of this aluminum-based pentafluoroorthotellurate chemistry the gallium analogs should also be synthesized. By a modified route salts of the anion [Ga(OTeF$_5$)$_4$]$^-$ are finally obtained. Attempts to obtain the gallium analogs of the above mentioned Lewis and Brønsted acids lead to the oxygen-bridged species Ga$_2$(Et)$_3$(OTeF$_5$)$_3$. This reactive dimer was used to form salts of the heteroleptic anion [Ga(Et)(OTeF$_5$)$_3$]$^-$. 
Zusammenfassung

<table>
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<tr>
<th>Abbreviation</th>
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<tr>
<td>a</td>
<td>activity</td>
</tr>
<tr>
<td>ACF</td>
<td>aluminum chlorofluoride</td>
</tr>
<tr>
<td>Alk</td>
<td>alkyl</td>
</tr>
<tr>
<td>Ar</td>
<td>aryl</td>
</tr>
<tr>
<td>BArF</td>
<td>tetrakis(3,5-bis(trifluoromethyl)phenyl)borate</td>
</tr>
<tr>
<td>BP86</td>
<td>generalized gradient approximation functional</td>
</tr>
<tr>
<td></td>
<td>exchange functional with Becke 1988 exchange</td>
</tr>
<tr>
<td></td>
<td>functional and the Perdew 1986 correlation</td>
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<tr>
<td></td>
<td>functional</td>
</tr>
<tr>
<td>c</td>
<td>concentration</td>
</tr>
<tr>
<td>Cp</td>
<td>cyclopentadienyl</td>
</tr>
<tr>
<td>Cp*</td>
<td>pentamethylcyclopentadienyl</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>ΔH</td>
<td>enthalpy</td>
</tr>
<tr>
<td>ΔrH°</td>
<td>standard enthalpy of reaction</td>
</tr>
<tr>
<td>e.g.</td>
<td>for example (Latin: exempli gratia)</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>et al.</td>
<td>and others (Latin: et alii)</td>
</tr>
<tr>
<td>exp.</td>
<td>experimental</td>
</tr>
<tr>
<td>FIA</td>
<td>fluoride ion affinity</td>
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<tr>
<td>FLP</td>
<td>frustrated Lewis pair</td>
</tr>
<tr>
<td>g</td>
<td>gaseous</td>
</tr>
<tr>
<td>G3</td>
<td>Gaussian-3 composite method</td>
</tr>
<tr>
<td>H0</td>
<td>Hammett acidity function</td>
</tr>
<tr>
<td>HS-AlF₃</td>
<td>high-surface aluminum fluoride</td>
</tr>
<tr>
<td>i-Pr</td>
<td>iso-propyl</td>
</tr>
</tbody>
</table>
$K_a$ equilibrium constant of the dissociation of a Brønsted acid
Me methyl
MeCN acetonitrile
Mes mesitylene
MP2 2nd order Møller-Plesset perturbation theory
n-Bu n-butyl
NMR nuclear magnetic resonance
PDZ double-ζ plus polarization basis set
Ph phenyl
pH negative decadic logarithm of the proton activity
p$K$ negative decadic logarithm of the equilibrium constant $K$
RI resolution of identity
solv solvent
SV(P) split valence basis set with polarization functions on heavy atoms (not hydrogen)
tol toluene
UV ultraviolet
vis visible
WCA weakly coordinating anion
XRD x-ray diffraction
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1 Introduction

In 1923 Johannes N. Brønsted and Thomas M. Lowry proposed independently from each other an acid-base concept, whereby acids are defined as proton donators and bases as proton acceptors.\textsuperscript{[1,2]} This proton-transfer-concept is not restricted to aqueous solutions, and thus, allows for greater universality compared to the previously reported Arrhenius definition. The proton-transfer from an acid HA to a base B generates the conjugate base $A^-$ and the conjugate acid $BH^+$ (Equation 1.1). In solution the reactants are in equilibrium with each other.

\begin{equation}
AH_{\text{acid}} + B_{\text{base}} \rightleftharpoons A^-_{\text{conjugate base}} + BH^+_{\text{conjugate acid}} \tag{1.1}
\end{equation}

In the same year Gilbert N. Lewis described a proton independent acid-base concept based on electron-pair acceptors (Lewis acid) and electron-pair donators (Lewis base) which form an acid-base complex (Equation 1.2).\textsuperscript{[3]} This definition includes reactions such as adduct formation, solvation, and coordination compounds, thus reactions that do not include ion transfer or ion formation. This concept is an extension of the Brønsted-Lowry theory.

\begin{equation}
A_{\text{acid}} + B_{\text{base}} \rightleftharpoons A-B_{\text{acid-base complex}} \tag{1.2}
\end{equation}

There are numerous types of Brønsted acids, such as hydrogen halides, organic and inorganic oxoacids or solid acids and these are applied in industrial chemistry, petrochemistry, electrochemistry, catalysis, and modern stereo- and regioselective synthetic chemistry.\textsuperscript{[4–8]} The broad usage is due to the unique properties of the proton. It is the only univalent cation with an empty $1s$ orbital, and thus, without valence electrons. Therefore, it is not prone to electronic repulsion. On the other side, the high charge accumulation on the small proton size leads to its strong electron affinity and polarization effect. As a result, protons in the condensed phase are always found associated with molecules, solvents
or ions. The free species exists only in the gas phase.\textsuperscript{[9]} The proton itself can also be understood as a Lewis acid, but conventional examples for this class of acids are neutral electron-deficient molecules, e.g. group 13 trihalides EX\textsubscript{3} (with E = B, Al, Ga, and X = F, Cl, Br, I), halogen compounds with unsaturated coordination (PF\textsubscript{5}, AsF\textsubscript{5} or SbF\textsubscript{5}) and non-metal oxides (SO\textsubscript{2}, SO\textsubscript{3}).\textsuperscript{[10]} The substitution of halogen atoms by partly or fully fluorinated aryl substituents increases the steric demand which made especially boron-based compounds widely used components in FLP (frustrated Lewis pair) chemistry.\textsuperscript{[11]} Lewis acids are of significant importance in industrial processes, being applied in olefine polymerization as Ziegler-Natta catalysts,\textsuperscript{[12]} and also in other polymerization, aldol or oxidation reactions\textsuperscript{[13,14]}

### 1.1 Lewis Superacids

The strength of a Lewis acid can be defined by its thermodynamic tendency to form a Lewis acid-base pair. Ranking the strength of Lewis acids is required for a precise distinction between conventional and superacidic Lewis acids. For this purpose different approaches have been reported. In all methods a reference Lewis base is used. The corresponding Lewis acid-base complex containing the chosen acid is spectroscopically analyzed and compared to the uncomplexed reference. Lappert used ethyl acetate as Lewis base and observed a blue shift of the carbonyl stretching frequency upon complex formation in the infrared spectra.\textsuperscript{[15]} In a comparable manner Lewis acid-base complexes with acetonitrile have been prepared and discussed regarding the resulting blue shift of the stretching mode of the C≡N bond.\textsuperscript{[16,17]} In both procedures the magnitude of the blue shift should correlate to the Lewis acidity of the parent acid. Gutmann and Beckett introduced an NMR spectroscopic method based on the chemical shift difference $\Delta\delta$ in the $^{31}$P NMR spectrum of triethylphosphine oxide before and after complexation with a certain Lewis acid,\textsuperscript{[18,19]} while Childs \textit{et al.} chose crotonaldehyde as reference and investigated the $\Delta\delta$ of the H3 proton in the $^{1}$H NMR spectrum.\textsuperscript{[20]} An increased $\Delta\delta$ value is considered as an increased Lewis acidity in both methods. The result of such an estimation of the Lewis acid strength is always dependent on the selected reference, and doubts about the comparability of these experimental scales and their dependence on the softness or
hardness of the acids and bases were noticed.[21]

