
Aluminum and Gallium Pentafluoroorthotellurates: Novel Superacids and Weakly Coordinating Anions

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Abstract

A one-pot synthesis of the Lewis acid $\text{Al}(\text{OTeF}_5)_3$ and the Brønsted acid $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ ($\text{Ar} = 1,2\text{-difluorobenzene}$) 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 $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ and the corresponding weakly coordinating anion (WCA) $[\text{Al}(\text{OTeF}_5)_4]^-$. Due to the non-oxidizing behavior of $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ the protonation of white phosphorus succeeded. For the first time, the structure of the $[\text{P}_4\text{H}]^+$ 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 $[\text{Al}(\text{OTeF}_5)_4]^-$. 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 $[\text{Ga}(\text{OTeF}_5)_4]^-$ are finally obtained. Attempts to obtain the gallium analogs of the above mentioned Lewis and Brønsted acids lead to the oxygen-bridged species $\text{Ga}_2(\text{Et})_3(\text{OTeF}_5)_3$. This reactive dimer was used to form salts of the heteroleptic anion $[\text{Ga}(\text{Et})(\text{OTeF}_5)_3]^-$.

Zusammenfassung

Es wird die Eintopfreaktion zur Synthese der Lewis-Säure $\text{Al}(\text{OTeF}_5)_3$ und der Brønsted-Säure $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ ($\text{Ar} = 1,2\text{-Difluorbenzol}$) beschrieben. Zusätzlich werden deren Eigenschaften bezüglich ihrer Säurestärke untersucht, woraufhin beide Verbindungen als Supersäuren eingestuft werden können. Die darauffolgende Arbeit beschäftigt sich hauptsächlich mit der Nutzung von $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ und dem korrespondierenden schwach koordinierenden Anion $[\text{Al}(\text{OTeF}_5)_4]^-$. Aufgrund der nicht-oxidierenden Eigenschaften von $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ ist es gelungen weißen Phosphor zu protonieren. Erstmals wird die Struktur des $[\text{P}_4\text{H}]^+$ -Kations in Lösung untersucht, wobei die erwartete Insertion des Protons in eine Kante des P_4 -Tetraeders bestätigt wird. Außerdem sind weitere Arene höherer Basizität mithilfe der Brønsted-Säure $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ protoniert und strukturell mittels Tieftemperatur-Einkristallröntgenbeugung analysiert worden. Die erhaltenen Areniumionen können am besten als kationische 1,4-Cyclohexadienyllderivate beschrieben werden. Die Stabilität solcher reaktiver Kationen wird durch die gleichzeitige Bildung des chemisch robusten und schwach koordinierenden Anions $[\text{Al}(\text{OTeF}_5)_4]^-$ ermöglicht. Zur universellen Verwendung dieses Anions sind nützliche Ausgangsverbindungen wie die Alkalimetallsalze, das Silber-, Trityl- oder Nitrosylsalz hergestellt worden. Inspiriert von den vielversprechenden Ergebnissen dieser aluminiumbasierten Pentafluororthotelluraten sollten auch die Galliumanaloga synthetisiert werden. Salze des $[\text{Ga}(\text{OTeF}_5)_4]^-$ -Anions sind über eine modifizierte Syntheseroute erhalten worden. Versuche zur Herstellung der analogen Lewis- und Brønsted-Säure führen allerdings zur sauerstoffverbrückten Spezies $\text{Ga}_2(\text{Et})_3(\text{OTeF}_5)_3$. Dieses reaktive Dimer wird im Folgenden für die Bildung von Salzen des heteroleptischen $[\text{Ga}(\text{Et})(\text{OTeF}_5)_3]^-$ -Anions genutzt.

List of Abbreviations

<i>a</i>	activity
ACF	aluminum chlorofluoride
Alk	alkyl
<i>Ar</i>	aryl
BArF	tetrakis(3,5-bis(trifluoromethyl)phenyl)borate
BP86	generalized gradient approximation functional with Becke 1988 exchange functional and the Perdew 1986 correlation functional
<i>c</i>	concentration
Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
DFT	density functional theory
ΔH	enthalpy
$\Delta_r H^\circ$	standard enthalpy of reaction
e.g.	for example (Latin: <i>exempli gratia</i>)
Et	ethyl
<i>et al.</i>	and others (Latin: <i>et alii</i>)
exp.	experimental
FIA	fluoride ion affinity
FLP	frustrated Lewis pair
g	gaseous
G3	Gaussian-3 composite method
H_0	Hammett acidity function
HS-AlF ₃	high-surface aluminum fluoride
<i>i</i> -Pr	<i>iso</i> -propyl

K_a	equilibrium constant of the dissociation of a Brønsted acid
Me	methyl
MeCN	acetonitrile
Mes	mesitylene
MP2	2nd order Møller-Plesset perturbation theory
<i>n</i> -Bu	<i>n</i> -butyl
NMR	nuclear magnetic resonance
PDZ	double- ζ plus polarization basis set
Ph	phenyl
pH	negative decadic logarithm of the proton activity
p <i>K</i>	negative decadic logarithm of the equilibrium constant <i>K</i>
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.^[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.



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).^[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.