Bartlett et al. introduced the concept of fluoride ion affinity (FIA). It is based on the ability of a Lewis acid to form a Lewis acid-base complex with a fluoride ion and the energy that is released upon this complex formation (Equation 1.3).[22] A high FIA value of a certain compound corresponds to a high Lewis acidity.

\[
A(g) + F^-(g) \rightarrow AF^-(g) \quad \text{FIA} = -\Delta H \quad (1.3)
\]

Because experimentally estimated FIA values showed discrepancies between different measuring techniques,[23] Christe et al. proposed a quantum-chemical approach that avoids the calculation of a naked fluoride ion by using the experimentally determined FIA value of carbonylfluoride (Equation 1.4) as a reference reaction.[24,25] Then, only the Lewis acid A, the complex AF\(^-\), as well as \([\text{CF}_3\text{O}]^-\) and COF\(_2\) needs to be calculated quantum-chemically (Equation 1.5).

\[
\text{COF}_2 + F^- \xrightarrow{\text{experimental}} [\text{CF}_3\text{O}]^- \quad \text{FIA}_{\text{exp.}} = 209 \text{kJ mol}^{-1} \quad (1.4)
\]

\[
A(g) + [\text{CF}_3\text{O}]^-_{(g)} \xrightarrow{\text{MP2/PDZ}} AF^-(g) + \text{COF}_2(g) \quad (1.5)
\]

In another approach the reaction energy of the isodesmic reaction shown in Equation 1.6 is quantum-chemically calculated using the G3 method[26] and then used as an anchor point.[27] The overall reaction (Equation 1.7) giving rise to the desired FIA value can then be performed on a comparably low DFT level ((RI)BP86/SV(P)).

\[
\text{Me}_3\text{SiF}_{(g)} \xrightarrow{\text{G3}} [\text{Me}_3\text{Si}]^+_{(g)} + F^-_{(g)} \quad \Delta_r H_{(G3)}^o = 958 \text{kJ mol}^{-1} \quad (1.6)
\]

\[
A(g) + \text{Me}_3\text{SiF}_{(g)} \xrightarrow{(RI)BP86/SV(P)} AF^-_{(g)} + [\text{Me}_3\text{Si}]^+_{(g)} \quad (1.7)
\]

This procedure can even be extended to chloride, hydride or methyl ion affinities using \(\text{Me}_3\text{SiY}\) and the corresponding ions \([\text{Me}_3\text{Si}]^+/Y^-\) with \(Y = \text{Cl}, \text{H}, \text{and Me}\) to evaluate the behavior of a Lewis acid towards softer bases than the fluoride ion. By this method the FIA value of 493 kJ mol\(^{-1}\) was received for molecular SbF\(_5\). Krossing et al. defined **Lewis superacids** as molecular Lewis acids which are stronger than monomeric SbF\(_5\) in the gas phase.[25] Using this definition and the previously described quantum-chemical approach[27] the aluminum-based Lewis acids AlCl\(_3\), AlBr\(_3\), AlI\(_3\), Al(C\(_6\text{F}_{5}\))\(_3\), Al(OC(CF\(_3\))\(_3\))\(_3\), the
boron-based Lewis acids $B(\text{CN})_3$, $B(\text{CF}_3)_3$, $F_4C_6(1,2-(B(C_6F_5)_2)_2)$, $\text{SiMe}_2\text{CH}_2\text{CB}_{11}\text{Cl}_{11}$, and the pentafluoroorthotellurates $B(\text{OTeF}_5)_3$, $\text{As}(\text{OTeF}_5)_5$, $\text{Sb}(\text{OTeF}_5)_5$ are Lewis superacids. More recent examples, like $B(C_6F_4\text{CF}_3)_3$, $\text{Al}(\text{N}(C_6F_5)_2)_3$, $B(\text{OC}_5\text{F}_4\text{N})_3$, $\text{Al}(\text{OC}_5\text{F}_4\text{N})_3$, $\text{Al}(\text{OC}(C_6\text{F}_5)_3)_3$, and $\text{Si}(\text{O}_2\text{C}_6\text{Cl}_4)_2$ underline the high interest in new Lewis superacids. Some of them have already been applied in C–H or C–F bond activation reactions. Furthermore, there are widely used solid-state Lewis acids like aluminum chlorofluoride (ACF with $\text{AlCl}_x\text{F}_{3-x}$ and $x = 0.05–0.3$) or high-surface aluminum fluoride (HS-AlF$_3$) that reach the acidity of SbF$_5$.}

### 1.2 Brønsted Superacids

In the condensed phase Brønsted acids may dissociate to some extent into solvated protons and solvated counterions (Equation 1.8). Historically the solvent is water, but also other solvents or the Brønsted acid itself can be used. The strength of a Brønsted acid is conventionally ranked by the pH scale (Equation 1.9), whereby the pH value is considered as negative decadic logarithm of the proton activity $a_{\text{H}^+}$. The pH scale is commonly used in diluted aqueous solution. In order to estimate the acidity of acids in different solvents and concentrated aqueous solution the $pK_a$ value based on the acidity constant $K_a$ was established (Equation 1.10). It denotes the ability of a certain Brønsted acid to dissociate in a medium and is listed for different solvents. To better describe very strong Brønsted acids, the Hammett acidity function $H_0$ (Equation 1.11 and 1.12) is used based on the protonation of a weakly basic indicator B forming $\text{BH}^+$ (e.g. para-nitroaniline, $pK_{\text{BH}^+} = 1.4$) and the equilibrium constant $K_{\text{BH}^+}$ of this reaction. The indicator changes its color upon protonation and the concentration $c_{\text{BH}^+}$ and $c_B$ are measured by UV-vis spectroscopy. Using the Hammett acidity function Gillespie et al. specified Brønsted acids that possess an acidity higher than that of 100% sulfuric acid ($H_0 \leq -12$) as Brønsted superacids.
Brønsted Superacids

\[
\text{AH}_{\text{(solv)}} + K_a^{-} \rightleftharpoons A^{-}_{\text{(solv)}} + H^+_{\text{(solv)}}
\]  
(1.8)

\[
\text{pH} = -\lg a_{H^+}
\]  
(1.9)

\[
pK_a = -\lg K_a
\]  
(1.10)

\[
B_{\text{(solv)}} + H^+_{\text{(solv)}} \rightleftharpoons K_{BH^+}BH^+_{\text{(solv)}}
\]  
(1.11)

\[
H_0 = pK_{BH^+} - \lg \frac{c_{BH^+}}{c_B}
\]  
(1.12)

However, the pH and pKₐ values are solvent-dependent. On the other hand, the Hammett scale is limited to liquid Brønsted acids, but solid Brønsted superacids such as H[HCB₁₁F₁₁], H[HCB₁₁Cl₁₁], H[CB₁₁H₅X₆], and H[HCB₁₁Me₅X₆] with X = Cl, Br have been reported.⁴⁵–⁴⁸ To estimate the strength of these compounds Reed et al. recommended to compare the ¹³C NMR chemical shift difference Δδ of the Cᵦ and Cᵦ carbon atom of mesityl oxide prior and upon protonation.⁴⁷ An increasing Δδ value should correlate with an enhanced Brønsted acidity. To describe the Brønsted acidity in a more general manner efforts have been made to develop a system-independent acidity scale. Two prominent examples are the gas phase acidity⁴⁹ or the “Unified pH Scale for All Phases”.⁵⁰

By means of the Hammett acidity function George A. Olah classifies Brønsted superacids in primary, binary, ternary, and solid types, while the first and second class are usually applied in synthetic chemistry.⁹ Primary Brønsted superacids are perchloric acid (HClO₄), halosulfuric acids (HSO₃Cl, HSO₃F), and triflic acid (CF₃SO₃H). The acidity can be even increased by the mixture of two Brønsted acids such as HF–HSO₃F, HF–CF₃SO₃F, and HB(HSO₄)₄ or by the preparation of conjugate Brønsted-Lewis superacids. The most prominent example of this type of binary Brønsted superacids is the HF–SbF₅ system which is considered as the strongest liquid superacid.⁹ Other examples of those superacids are easily accessible too (magic acid HSO₃F–SbF₅, oleum H₂SO₄–SO₃, HF–PF₅, HF–AsF₅, HBr–AlBr₃ or HCl–AlCl₃).⁹

Fundamental questions can be answered with the help of Brønsted superacids. Olah received the Nobel Prize in 1994 for his contribution to carbocation chemistry.⁵¹,⁵² When Olah started his research in 1960s carbocations were generally considered to be unstable and short-lived. The usage of Brønsted (and Lewis) superacids in low-nucleophilic solvent like SO₂ClF at low temperatures allowed him to study highly reactive alkyl car-
bocations by NMR spectroscopy.\cite{53} Olah also provided a classification of carbocations in two distinct types, trivalent ("classical") carbenium ions containing an \(sp^2\)-hybridized electron-deficient carbon center and penta(or higher)-coordinated ("nonclassical") car-
bonium ions which contain fivefold (or higher) coordinated carbon atoms necessitating 
three-center (or multicenter) two-electron bonds.\cite{9} The simplest representative of a car-
benium ion is the methenium ion [CH\(_3\)]\(^+\), whereas the methonium ion [CH\(_3\)]\(^+\) is the simplest example of a carbonium ion. More recently Malischewski \textit{et al.} showed that superacidic chemistry can still contribute fundamentally to research by protonation of ferrocene yielding [Cp\(_2\)FeH][PF\(_6\)],\cite{54} the synthesis of the decamethylferrocene dication ([Cp\(_2\)Fe][SbF\(_6\)]),\cite{55} and the preparation of the hexamethylbenzene dication ([C\(_6\)(CH\(_3\))\(_6\)][SbF\(_6\)]) which is in agreement with the Wade’s rules of pentagonal-
pyramidal geometry.\cite{56} In order to stabilize and isolate these reactive cations weakly 
coordinating anions (WCAs) such as [PF\(_6\)]\(^-\), [SbF\(_6\)]\(^-\), and [Sb\(_2\)F\(_{11}\)]\(^-\) are necessary. A 
major drawback of these binary Brønsted superacids are oxidation reactions which lead to 
cation and anion decomposition.\cite{57} As a consequence, scientists focused on the preparation 
of non-oxidizing Brønsted superacids with highly stable counterions.

\section*{1.3 Weakly Coordinating Anions}

Weakly coordinating anions have been exploited to synthesize and isolate reactive cationic 
species of interest, in which those cations are labile towards coordination, highly elec-
trophilic, strong oxidants or they show fundamental structural or bonding features.\cite{58} There 
are several examples where WCAs contribute in catalysis or as components in electrolytes and ionic liquids.\cite{59,60} End of the 20th century WCAs encompassed [BF\(_4\)]\(^-\), 
[ClO\(_4\)]\(^-\), [AlX\(_4\)]\(^-\), [EF\(_6\)]\(^-\), and [CF\(_3\)SO\(_3\)]\(^-\) (with X = Cl, Br, I, and E = P, As, Sb), but 
later on single-crystal x-ray diffraction studies disclosed more and more their obvious 
ability to coordinate a cation.\cite{61–67} The search for cationic species without a strong 
fluence of the counterion led to an improved anion design. An ideal modern WCA should 
combine the following features.\cite{68}
Weakly Coordinating Anions

- Ideally, WCAs possess a monovalent negative charge, although there are di- and trivalent anions also described.
- The negative charge should be completely dispersed over the entire molecule.
- A large size of the anion is desired.
- The polarizability of its surface should be low.
- Nucleophilic and basic sites of the WCA should be shielded.
- The WCA is built of chemically robust moieties.

These properties allow solubility in low-polar solvents, stability against reactive cations, and minimized Coulomb interactions and therefore prevent ion pairing and the decomposition of the anion and cation. To fulfill these requirements modern weakly coordinating anions commonly consist of partially or fully fluorinated entities at the periphery.

The choice to utilize a certain WCA depends on the nature of the cation. Whenever structural or bonding properties of a cationic species are investigated, as in the case of the 2-norbonyl cation \(\text{[C}_7\text{H}_{11}]^+\)\[^{[69]}\] or the homopolyatomic phosphorus cation \(\text{[P}_{9}]^+\)\[^{[70]}\], a bulky anion with an evenly delocalized charge is required to suppress cation-anion interactions. The same is true for weakly bound complex cations, such as silver acetylene\[^{[71]}\] and ethene\[^{[72]}\] complexes. In the case of strongly oxidizing cations, like \(\text{[XeF]}^+\), the demand for weak coordination is not as necessary as the anion’s stability against oxidation.\[^{[73]}\] For highly electrophilic cations, e.g. silylium cations, a hindered access to existent nucleophilic or basic sites and the overall chemical robustness of the anion is most important.\[^{[74]}\]

At the present time there is no modern WCA available which complies the full set of requirements and withstand all types of reactive cations. All of them combine certain advantages and drawbacks, hence four commonly used WCA classes are introduced and discussed in the following sections.

1.3.1 Fluorinated Alkyl- and Arylborate Anions

The tetrakis(pentafluorophenyl)borate anion \(\text{[B(\text{C}_6\text{F}_5)}_4]^-\) (Figure 1.1, left) was already reported by Massey \textit{et al.} in 1964.\[^{[75]}\] Substitution of the fluoride in \textit{para} position by trialkylsilyl groups\[^{[76,77]}\] improved the poor thermal stability, solubility in aromatic solvents, and crystallizability. However, these latter derivatives were found to be slightly more
strongly coordinating. Twenty years later the chemically more stable and well soluble tetrakis(3,5-bis(trifluoromethyl)phenyl)borate anion (Figure 1.1, middle), better known as BArF anion, was first synthesized. Its cheap and easy synthesis results in widespread utility for applications such as polymerization and homogeneous catalysis. The CF$_3$ group has also been replaced by larger fluoroalkyl groups such as CF(CF$_3$)$_2$, C$_4$F$_9$, C(CF$_3$)$_2$OCH$_3$, C(CF$_3$)$_2$OCH$_2$CF$_3$, and C$_6$F$_{13}$. Still the arylborate anions tent to coordinate via fluorine atoms or the π system of the arene. Furthermore, they are not compatible with strong oxidants and prone to degradation by fluoride abstraction and aryl transfer. The comparably small [B(CF$_3$)$_4$]$^-$ anion (Figure 1.1, right) possesses a high chemical stability. It is one of few anions known to successfully stabilize the pentanitrogen cation but is not stable against concentrated sulfuric acid.