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.^[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.^[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_3 (with $E = B, Al, Ga$, and $X = F, Cl, Br, I$), halogen compounds with unsaturated coordination (PF_5, AsF_5 or SbF_5) and non-metal oxides (SO_2, SO_3).^[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.^[11] Lewis acids are of significant importance in industrial processes, being applied in olefine polymerization as Ziegler-Natta catalysts,^[12] and also in other polymerization, aldol or oxidation reactions^[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.^[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 $C \equiv N$ bond.^[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,^[18,19] while Childs *et al.* chose crotonaldehyde as reference and investigated the $\Delta\delta$ of the H3 proton in the 1H NMR spectrum.^[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]

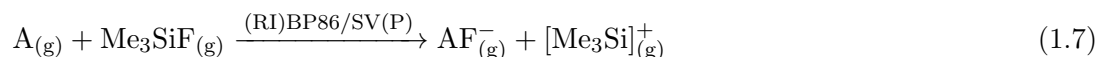
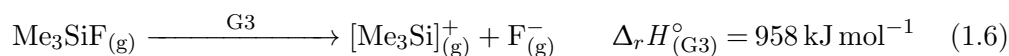
Bartlett *et al.* introduced the concept of fluoride ion affinity (FIA). It is based on the ability of a Lewis acid to form a Lewis acid-base complex with a fluoride ion and the energy that is released upon this complex formation (Equation 1.3).^[22] A high FIA value of a certain compound corresponds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



Because experimentally estimated FIA values showed discrepancies between different measuring techniques,^[23] Christie *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 $[CF_3O]^-$ and COF_2 needs to be calculated quantum-chemically (Equation 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)).

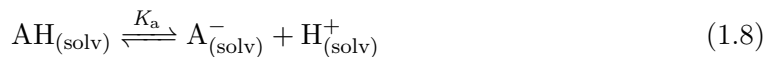


This procedure can even be extended to chloride, hydride or methyl ion affinities using Me_3SiY and the corresponding ions $[Me_3Si]^+/Y^-$ with $Y = Cl, H,$ and Me to evaluate the behavior of a Lewis acid towards softer bases than the fluoride ion. By this method the FIA value of 493 kJ mol^{-1} was 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 , $Al(C_6F_5)_3$, $Al(OC(CF_3)_3)_3$, the

boron-based Lewis acids $B(CN)_3$, $B(CF_3)_3$, $F_4C_6(1,2-(B(C_6F_5)_2)_2)$, $SiMe_2CH_2CB_{11}Cl_{11}$, and the pentafluoroorthotellurates $B(OTeF_5)_3$, $As(OTeF_5)_5$, $Sb(OTeF_5)_5$ are Lewis superacids. More recent examples, like $B(C_6F_4CF_3)_3$,^[28] $Al(N(C_6F_5)_2)_3$,^[29] $B(OC_5F_4N)_3$,^[30] $Al(OC_5F_4N)_3$,^[30] $Al(OC(C_6F_5)_3)_3$,^[31] and $Si(O_2C_6Cl_4)_2$ ^[32] underline the high interest in new Lewis superacids. Some of them have already been applied in C–H or C–F bond activation reactions.^[33,34] Furthermore, there are widely used solid-state Lewis acids like aluminum chlorofluoride (ACF with $AlCl_xF_{3-x}$ and $x = 0.05-0.3$) or high-surface aluminum fluoride (HS- AlF_3) that reach the acidity of SbF_5 .^[21,35,36]

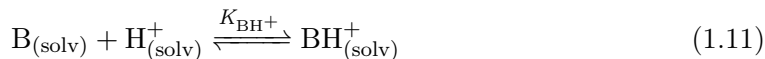
1.2 Brønsted Superacids

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_{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.^[37-41] 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 BH^+ (e.g. *para*-nitroaniline, $pK_{BH^+} = 1.4$) and the equilibrium constant K_{BH^+} of this reaction. The indicator changes its color upon protonation and the concentration c_{BH^+} and c_B are measured by UV-vis spectroscopy.^[42] 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**.^[43,44]



$$\text{pH} = -\lg a_{\text{H}^+} \quad (1.9)$$

$$\text{p}K_a = -\lg K_a \quad (1.10)$$



$$H_0 = \text{p}K_{\text{BH}^+} - \lg \frac{c_{\text{BH}^+}}{c_{\text{B}}} \quad (1.12)$$

However, the pH and p*K*_a 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 C_α and C_β 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 acidity^[49] 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.^[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”) carbonium ions which contain fivefold (or higher) coordinated carbon atoms necessitating three-center (or multicenter) two-electron bonds.^[9] The simplest representative of a carbenium ion is the methenium ion $[\text{CH}_3]^+$, whereas the methonium ion $[\text{CH}_5]^+$ is the simplest example of a carbonium ion. More recently Malischewski *et al.* showed that superacidic chemistry can still contribute fundamentally to research by protonation of ferrocene yielding $[\text{Cp}_2\text{FeH}][\text{PF}_6]$,^[54] the synthesis of the decamethylferrocene dication ($[\text{Cp}_2^*\text{Fe}][\text{SbF}_6]_2$ and $[\text{Cp}_2^*\text{Fe}][\text{Sb}_2\text{F}_{11}]_2$),^[55] and the preparation of the hexamethylbenzene dication ($[\text{C}_6(\text{CH}_3)_6][\text{SbF}_6]_2$) which is in agreement with the Wade’s rules of pentagonal-pyramidal geometry.^[56] In order to stabilize and isolate these reactive cations weakly coordinating anions (WCAs) such as $[\text{PF}_6]^-$, $[\text{SbF}_6]^-$, and $[\text{Sb}_2\text{F}_{11}]^-$ are necessary. A major drawback of these binary Brønsted superacids are oxidation reactions which lead to cation and anion decomposition.^[57] As a consequence, scientists focused on the preparation of non-oxidizing Brønsted superacids with highly stable counterions.