![Figure 1.1. Structural formula of selected fluorinated alkyl- and arylborate anions; [B(C$_6$F$_5$)$_4$]$^-$ (left), [B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$]$^-$ (middle), and [B(CF$_3$)$_4$]$^-$ (right).](image)

1.3.2 Carborane Anions

Another class of boron-based weakly coordinating anions comprises the carborane anions. The most common representative of this group is the vertex carba-closo-carborane anion [HCB$_{11}$H$_{11}$]$^-$ which is structurally related to the dodecaborane dianion [B$_{12}$H$_{12}$]$^{2-}$. The B–H bonds are strongly bound and already weakly coordinating. Nevertheless, the halogenated derivatives [HCB$_{11}$H$_5$X$_6$]$^-$ and [HCB$_{11}$X$_{11}$]$^-$ (X = Cl, Br or I) are more resistant against oxidants and delocalize the negative charge more effectively (Figure 1.2, left and middle). To improve the solubility of this type of WCAs methyl groups have been introduced at the hydrogen positions, leading to [HCB$_{11}$Me$_5$X$_6$]$^-$ (X = Cl, Br, I; Figure 1.2, right). With the halogenated carborane anions the successful
Weakly Coordinating Anions

preparation of silylium ions $[\text{Si}(i-\text{Pr})_3]^+$ and $[\text{Si}(\text{Mes})_3]^+$, carbocations, the fullerene ions $[\text{C}_{60}]^+$ and $[\text{HC}_{60}]^+$ and protonated arenes have been reported. In 2006 the acidity of carborane Brønsted acids were even enhanced and the so called “Strongest Brønsted Acid” $\text{H}[\text{HCB}_{11}\text{Cl}_{11}]$ was presented by Reed et al. While the chlorine and bromine substituted carborane anions show a stronger coordination ability, it was possible to prepare the perfluorinated anions $[\text{HCB}_{11}\text{F}_{11}]^-$ and $[\text{HCB}_{11}(\text{CF}_3)_n\text{F}_{11-n}]^-$ with $n = 5, 6, 10, 11$. The class of carborane anions stands out among the other weakly coordinating anions due to their robustness and their versatile application in fundamental research. The poor availability - only in milligram scale - is their disadvantage.

![Figure 1.2. Structural formula of selected carborane anions; $[\text{HCB}_{11}\text{H}_3\text{Cl}_6]^-$ (left), $[\text{HCB}_{11}\text{Cl}_{11}]^-$ (middle), and $[\text{HCB}_{11}\text{Me}_5\text{Cl}_6]^-$ (right). Chlorine atoms are colored for clarity.]

1.3.3 Alkoxyaluminate Anions

Weakly coordinating anions based on aluminum are mainly represented by the group of alkoxyaluminates. The first representative, the $[\text{Al}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4]^-$ anion (Figure 1.3, left), is known since 1996. Until now, many derivatives (Figure 1.3, middle and right) have been reported, e.g. $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$, $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$, $[\text{Al}(\text{OC}(\text{Me})(\text{CF}_3)_2)_4]^-$, and $[\text{Al}(\text{Oi-Pr})_4]^-$.

The tetrakis(perfluoro-tert-butoxy)aluminate anion $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ was found to be the most stable compound out of this class. The easy, cheap and fast preparation and the very weak coordination strength leads to its utilization in fundamental and applied chemistry. A whole range of different reactive cations has been synthesized, such as Brønsted acids, electrophiles, weakly bound complexes, weakly bound complexes, carbonyl complexes or oxidizing cations. Moreover, it has been shown that alkoxyaluminate anions score very high ionicities in ionic liquids and are applied as component in electrolytes of lithium-sulfur batteries or homogeneous catalysis.
However, in attempts to synthesize extremely electrophilic silylium cations ([SiR$_3$]$^+$, R = Me, Et, i-Pr), even the most robust anion of its class degrade via fluoride abstraction.$^{[128]}$

![Structural formula of selected fluorinated alkoxyaluminate anions](image)

**Figure 1.3.** Structural formula of selected fluorinated alkoxyaluminate anions; [Al(OC(Ph)(CF$_3$)$_2$)$_4$]$^-$ (left), [Al(OCH(CF$_3$)$_2$)$_4$]$^-$ (middle), and [Al(OC(CF$_3$)$_3$)$_4$]$^-$ (right).

### 1.3.4 Pentafluoroorthotellurate Anions

Formal substitution of the fluorido ligand in [BF$_4$]$^-$ and [MF$_6$]$^-$ (with M = As, Nb, Sb, Ta, and Bi) by the OTeF$_5$ ligand gives rise to the class of pentafluoroorthotellurate anions. The boron- and antimony-based derivatives (Figure 1.4) are the most commonly used anions of them and they were already reported in 1981 and 1994, respectively.$^{[129,130]}$

Especially the sixfold coordinated anions combine chemical robustness with bulky shape and a good charge delocalization. Still, pentafluoroorthotellurate anions have not been as frequently used as the alkyl- and arylborate and alkoxyaluminate anions. The main reason for that are comparably expensive starting materials (Te(OH)$_6$ and HSO$_3$F) and the need for strict exclusion of moisture due to the degradation of HOTeF$_5$ into toxic decomposition products (e.g. HF). A more detailed insight to the OTeF$_5$ group properties and its chemistry is provided in the following section.
1.3.5 Conclusion

In summary, the design of weakly coordinating anions changed over the last fifty years. In the last decades many reviewing articles were published emphasizing the fast developments in this field,[68,78,92,131–133] but the “Myth of the Non-Coordinating Anion”[134] is still present and has been overcome only linguistically by using superlatives.[135,136] The requirement for WCAs is nowadays more focused on chemical resistance rather than to low coordination ability and charge dispersion. The space-filling model of weakly coordinating anions provides a first impression of the anion size as well as the shielding of nucleophilic and basic sites (Figure 1.5, upper trace). The basic oxygen atoms in [Al(OC(CF$_3$)$_3$)$_4$]$^-$ and [Sb(OTeF$_5$)$_6$]$^-$ (Figure 1.5 e and f) are better protected than the aromatic ring systems of the tetrakis(3,5-bis(trifluoromethyl)phenyl)borate anion (Figure 1.5 c). The charge delocalization of those anions is often visualized by the electrostatic potential energy map plotted on a given isosurface of the electron density (isodensity surface, Figure 1.5, lower trace). A high accumulation of negative charge at the surface, for example in [SbF$_6$]$^-$ (red colored in Figure 1.5 a) or on basic sites, for example in [Al(OC(CF$_3$)$_3$)$_4$]$^-$ (orange colored in Figure 1.5 e), are visible. The examples of arylborate, carborane, alkoxyaluminate, and pentafluoroorthotellurate anions given in Figure 1.5 clearly demonstrate their well dispersed negative charge (yellow/green).
1.4 Pentafluoroorthotellurates

In 1964 Engelbrecht and Sladky accidentally prepared pentafluoroorthotelluric acid HOTeF$_5$ from barium tellurate BaTeO$_4$ and fluorosulfonic acid HSO$_3$F which paved the way for the further chemistry of pentafluoroorthotellurates.$^{137}$ They described the formed acid as colorless and volatile solid which melts at 40 $^\circ$C and solidifies from the melt in a glass-like manner. Attempts to dissolve HOTeF$_5$ in water showed its fast hydrolysis to telluric acid Te(OH)$_6$ and hydrofluoric acid HF. Only one year later the ammonium, pyridinium, and first alkali salts of the [OTeF$_5$]$^-$ anion were obtained by the reaction of HOTeF$_5$ with ammonia, pyridine, and alkali chlorides (Equations 1.13-1.15), respectively.$^{138}$

\[
\begin{align*}
\text{HOTeF}_5 + \text{MCl} & \rightarrow \text{MOTeF}_5 + \text{HCl}, \text{with M = K, Cs} \\
\text{HOTeF}_5 + \text{NH}_3 & \rightarrow [\text{NH}_4][\text{OTeF}_5] \\
\text{HOTeF}_5 + \text{C}_5\text{H}_5\text{N} & \rightarrow [\text{C}_5\text{H}_6\text{N}][\text{OTeF}_5]
\end{align*}
\]

The synthesis of B(OTeF$_5$)$_3$,$^{139}$ AgOTeF$_5$,$^{140,141}$ and Xe(OTeF$_5$)$_2$,$^{142-144}$ in the early 1970s extended the synthetic scope of OTeF$_5$ derivatives. Together with HOTeF$_5$ itself...
these three compounds became widely used starting materials to introduce the $\text{OTeF}_5$ ligand to main group (Table 1.4) and transition metal compounds.\cite{145} The Lewis superacid $\text{B(OTeF}_5)_3$ acts as a $\text{OTeF}_5$ group transfer reagent for element fluorides ($\text{E(OTeF}_5)_n$, Equation 1.16). While the driving force of this reaction is the release of gaseous BF$_3$, it enables the synthesis of $\text{Sb(OTeF}_5)_3$, $\text{Xe(OTeF}_5)_4$, $\text{As(OTeF}_5)_5$, $\text{Xe(OTeF}_5)_6$, and $\text{U(OTeF}_5)_6$.\cite{146, 147, 148, 149} $\text{AgOTeF}_5$ is used as a reactant for element chlorides ($\text{ECl}_n$) resulting in the formation of insoluble $\text{AgCl}$ (Equation 1.17). By this route $\text{Si(OTeF}_5)_4$ or $\text{Me}_3\text{GeOTeF}_5$ have been prepared.\cite{150} While these approaches are simple metathesis reactions, an oxidative addition of an $\text{OTeF}_5^-$ radical is achieved using $\text{Xe(OTeF}_5)_2$ (Equation 1.18) leading to compounds in a high oxidation state such as $\text{I}^V(\text{OTeF}_5)_5$ or $\text{Te}^{VI}(\text{OTeF}_5)_6$.\cite{151, 152}

\begin{align*}
  n \text{B(OTeF}_5)_3 + 3 \text{E(OTeF}_5)_n & \rightarrow 3 \text{E(OTeF}_5)_n + n \text{BF}_3 \uparrow \\
  n \text{AgOTeF}_5 + \text{ECl}_n & \rightarrow \text{E(OTeF}_5)_n + n \text{AgCl} \downarrow \\
  \text{Xe(OTeF}_5)_2 + \text{EX}_n & \rightarrow \text{EX}_n(\text{OTeF}_5)_2 + \text{Xe} \uparrow
\end{align*}

with $\text{E} =$ element and $X = \text{F or OTeF}_5$

In contrast to the previously synthesized Xe$^{II}$ compounds $\text{Xe(OOSO}_2\text{F})_2$ and $\text{Xe(OClO}_3)_2$, the pentafluoroorthotellurate derivative $\text{Xe(OTeF}_5)_2$ shows a surprisingly high thermal stability with a decomposition temperature of 150 °C.\cite{142} This led scientists to the investigation of the electron withdrawing properties of the $\text{OTeF}_5$ group and its comparison to the fluorido ligand. Therefore, Schrobilgen et al. investigated chemical shift differences in $^1\text{H}$ NMR spectra between the methyl and the methylene protons in $\text{CH}_3\text{-CH}_2\text{-X}$ with $X = \text{I, Br, Cl, F or OTeF}_5$ and multinuclear NMR together with Mößbauer\cite{155} studies on a variety of $\text{OTeF}_5$ derivatives of xenon, iodine, and tellurium. As a result, they concluded weaker electron withdrawing properties of the $\text{OTeF}_5$ group compared to a fluorido ligand. However, Seppelt et al. reported opposing results based on the preference of the $\text{OTeF}_5$ group for equatorial positions in the square pyramidal compounds $\text{IF}_x(\text{OTeF}_5)_{5-x}$. Also infrared and multinuclear NMR experiments of $\text{OPF}_2\text{X}$ with $X = \text{Br, Cl, F or OTeF}_5$, and $^1\text{H}$ NMR chemical shifts of $\text{CH}_3\text{X}$ with $X = \text{I, Br, Cl, F or OTeF}_5$ indicated higher electron withdrawing properties.\cite{145, 151, 154} Regardless of the definite classification of their electron withdrawing behavior, one fundamental difference between the fluoride and the pentafluoroorthotellurate ion is the
higher steric demand of the OTeF$_5$ group. Consequently, few examples of oxygen-bridged pentafluoroorthotellurates characterized by x-ray diffraction are described, whereby [Au(OTeF$_5$)$_3$]$^2$,$^{156}$ [Tl(OTeF$_5$)$_3$]$^2$,$^{157}$ and [Hg$_2$(OTeF$_5$)$_6$]$^{2-}$,$^{158}$ are the only known homoleptic examples (Table 1.2). In contrast, in metal fluoride chemistry the formation of fluorine bridges between metal centers such as in AuF$_3$, AuF$_5$, and [Sb$_2$F$_{11}$]$^-$ is a common structural motif.$^{73,159-161}$

As a result of the bulky size, the low accessibility of oxygen-bridges, and low intermolecular interactions of the OTeF$_5$ groups neutral covalent derivatives such as HOTeF$_5$, B(OTeF$_5$)$_3$, Xe(OTeF$_5$)$_2$, and Te(OTeF$_5$)$_6$ are relatively volatile.$^{137,139,142,152}$ Moreover, as mentioned above, monovalent anions of the type [E(OTeF$_5$)$_n$]$^-$ are versatile weakly coordinating anions. Besides the tetracoordinated [B(OTeF$_5$)$_4$]$^-$,$^{129,162}$ several hexacoordinated [M(OTeF$_5$)$_6$]$^-$ monoanions (M = As,$^{130,163}$ Sb,$^{130,164}$ Nb,$^{164,165}$ Ta$^{165}$, Bi$^{130}$) have been reported (Table 1.3).