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 electrophilic, strong oxidants or they show fundamental structural or bonding features.^[58] There are several examples where WCAs contribute in catalysis or as components in electrolytes and ionic liquids.^[59,60] End of the 20th century WCAs encompassed $[\text{BF}_4]^-$, $[\text{ClO}_4]^-$, $[\text{AlX}_4]^-$, $[\text{EF}_6]^-$, and $[\text{CF}_3\text{SO}_3]^-$ (with $\text{X} = \text{Cl}, \text{Br}, \text{I}$, and $\text{E} = \text{P}, \text{As}, \text{Sb}$), but later on single-crystal x-ray diffraction studies disclosed more and more their obvious ability to coordinate a cation.^[61–67] The search for cationic species without a strong influence of the counterion led to an improved anion design. An ideal modern WCA should combine the following features:^[68]

- 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-norbornyl 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 *et al.* in 1964.^[75] Substitution of the fluoride in *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.^[78] 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.^[79–81] Its cheap and easy synthesis results in widespread utility for applications such as polymerization and homogeneous catalysis.^[82–84] The CF_3 group has also been replaced by larger fluoroalkyl groups such as $\text{CF}(\text{CF}_3)_2$,^[81] C_4F_9 ,^[81] $\text{C}(\text{CF}_3)_2\text{OCH}_3$,^[85] $\text{C}(\text{CF}_3)_2\text{OCH}_2\text{CF}_3$,^[85] and C_6F_{13} .^[86] Still the arylborate anions tend to coordinate via fluorine atoms^[87] or the π system of the arene.^[88] Furthermore, they are not compatible with strong oxidants^[68] and prone to degradation by fluoride abstraction^[89] and aryl transfer.^[78] The comparably small $[\text{B}(\text{CF}_3)_4]^-$ anion^[90] (Figure 1.1, right) possesses a high chemical stability. It is one of few anions known to successfully stabilize the pentanitrogen cation,^[91] but is not stable against concentrated sulfuric acid.^[92]

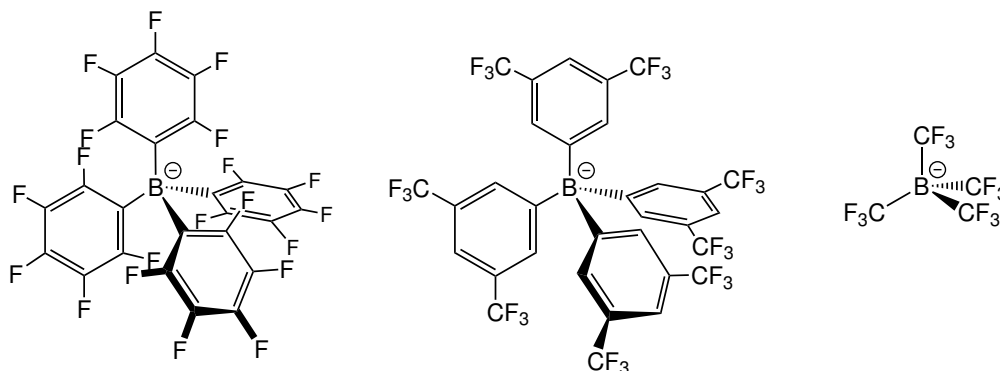


Figure 1.1. Structural formula of selected fluorinated alkyl- and arylborate anions; $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ (left), $[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$ (middle), and $[\text{B}(\text{CF}_3)_4]^-$ (right).

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 $[\text{HCB}_{11}\text{H}_{11}]^-$ ^[93,94] which is structurally related to the dodecaborane dianion $[\text{B}_{12}\text{H}_{12}]^{2-}$. The B–H bonds are strongly bound and already weakly coordinating. Nevertheless, the halogenated derivatives $[\text{HCB}_{11}\text{H}_5\text{X}_6]^-$ ^[95–97] and $[\text{HCB}_{11}\text{X}_{11}]^-$ ^[98,99] ($\text{X} = \text{Cl}, \text{Br}$ or I) are more resistant against oxidants and delocalize the negative charge more effectively (Figure 1.2, left and middle).^[100,101] To improve the solubility of this type of WCAs methyl groups have been introduced at the hydrogen positions, leading to $[\text{HCB}_{11}\text{Me}_5\text{X}_6]^-$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; Figure 1.2, right).^[102] With the halogenated carborane anions the successful

preparation of silylium ions $[\text{Si}(i\text{-Pr})_3]^+$ ^[74] and $[\text{Si}(\text{Mes})_3]^+$,^[103] carbocations,^[104,105] the fullerene ions $[\text{C}_{60}]^+$ and $[\text{HC}_{60}]^+$ ^[45] and protonated arenes^[46,106] 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.*^[107] While the chlorine and bromine substituted carborane anions show a stronger coordination ability,^[88] 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 $n = 5, 6, 10, 11$.^[48,108–110] 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.