### Table 1.2. Overview of oxygen-bridged pentafluoroorthotellurates.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Bridging motif$^a$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(solv)$_2$(OTeF$_5$)$_2$]$^2$,$^{166}$</td>
<td>Zn–O–Zn</td>
<td>nitrobenzene</td>
</tr>
<tr>
<td>Ag$_2$(solv)Pd(OTeF$_5$)$_4$,$^{167}$</td>
<td>Ag–O–Pd</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>Ag$_2$(solv)Pd(OTeF$_5$)$_3$,$^{168}$</td>
<td>Ag–O–Pd</td>
<td>1,2-dichloroethane</td>
</tr>
<tr>
<td>[Ag(solv)(OTeF$_5$)$_2$]$^2$,$^{168}$</td>
<td>Ag–O–Ag</td>
<td>dichloromethane</td>
</tr>
<tr>
<td>[Ag(solv)(OTeF$_5$)$_2$]$_2$,$^{168,169}$</td>
<td>Ag–O–Ag</td>
<td>1,2-dichloroethane</td>
</tr>
<tr>
<td>[Ag(solv)(OTeF$_5$)$_2$]$_2$,$^{170}$</td>
<td>Ag–O–Ag</td>
<td>1,2,3-trichloropropane</td>
</tr>
<tr>
<td>[Ag(solv)(OTeF$_5$)$_2$]$_2$,$^{171}$</td>
<td>Ag–O–Ag</td>
<td>toluene</td>
</tr>
<tr>
<td>[Au(OTeF$_5$)$_3$]$_2$,$^{156}$</td>
<td>Au–O–Au</td>
<td>–</td>
</tr>
<tr>
<td>[N(CH$_3$)$_4$]$_2$[Hg$_2$(OTeF$_5$)$_6$]$^2$,$^{158}$</td>
<td>Hg–O–Hg</td>
<td>–</td>
</tr>
<tr>
<td>[Hg(solv)$_2$(OTeF$_5$)$_2$]$_2$,$^{172}$</td>
<td>Hg–O–Hg</td>
<td>thiazyl trifluoride</td>
</tr>
<tr>
<td>[Tl(solv)$_2$(OTeF$_5$)$_3$]$_2$·solv$^{173,174}$</td>
<td>Tl–O–Tl</td>
<td>mesitylene</td>
</tr>
<tr>
<td>[Tl(OTeF$_5$)$_3$]$_2$·solv$^{157}$</td>
<td>Tl–O–Tl</td>
<td>SO$_2$ClF</td>
</tr>
</tbody>
</table>

$^a$O represents the oxygen atom from the OTeF$_5$ group in bridging position.

Additionally, the di- and trivalent anions [Ti(OTeF$_5$)$_6$]$^{2-}$,$^{164,175}$ [Zr(OTeF$_5$)$_6$]$^{2-}$,$^{164}$ [Hf(OTeF$_5$)$_6$]$^{2-}$,$^{164}$ [Hg(OTeF$_5$)$_4$]$^{2-}$,$^{158}$ and [Hg(OTeF$_5$)$_5$]$^{3-}$,$^{158}$ have been investigated. The most commonly used WCA is the hexakis(pentafluoroorthotellurate)antimonate. A number of synthetically useful [Sb(OTeF$_5$)$_6$]$^-$ salts have been synthesized, such as the silver, cesium, trityl, and tetraalkylammonium salts. There are different routes to the desired salts of the antimonate. A simple one-step procedure has been developed to
form the silver salt from SbCl₅ and AgOTeF₅ (Equations 1.19). With Ag[Sb(OTeF₅)₆] metathesis reactions have been carried out which led to the alkali salt Cs[Sb(OTeF₅)₆] and the trityl salt [CPh₃][Sb(OTeF₅)₆] (Equation 1.20 and 1.21). In a three-step route the tetramethyl- and tetraethylammonium salts have been prepared (Equations 1.22-1.24).

\[
\text{SbCl}_5 + 6 \text{AgOTeF}_5 \rightarrow \text{Ag}[\text{Sb(OTeF}_5)_6] + 5 \text{AgCl}_\downarrow \quad (1.19)
\]

\[
\text{Ag}[\text{Sb(OTeF}_5)_6] + \text{CsBr} \rightarrow \text{Cs}[\text{Sb(OTeF}_5)_6] + \text{AgBr}_\downarrow \quad (1.20)
\]

\[
\text{Ag}[\text{Sb(OTeF}_5)_6] + \text{CPh}_3\text{Cl} \rightarrow [\text{CPh}_3][\text{Sb(OTeF}_5)_6] + \text{AgCl}_\downarrow \quad (1.21)
\]

\[
\text{SbF}_3 + \text{B(OTeF}_5)_3 \rightarrow \text{Sb(OTeF}_5)_3 \quad (1.22)
\]

\[
[\text{N(Alk)}_4][\text{Sb(OTeF}_5)_4] + \text{Xe(OTeF}_5)_2 \rightarrow [\text{N(Alk)}_4][\text{Sb(OTeF}_5)_6] + \text{Xe}_\uparrow \quad (1.24)
\]

with Alk = Me, Et

In the reaction of Xe(OTeF₅)₂ with Sb(OTeF₅)₃ a strongly oxidizing xenonium cation ([XeOTeF₅]⁺) is formed along with the weakly coordinating hexakis(pentafluoroorthotellurato)antimonate (Equation 1.25). The reactivity of this cation has already been demonstrated by the oxidative elimination of a chlorine atom of CCl₄ leading to the highly electrophilic [CCl₃]⁺ carbocation (Equation 1.26). By a similar route the [CBr₃]⁺ and [C(OTeF₅)₃]⁺ cations are also accessible.

\[
2 \text{Xe(OTeF}_5)_2 + \text{Sb(OTeF}_5)_3 \rightarrow [\text{XeOTeF}_5][\text{Sb(OTeF}_5)_6] + \text{Xe}_\uparrow \quad (1.25)
\]

\[
[\text{XeOTeF}_5][\text{Sb(OTeF}_5)_6] + \text{CCl}_4 \rightarrow [\text{CCl}_3][\text{Sb(OTeF}_5)_6] + \text{ClOTeF}_5 + \text{Xe}_\uparrow \quad (1.26)
\]

The utilization of [Sb(OTeF₅)₆]⁻ in order to stabilize other oxidizing cations such as [Br(OTeF₅)₂]⁺ and [SbX₄]⁺ (with X = Cl, Br) and the reducing cation [Te₄]²⁺ as well as the weakly bound complex cations [Ag₂Se₆(SO₂)₂]²⁺ and [Ag(S₈)₂]⁺ further illustrates its robustness and versatile application.
Table 1.3. Overview of salts containing OTeF$_5$-based weakly coordinating anions.

<table>
<thead>
<tr>
<th>Anion</th>
<th>Cation</th>
<th>Anion</th>
<th>Cation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[B(OTeF$_5$)$_4$]$^-$</td>
<td>Ag$^+$$^{[162]}$</td>
<td>[Sb(OTeF$_5$)$_6$]$^-$</td>
<td>Ag$^+$$^{[164]}$</td>
</tr>
<tr>
<td></td>
<td>[Ag(CO)]$^+$$^{[184]}$</td>
<td>CS$^+$$^{[176]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Ag(CO)$_2$]$^+$$^{[185]}$</td>
<td>[N(Me)$_4$]$^+$$^{[130]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>K$^+$</td>
<td>[N(Et)$_4$]$^+$$^{[130]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cs$^+$$^{[129]}$</td>
<td>[N(n-Bu)$_4$]$^+$$^{[164]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ti$_4$$^{+174,187}$</td>
<td>[CPh$_3$]$^+$$^{[164]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[N(Me)$_4$]$^+$$^{[188]}$</td>
<td>Te$_4$$^{2+}$$^{[180]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[CPh$_3$]$^+$$^{[162]}$</td>
<td>[Cl$_4$TeF$^-$$TeCl$_4$]$^{+180}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[C$_6$F$_5$Xe]$^+$</td>
<td>[C$_6$F$_5$Cl]$^{+178}$</td>
<td></td>
</tr>
<tr>
<td>[As(OTeF$_5$)$_6$]$^-$</td>
<td>Cs$^+$$^{[163]}$</td>
<td>[CBr$_3$]$^{+178}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[N(Me)$_4$]$^+$$^{[130]}$</td>
<td>[C(OTeF$_5$)$_3$]$^+$$^{[178]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[AsCl$_4$]$^+$$^{[189]}$</td>
<td>[Br$_2$(OTeF$_5$)$_2$]$^+$$^{[178]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[AsBr$_4$]$^+$$^{[189]}$</td>
<td>[XeOTeF$_5$]$^{+177,178}$</td>
<td></td>
</tr>
<tr>
<td>[Nb(OTeF$_5$)$_6$]$^-$</td>
<td>Cs$_4$$^{+165}$</td>
<td>Ag$_2$Se$_6$(SO$_2$)$_2$$^{2+}$$^{[181,182]}$</td>
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</tr>
<tr>
<td></td>
<td>Ag$^+$$^{[164,190]}$</td>
<td>[Ag(S)$_2$]$^+$$^{[183]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Ag(CO)]$^+$$^{[191]}$</td>
<td>[SbCl$_4$]$^{+179}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[Ag(CO)$_2$]$^+$$^{[191]}$</td>
<td>[SbBr$_4$]$^{+179}$</td>
<td></td>
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<tr>
<td></td>
<td>[Ag(CO)$_3$]$^+$$^{[192]}$</td>
<td>[Ta(OTeF$_5$)$_6$]$^-$</td>
<td>Cs$_4$$^{+165}$</td>
</tr>
<tr>
<td></td>
<td>[N(Et)$_4$]$^+$$^{[165]}$</td>
<td>[N(Et)$_4$]$^+$$^{[165]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[N(n-Bu)$_4$]$^+$$^{[164,165,190]}$</td>
<td>[N(n-Bu)$_4$]$^+$$^{[165]}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>[CPh$_3$]$^+$$^{[164]}$</td>
<td>[Bi(OTeF$_5$)$_6$]$^-$</td>
<td>[N(Me)$_4$]$^+$$^{[130]}$</td>
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</tbody>
</table>
Figure 1.6. Plot of the calculated fluoride ion affinities of selected Lewis acids at (RI)PB86/SV(P) level of theory.\cite{27}
Table 1.4. Overview of pentafluoroorthotellurates of main group elements.

<table>
<thead>
<tr>
<th>Group 1</th>
<th>Group 13</th>
<th>Group 14</th>
<th>Group 15</th>
<th>Group 16</th>
<th>Group 17</th>
<th>Group 18</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOPeF₅ [138]</td>
<td>[Li(OPeF₅)₄] [129]</td>
<td>[C(OPeF₅)₅]⁺ [178]</td>
<td>PO(OPeF₅)₂ [146]</td>
<td>HSO₂(OPeF₅) [197]</td>
<td>ClOTeF₅ [194]</td>
<td>Xe(OPeF₅)₄ [142–144,198]</td>
</tr>
<tr>
<td>NaOPeF₅ [138]</td>
<td>[Na(OPeF₅)₄] [154]</td>
<td>POF₂(OPeF₅)₂ [151]</td>
<td>PO₂F(OPeF₅) [197]</td>
<td>SO₂(OPeF₅) [197]</td>
<td>BrOTeF₅ [199]</td>
<td>XeF(OTeF₅)₂ [143,198,200]</td>
</tr>
<tr>
<td>KOPeF₅ [138]</td>
<td>EtOPeF₅ [154]</td>
<td>As(OPeF₅)₃ [150,193]</td>
<td>SO₂Cl(OPeF₅) [197]</td>
<td>[BrOPeF₅]₂⁺ [178]</td>
<td>IO(OPeF₅)₂ [159]</td>
<td>[XeOTeF₅]⁺ [177,178,201–204]</td>
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<tr>
<td>RbOPeF₅ [138]</td>
<td>Si(OPeF₅)₄ [150]</td>
<td>As₂(OPeF₅) [150]</td>
<td>SO₂(OPeF₅)₂ [197]</td>
<td>IOTeF₅ [199]</td>
<td>I(OTeF₅)₃ [199]</td>
<td>XeF₄ n(OTeF₅)ₙ (n = 1–4) [208]</td>
</tr>
<tr>
<td>CsOPeF₅ [138]</td>
<td>Me₃GeOPeF₅ [150]</td>
<td>As(OPeF₅)₆ [163]</td>
<td>SeOF(OPeF₅) [208]</td>
<td>ICl(OPeF₅)₂ [209]</td>
<td>[XeF₃(3-n)(OTeF₅)ₙ]⁺ (n = 1–3) [210]</td>
<td></td>
</tr>
<tr>
<td>RbOPeF₅ [138]</td>
<td>Me₃SnOPeF₅ [150]</td>
<td>[AsF₅(OPeF₅)]⁻ [205]</td>
<td>SeO(OPeF₅) [208]</td>
<td>I(OTeF₅)₄ [209]</td>
<td>XeF₆(6-n)(OTeF₅)ₙ (n = 1–6) [147,206]</td>
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<tr>
<td>CsOPeF₅ [138]</td>
<td></td>
<td>[Sb(OPeF₅)₄] [146]</td>
<td>F₅TeOPeF₅ [142]</td>
<td>IO(OPeF₅)₃ [151]</td>
<td>XeF₆(4-n)(OTeF₅)ₙ (n = 1–4) [147,206]</td>
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(continued)
1.5 References


1 Introduction


1 Introduction


2 Objectives

Since the pentafluoroorthotellurate (OTeF$_5$) group combines chemical robustness, high steric demand and electron withdrawing properties comparable to that of the fluorido ligand, a wide variety of pentafluoroorthotellurate-containing compounds across the periodic table have been prepared. Among these are strong Lewis acids such as B(OTeF$_5$)$_3$, the Brønsted acid HOTeF$_5$, and weakly coordinating anions (WCAs) like [Sb(OTeF$_5$)$_6$]$^-$. However, their application in synthetic chemistry is so far rather limited.

Until now aluminum- and gallium-based pentafluoroorthotellurates have not been successfully prepared, although Lewis acids (e.g. AlCl$_3$, Ga(OSO$_2$CF$_3$)$_3$), Brønsted acids (e.g. HCl–AlCl$_3$, HBr–AlBr$_3$), and WCAs (e.g. [Al(OC(CF$_3$)$_3$)$_4$]$^-$, [Ga(C$_6$F$_5$)$_4$]$^-)$ containing these metals are broadly used.

Objective of this thesis is the synthesis and characterization of aluminum- and gallium-based pentafluoroorthotellurates. Different substance classes, such as Lewis acids, Brønsted acids, and weakly coordinating anions are imaginable and expected to possess promising properties. Especially in the case of the latter the stability towards reactive cations and the facile preparation of useful salts as starting material for further investigations should be demonstrated.
3 Publications

3.1 Superacids Based on Pentafluoroorthotellurate Derivatives of Aluminum

Anja Wiesner, Thomas W. Gries, Simon Steinhauer, Helmut Beckers, and Sebastian Riedel*

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Author contribution
Anja Wiesner designed the project, performed the main experiments, the product characterization, quantum-chemical calculations and wrote the publication. Thomas W. Gries did some of the experiments on the project during his Bachelor thesis that was supervised by Anja Wiesner. Simon Steinhauer, Helmut Beckers, and Sebastian Riedel supervised the project, provided scientific guidelines and suggestions and corrected the manuscript.
The pages 33–36 contain the printed article which is available at https://doi.org/10.1002/anie.201702807.