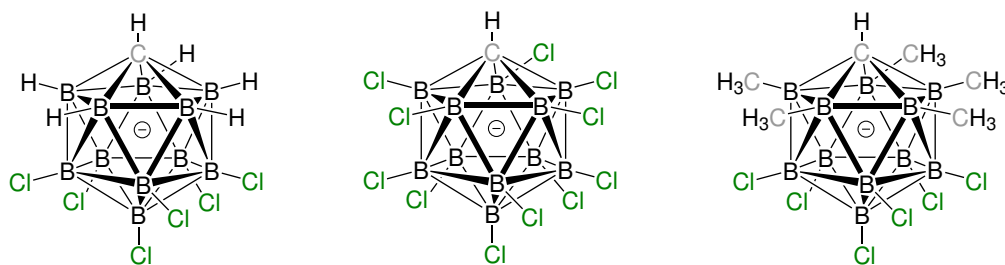


Figure 1.2. Structural formula of selected carborane anions; $[\text{HCB}_{11}\text{H}_5\text{Cl}_6]^-$ (left), $[\text{HCB}_{11}\text{Cl}_{11}]^-$ (middle), and $[\text{HCB}_{11}\text{Me}_5\text{Cl}_6]^-$ (right). Chlorine atoms are colored for clarity.

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.^[111] 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 $[\text{Al}(\text{O}i\text{-Pr})_4]^-$. 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.^[112] 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,^[113,114] electrophiles,^[115–118] weakly bound complexes,^[71,72,119–122] carbonyl complexes^[123,124] or oxidizing cations.^[122,125] Moreover, it has been shown that alkoxyaluminate anions score very high ionicities in ionic liquids^[68] and are applied as component in electrolytes of lithium-sulfur batteries^[126] or homogeneous catalysis.^[127]

However, in attempts to synthesize extremely electrophilic silylium cations ($[\text{SiR}_3]^+$, R = Me, Et, *i*-Pr), even the most robust anion of its class degrade via fluoride abstraction.^[128]

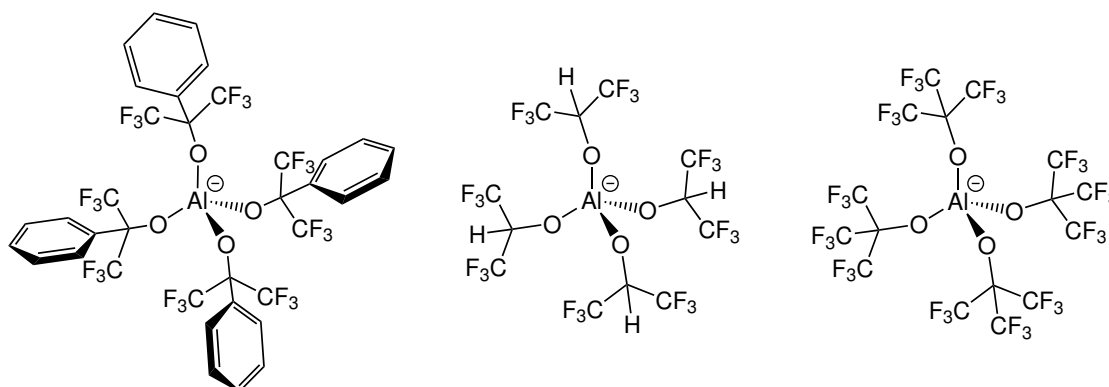


Figure 1.3. Structural formula of selected fluorinated alkoxyaluminate anions; $[\text{Al}(\text{OC}(\text{Ph})(\text{CF}_3)_2)_4]^-$ (left), $[\text{Al}(\text{OCH}(\text{CF}_3)_2)_4]^-$ (middle), and $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ (right).

1.3.4 Pentafluoroorthotellurate Anions

Formal substitution of the fluoro ligand in $[\text{BF}_4]^-$ and $[\text{MF}_6]^-$ (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 ($\text{Te}(\text{OH})_6$ and HSO_3F) 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.

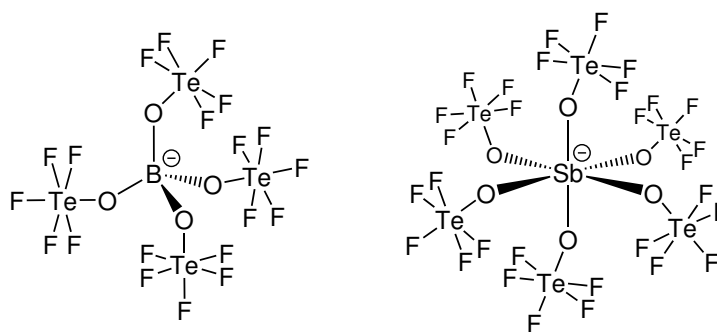


Figure 1.4. Structural formula of the pentafluororthotellurate anions $[\text{B}(\text{OTeF}_5)_4]^-$ and $[\text{Sb}(\text{OTeF}_5)_6]^-$.

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 $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ and $[\text{Sb}(\text{OTeF}_5)_6]^-$ (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 $[\text{SbF}_6]^-$ (red colored in Figure 1.5 a) or on basic sites, for example in $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$ (orange colored in Figure 1.5 e), are visible. The examples of arylborate, carborane, alkoxyaluminate, and pentafluororthotellurate anions given in Figure 1.5 clearly demonstrate their well dispersed negative charge (yellow/green).