The pages 37–63 contain the supporting information of the article which is available under the same URL.
3.2 Salts of the Weakly Coordinating Anion $[\text{Al}(\text{OTeF}_5)_4]$含 Reactive Counterions

Kurt F. Hoffmann, Anja Wiesner, Noah Subat, Simon Steinhauer, and Sebastian Riedel*


https://doi.org/10.1002/zaac.201800174

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Author contribution
Anja Wiesner and Kurt F. Hoffmann equally contributed to the design of the project, performed the main experiments and the product characterization. Kurt F. Hoffmann wrote the manuscript. Noah Subat did some of the experiments on the project during his research internship that was supervised by Anja Wiesner. Simon Steinhauer and Sebastian Riedel supervised the project, provided scientific guidelines and suggestions and corrected the manuscript.
The pages 67–71 contain the printed article which is available at
https://doi.org/10.1002/zaac.201800174.
3.3 \([P_4H][Al(OTeF_5)_4]\): Protonation of White Phosphorus with the Brønsted Superacid \(H[Al(OTeF_5)_4](solv)\)

Anja Wiesner, Simon Steinhauer, Helmut Beckers, Christian Müller*, and Sebastian Riedel*


https://doi.org/10.1039/C8SC03023E

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Author contribution
Anja Wiesner carried out the experiments, the product characterization, most of the quantum-chemical calculations and wrote the major part of manuscript. Sebastian Riedel performed the quantum-chemical calculations at the CCSD(T)/aug-cc-pVTZ level of theory. Christian Müller wrote the introduction of the publication and supervised the project, provided scientific guidelines and suggestions and corrected the manuscript together with Simon Steinhauer, Helmut Beckers, and Sebastian Riedel.
The pages 75–79 contain the printed article which is available at 
https://doi.org/10.1039/C8SC03023E.

The pages 81–91 contain the supporting information of the article
which is available under the same URL.
3.4 Oxygen-Bridged \( \text{Ga}_2(\text{Et})_3(\text{OTeF}_5)_3 \) and the Weakly Coordinating Anions \([\text{Ga}(\text{Et})(\text{OTeF}_5)_3]^–\) and \([\text{Ga}(\text{OTeF}_5)_4]^–\)

Anja Wiesner, Lukas Fischer, Simon Steinhauer, Helmut Beckers, and Sebastian Riedel*


https://doi.org/10.1002/chem.201901651

Author contribution
Anja Wiesner designed the project, performed the main experiments, the product characterization, quantum-chemical calculations and wrote the publication. Lukas Fischer did some of the experiments on the project during his research internship that was supervised by Anja Wiesner. Simon Steinhauer, Helmut Beckers, and Sebastian Riedel supervised the project, provided scientific guidelines and suggestions and corrected the manuscript.
The pages 95–102 contain the printed article which is available at https://doi.org/10.1002/chem.201901651.

The pages 103–121 contain the supporting information of the article which is available under the same URL.
4 Summary

A facile one-pot synthesis of the novel aluminum-based Lewis superacid \( \text{Al(OTeF}_5\text{)}_3 \) is reported starting from triethylaluminum and pentafluoroorthotelluric acid. Quantum-chemical investigations suggest that this thermally unstable Lewis acid forms an oxygen-bridged dimer in the solid state. In addition, the soluble and temperature-stable acetonitrile adduct of the Lewis superacid \( \text{MeCN} \rightarrow \text{Al(OTeF}_5\text{)}_3 \) has been prepared. It is a promising starting material for further Lewis acid-mediated reactions.

With \( \text{Al(OTeF}_5\text{)}_3 \) and one additional equivalent pentafluoroorthotelluric acid, the Brønsted superacid \([Ar\text{H}][\text{Al(OTeF}_5\text{)}_4]\) \((Ar = 1,2\text{-difluorobenzene})\) is formed. This Brønsted acid readily reacts with halides by elimination of hydrogen halides and the formation of the corresponding salt of the weakly coordinating anion \(\text{[Al(OTeF}_5\text{)}_4^-}\). By this route several synthetically useful salts such as the alkali metal, silver, trityl or nitrosonium salts are accessible. The Brønsted superacid \([Ar\text{H}][\text{Al(OTeF}_5\text{)}_4]\) has also been applied to protonate weak bases.

For this purpose, benzene or mesitylene have been treated with \([Ar\text{H}][\text{Al(OTeF}_5\text{)}_4]\) and the resulting benzenium and mesitylenium cations were obtained and fully characterized. These cations are best described as 1,4-cyclohexadienyl cations and are stabilized by the weakly coordinating anion \(\text{[Al(OTeF}_5\text{)}_4^-}\). Furthermore, it was possible to protonate white phosphorus taking advantage of the non-oxidizing nature of \([Ar\text{H}][\text{Al(OTeF}_5\text{)}_4]\). For the first time, the structure of the reactive \([P_4\text{H}]^+\) cation in solution was spectroscopically investigated. An insertion of the proton into the \(P_4\) tetrahedron and the formation of a three-center two-electron P–H–P bond is observed in agreement with quantum-chemical calculations.

When changing from aluminum- to gallium-based pentafluoroorthotellurates surprisingly different reaction products were obtained. Instead of a homoleptic Lewis or Brønsted acid the reaction of triethylgallium with pentafluoroorthotelluric acid leads to the formation
of the heteroleptic Ga$_2$(Et)$_3$(OTeF$_3$)$_3$. This compound can be described as an oxygen-bridged dimer, however it can also be understood as a contact ion pair of $[\text{Ga(Et)}_2]^+$ and the weakly coordinating anion $[\text{Ga(Et)(OTeF}_5)_3]^-$. Salts of the latter and of the homoleptic anion $[\text{Ga(OTeF}_5)_4]^{-}$ were also successfully synthesized and characterized.
5 Publications and Conference Contributions

Publication List

https://doi.org/10.1002/chem.201901651

https://doi.org/10.1039/c8sc03023e

https://doi.org/10.1002/zaac.201800174

https://doi.org/10.1039/c8cc05233f
Superacids Based on Pentaffluoroorthotellurate Derivatives of Aluminum.
https://doi.org/10.1002/anie.201702807

Taming the High Reactivity of Gold(III) Fluoride. Fluorido Gold(III) Complexes with N-Based Ligands.
https://doi.org/10.1002/chem.201702663

[7] K. Sonnenberg, P. Pröhm, S. Steinhauer, **A. Wiesner**, C. Müller, S. Riedel,
https://doi.org/10.1002/zaac.201600337

[8] R. Brückner, P. Pröhm, **A. Wiesner**, S. Steinhauer, C. Müller, S. Riedel,
https://doi.org/10.1002/anie.201604348
Conference Contributions – Oral Presentations

[1] A. Wiesner, S. Riedel,
18. Deutscher Fluortag, 2018, Schmitten, Germany.
Aluminatbasierte Brønsted-Säuren und Methylierungsmittel.

[2] A. Wiesner, S. Riedel,
17. Deutscher Fluortag, 2016, Schmitten, Germany.
New pentafluoroorthotellurate based compounds.

Conference Contributions – Poster Presentations

The weakly coordinating anion [Al(OTeF$_5$)$_4$]$^-$ - Stabilization if elusive cations and Brønsted superacids.

255th ACS National Meeting and Exposition, 2018, New Orleans, USA.
[Al(OTeF$_5$)$_4$]$^-$ - A Novel Weakly Coordinating Anion.

GDCh-Wissenschaftsforum Chemie, 2017, Berlin, Germany.
[Al(OTeF$_5$)$_4$]$^-$ - A Novel Weakly Coordinating Anion.

Investigation of New Pentafluoroorthotellurate Derivatives of Aluminum.

18th European Symposium on Fluorine Chemistry, 2016, Kiev, Ukraine.
New Aluminum Pentafluoroorthotellurates.