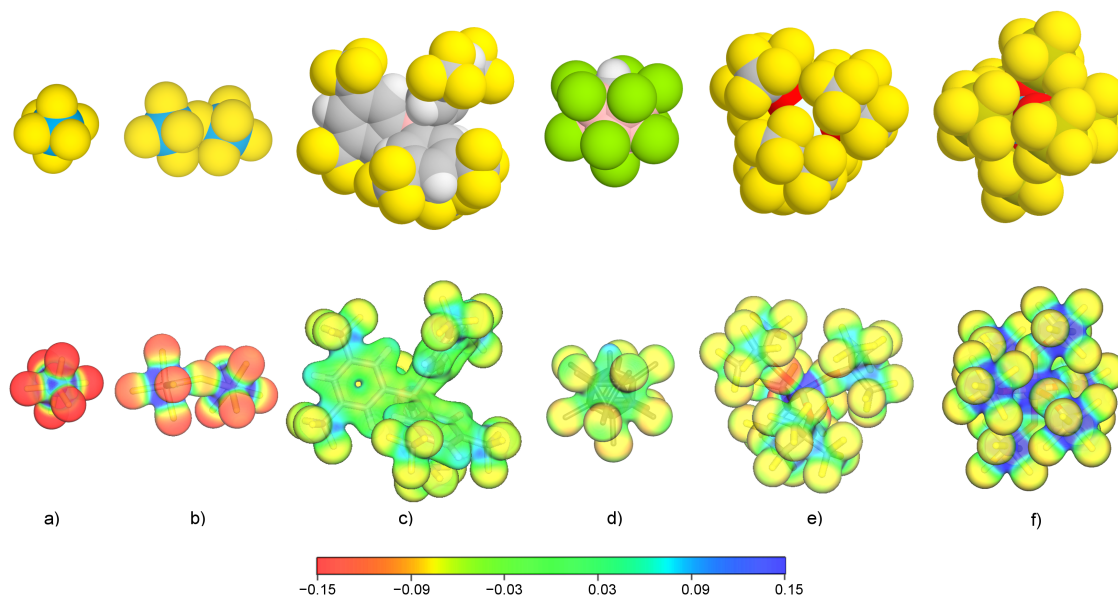
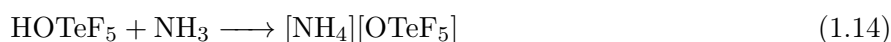


Figure 1.5. Space-filling model (upper trace) and calculated electrostatic potential plotted on the electron density (lower trace, (RI)PB86/SV(P), isovalue: $0.025 \text{ e bohr}^{-3}$) of a) $[\text{SbF}_6]^-$, b) $[\text{Sb}_2\text{F}_{11}]^-$, c) $[\text{B}(3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3)_4]^-$, d) $[\text{HCB}_{11}\text{Cl}_{11}]^-$, e) $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$, and f) $[\text{Sb}(\text{OTeF}_5)_6]^-$.

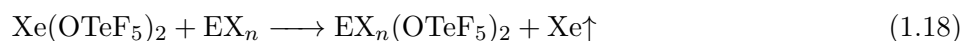
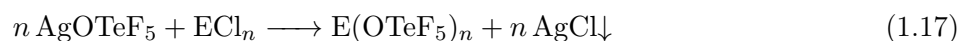
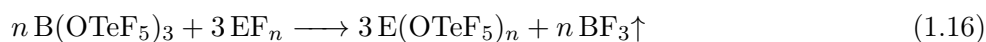
1.4 Pentafluoroorthotellurates

In 1964 Engelbrecht and Sladky accidentally prepared pentafluoroorthotelluric acid HOTeF_5 from barium tellurate BaTeO_4 and fluorosulfonic acid HSO_3F which paved the way for the further chemistry of pentafluoroorthotellurates.^[137] They described the formed acid as colorless and volatile solid which melts at $40 \text{ }^\circ\text{C}$ and solidifies from the melt in a glass-like manner. Attempts to dissolve HOTeF_5 in water showed its fast hydrolysis to telluric acid $\text{Te}(\text{OH})_6$ and hydrofluoric acid HF . Only one year later the ammonium, pyridinium, and first alkali salts of the $[\text{OTeF}_5]^-$ anion were obtained by the reaction of HOTeF_5 with ammonia, pyridine, and alkali chlorides (Equations 1.13-1.15), respectively.^[138]



The synthesis of $\text{B}(\text{OTeF}_5)_3$,^[139] AgOTeF_5 ,^[140,141] and $\text{Xe}(\text{OTeF}_5)_2$ ^[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 OTeF_5 ligand to main group (Table 1.4) and transition metal compounds.^[145] The Lewis superacid $\text{B}(\text{OTeF}_5)_3$ acts as a OTeF_5 group transfer reagent for element fluorides (EF_n , Equation 1.16). While the driving force of this reaction is the release of gaseous BF_3 , it enables the synthesis of $\text{Sb}(\text{OTeF}_5)_3$,^[146] $\text{Xe}(\text{OTeF}_5)_4$,^[147] $\text{As}(\text{OTeF}_5)_5$,^[146] $\text{Xe}(\text{OTeF}_5)_6$,^[148] and $\text{U}(\text{OTeF}_5)_6$.^[149] AgOTeF_5 is used as a reactant for element chlorides (ECl_n) resulting in the formation of insoluble AgCl (Equation 1.17). By this route $\text{Si}(\text{OTeF}_5)_4$ or $\text{Me}_3\text{GeOTeF}_5$ have been prepared.^[150] While these approaches are simple metathesis reactions, an oxidative addition of an OTeF_5 radical is achieved using $\text{Xe}(\text{OTeF}_5)_2$ (Equation 1.18) leading to compounds in a high oxidation state such as $\text{I}^{\text{V}}(\text{OTeF}_5)_5$ ^[151] or $\text{Te}^{\text{VI}}(\text{OTeF}_5)_6$.^[152]



with E = element and X = F or OTeF_5

In contrast to the previously synthesized Xe^{II} compounds $\text{Xe}(\text{OSO}_2\text{F})_2$ and $\text{Xe}(\text{OCIO}_3)_2$ ^[153] the pentafluoroorthotellurate derivative $\text{Xe}(\text{OTeF}_5)_2$ shows a surprisingly high thermal stability with a decomposition temperature of 150 °C.^[142] This led scientists to the investigation of the electron withdrawing properties of the OTeF_5 group and its comparison to the fluoro ligand. Therefore, Schrobilgen *et al.* investigated chemical shift differences in ^1H NMR spectra between the methyl and the methylene protons in $\text{CH}_3\text{-CH}_2\text{-X}$ with X = I, Br, Cl, F or OTeF_5 ^[154,155] and multinuclear NMR together with Mößbauer^[155] studies on a variety of OTeF_5 derivatives of xenon, iodine, and tellurium. As a result, they concluded weaker electron withdrawing properties of the OTeF_5 group compared to a fluoro ligand. However, Seppelt *et al.* reported opposing results based on the preference of the 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 OPF_2X with X = Br, Cl, F or OTeF_5 , and ^1H NMR chemical shifts of CH_3X with X = I, Br, Cl, F or OTeF_5 indicated higher electron withdrawing properties.^[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 $[\text{Au}(\text{OTeF}_5)_3]_2$,^[156] $[\text{Tl}(\text{OTeF}_5)_3]_2$,^[157] and $[\text{Hg}_2(\text{OTeF}_5)_6]^{2-}$ ^[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 $[\text{Sb}_2\text{F}_{11}]^-$ 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 , $\text{B}(\text{OTeF}_5)_3$, $\text{Xe}(\text{OTeF}_5)_2$, and $\text{Te}(\text{OTeF}_5)_6$ are relatively volatile.^[137,139,142,152] Moreover, as mentioned above, monovalent anions of the type $[\text{E}(\text{OTeF}_5)_n]^-$ are versatile **weakly coordinating anions**. Besides the tetracoordinated $[\text{B}(\text{OTeF}_5)_4]^-$,^[129,162] several hexacoordinated $[\text{M}(\text{OTeF}_5)_6]^-$ monoanions ($\text{M} = \text{As}$,^[130,163] Sb ,^[130,164] Nb ,^[164,165] Ta ^[165], Bi ^[130]) have been reported (Table 1.3).

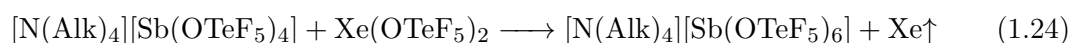
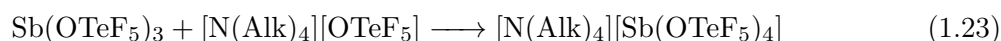
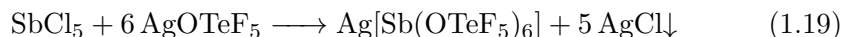
Table 1.2. Overview of oxygen-bridged pentafluoroorthotellurates.

Compound	Bridging motif ^a	Solvent
$[\text{Zn}(\text{solv})_2(\text{OTeF}_5)_2]_2$ ^[166]	Zn–O–Zn	nitrobenzene
$\text{Ag}_2(\text{solv})\text{Pd}(\text{OTeF}_5)_4$ ^[167]	Ag–O–Pd	dichloromethane
$\text{Ag}_2(\text{solv})\text{Pd}(\text{OTeF}_5)_4$ ^[168]	Ag–O–Pd	1,2-dichloroethane
$[\text{Ag}(\text{solv})(\text{OTeF}_5)]_2$ ^[168]	Ag–O–Ag	dichloromethane
$[\text{Ag}(\text{solv})(\text{OTeF}_5)]_2$ ^[168,169]	Ag–O–Ag	1,2-dichloroethane
$[\text{Ag}(\text{solv})(\text{OTeF}_5)]_2$ ^[170]	Ag–O–Ag	1,2,3-trichloropropane
$[\text{Ag}(\text{solv})(\text{OTeF}_5)]_2$ ^[171]	Ag–O–Ag	toluene
$[\text{Au}(\text{OTeF}_5)_3]_2$ ^[156]	Au–O–Au	–
$[\text{N}(\text{CH}_3)_4]_2[\text{Hg}_2(\text{OTeF}_5)_6]$ ^[158]	Hg–O–Hg	–
$[\text{Hg}(\text{solv})_2(\text{OTeF}_5)_2]_2$ ^[172]	Hg–O–Hg	thiazyl trifluoride
$[\text{Tl}(\text{solv})_2(\text{OTeF}_5)]_2 \cdot \text{solv}$ ^[173,174]	Tl–O–Tl	mesitylene
$[\text{Tl}(\text{OTeF}_5)_3]_2 \cdot \text{solv}$ ^[157]	Tl–O–Tl	SO_2ClF

^aO represents the oxygen atom from the OTeF_5 group in bridging position.

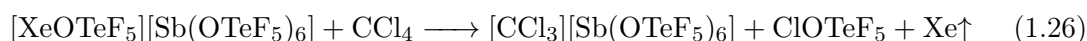
Additionally, the di- and trivalent anions $[\text{Ti}(\text{OTeF}_5)_6]^{2-}$,^[164,175] $[\text{Zr}(\text{OTeF}_5)_6]^{2-}$,^[164] $[\text{Hf}(\text{OTeF}_5)_6]^{2-}$,^[164] $[\text{Hg}(\text{OTeF}_5)_4]^{2-}$,^[158] and $[\text{Hg}(\text{OTeF}_5)_5]^{3-}$ ^[158] have been investigated. The most commonly used WCA is the hexakis(pentafluoroorthotellurato)antimonate. A number of synthetically useful $[\text{Sb}(\text{OTeF}_5)_6]^-$ 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 SbCl_5 and AgOTeF_5 (Equations 1.19).^[164] With $\text{Ag}[\text{Sb}(\text{OTeF}_5)_6]$ metathesis reactions have been carried out which led to the alkali salt $\text{Cs}[\text{Sb}(\text{OTeF}_5)_6]$ ^[176] and the trityl salt $[\text{CPh}_3][\text{Sb}(\text{OTeF}_5)_6]$ ^[164] (Equation 1.20 and 1.21). In a three-step route the tetramethyl- and tetraethylammonium salts have been prepared (Equations 1.22-1.24).



with $\text{Alk} = \text{Me}, \text{Et}$

In the reaction of $\text{Xe}(\text{OTeF}_5)_2$ with $\text{Sb}(\text{OTeF}_5)_3$ a strongly oxidizing xenonium cation ($[\text{XeOTeF}_5]^+$) is formed along with the weakly coordinating hexakis(pentafluoroorthotellurato)antimonate (Equation 1.25).^[177] The reactivity of this cation has already been demonstrated by the oxidative elimination of a chlorine atom of CCl_4 leading to the highly electrophilic $[\text{CCl}_3]^+$ carbocation (Equation 1.26). By a similar route the $[\text{CBr}_3]^+$ and $[\text{C}(\text{OTeF}_5)_3]^+$ cations are also accessible.^[178]



The utilization of $[\text{Sb}(\text{OTeF}_5)_6]^-$ in order to stabilize other oxidizing cations such as $[\text{Br}(\text{OTeF}_5)_2]^+$ ^[178] and $[\text{SbX}_4]^+$ (with $\text{X} = \text{Cl}, \text{Br}$)^[179] and the reducing cation $[\text{Te}_4]^{2+}$ ^[180] as well as the weakly bound complex cations $[\text{Ag}_2\text{Se}_6(\text{SO}_2)_2]^{2+}$ ^[181,182] and $[\text{Ag}(\text{S}_8)_2]^+$ ^[183] further illustrates its robustness and versatile application.

Table 1.3. Overview of salts containing OTeF₅-based weakly coordinating anions.

Anion	Cation	Anion	Cation
[B(OTeF ₅) ₄] ⁻	Ag ^{+ [162]}	[Sb(OTeF ₅) ₆] ⁻	Ag ^{+ [164]}
	[Ag(CO)] ^{+ [184]}		Cs ^{+ [176]}
	[Ag(CO) ₂] ^{+ [185]}		[N(Me) ₄] ^{+ [130]}
	K ^{+ [186]}		[N(Et) ₄] ^{+ [130]}
	Cs ^{+ [129]}		[N(<i>n</i> -Bu) ₄] ^{+ [164]}
	Tl ^{+ [174, 187]}		[CPh ₃] ^{+ [164]}
	[N(Me) ₄] ^{+ [188]}		[Te ₄] ^{+ [180]}
	[N(<i>n</i> -Bu) ₄] ^{+ [174]}		[TeBr ₃] ^{+ [180]}
	[CPh ₃] ^{+ [162]}		[Cl ₃ Te-F-TeCl ₃] ^{+ [180]}
	[C ₆ F ₅ Xe] ^{+ [186]}		[CCl ₃] ^{+ [178]}
	[As(OTeF ₅) ₆] ⁻		Cs ^{+ [163]}
[N(Me) ₄] ^{+ [130]}		[C(OTeF ₅) ₃] ^{+ [178]}	
[AsCl ₄] ^{+ [189]}		[Br(OTeF ₅) ₂] ^{+ [178]}	
[AsBr ₄] ^{+ [189]}		[XeOTeF ₅] ^{+ [177, 178]}	
[Nb(OTeF ₅) ₆] ⁻	Cs ^{+ [165]}	[Ag ₂ Se ₆ (SO ₂) ₂] ^{+ [181, 182]}	
	Ag ^{+ [164, 190]}	[Ag(S ₈) ₂] ^{+ [183]}	
	[Ag(CO)] ^{+ [191]}	[SbCl ₄] ^{+ [179]}	
	[Ag(CO) ₂] ^{+ [191]}	[SbBr ₄] ^{+ [179]}	
	[Ag(CO) ₃] ^{+ [192]}	[Ta(OTeF ₅) ₆] ⁻	
	[N(Et) ₄] ^{+ [165]}	Cs ^{+ [165]}	
	[N(<i>n</i> -Bu) ₄] ^{+ [164, 165, 190]}	[N(Et) ₄] ^{+ [165]}	
	[CPh ₃] ^{+ [164]}	[N(<i>n</i> -Bu) ₄] ^{+ [165]}	
		[Bi(OTeF ₅) ₆] ⁻	
		[N(Me) ₄] ^{+ [130]}	

Besides the weakly coordinating anions, the neutral derivatives B(OTeF₅)₃, As(OTeF₅)₅, and Sb(OTeF₅)₅ are stronger Lewis acids than their fluoride analogs and are referred to **Lewis superacids**. The antimony pentafluorooorthotellurate, Sb(OTeF₅)₅, is claimed to be the strongest Lewis acid known but it has never been successfully synthesized.^[146, 193] According to the fluoride ion affinity scale Sb(OTeF₅)₅ has the highest FIA value (Figure 1.6). Even if Lewis acids sharing the same central atom are compared among each other the pentafluorooorthotellurates show the highest FIA values.

Despite this excellent properties only a few OTeF₅-based Lewis acids have been prepared so far. Apart from their characterization and the application of B(OTeF₅)₃ as OTeF₅ transfer reagent, they have not been further used in synthetic chemistry.

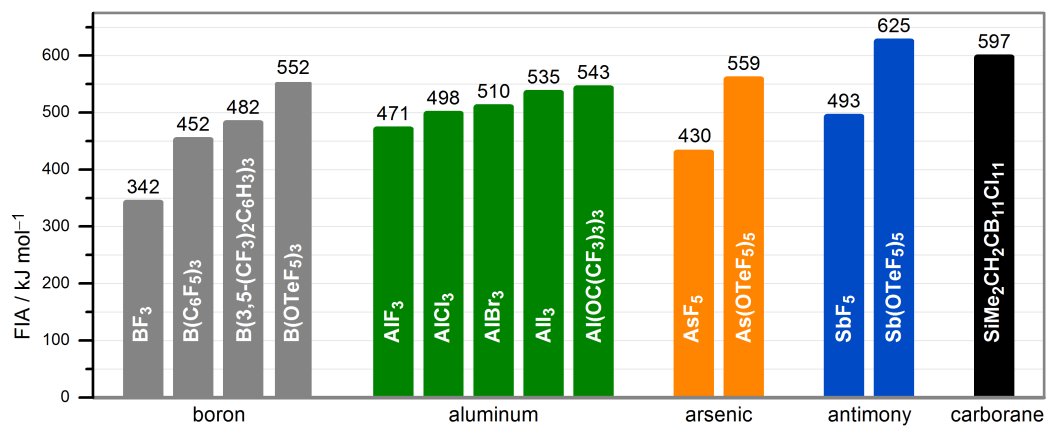


Figure 1.6. Plot of the calculated fluoride ion affinities of selected Lewis acids at (RI)PB86/SV(P) level of theory.^[27]

Table 1.4. Overview of pentafluororthotellurates of main group elements.

Group 1	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
HOTeF_5 ^[137,194]	$\text{B}(\text{OTeF}_5)_3$ ^[129,139]	$\text{C}(\text{OTeF}_5)_4$ ^[178]	$\text{P}(\text{OTeF}_5)_3$ ^[146]	$\text{F}_5\text{TeOOTeF}_5$ ^[194]	FOTeF_5 ^[195]	$\text{Kr}(\text{OTeF}_5)_2$ ^[196]
LiOTeF_5 ^[138]	$[\text{B}(\text{OTeF}_5)_4]^-$ ^[129]	$[\text{C}(\text{OTeF}_5)_3]^+$ ^[178]	$\text{PO}(\text{OTeF}_5)_3$ ^[146]	$\text{HSO}_3(\text{OTeF}_5)$ ^[197]	ClOTeF_5 ^[194]	$\text{Xe}(\text{OTeF}_5)_2$ ^[142-144,198]
NaOTeF_5 ^[138]	$[\text{FB}(\text{OTeF}_5)_3]^-$ ^[151]	MeOTeF_5 ^[154]	$\text{POF}_2(\text{OTeF}_5)_3$ ^[151]	$\text{SO}_2\text{F}(\text{OTeF}_5)$ ^[197]	BrOTeF_5 ^[199]	$\text{XeF}(\text{OTeF}_5)$ ^[143,198,200]
KOTeF_5 ^[138]	TlOTeF_5 ^[173,174]	EtOTeF_5 ^[154]	$\text{As}(\text{OTeF}_5)_3$ ^[150,193]	$\text{SO}_2\text{Cl}(\text{OTeF}_5)$ ^[197]	$[\text{Br}(\text{OTeF}_5)_2]^+$ ^[178]	$\text{Xe}(\text{OSeF}_5)(\text{OTeF}_5)$ ^[198]
RbOTeF_5 ^[138]	$\text{Tl}(\text{OTeF}_5)_3$ ^[157]	$\text{Si}(\text{OTeF}_5)_4$ ^[150]	$\text{AsF}_2(\text{OTeF}_5)$ ^[150]	$\text{SO}_2(\text{OTeF}_5)_2$ ^[197]	IOTeF_5 ^[199]	$[\text{XeOTeF}_5]^+$ ^[177,178,201-204]
CsOTeF_5 ^[138]		$\text{Me}_3\text{SiOTeF}_5$ ^[150]	$\text{As}(\text{OTeF}_5)_5$ ^[146,163]	NSOTeF_5 ^[205]	$\text{I}(\text{OTeF}_5)_3$ ^[199]	$\text{XeF}_{(4-n)}(\text{OTeF}_5)_n$ ($n = 1-4$) ^[147,206,207]
		$\text{Me}_3\text{GeOTeF}_5$ ^[150]	$[\text{As}(\text{OTeF}_5)_6]^-$ ^[163]	$\text{SeOF}(\text{OTeF}_5)$ ^[208]	$\text{ICl}(\text{OTeF}_5)_2$ ^[209]	$[\text{XeF}_{(3-n)}(\text{OTeF}_5)_n]^+$ ($n = 1-3$) ^[210]
		$\text{Me}_3\text{SnOTeF}_5$ ^[150]	$[\text{AsF}_5(\text{OTeF}_5)]^-$ ^[205]	$\text{SeO}(\text{OTeF}_5)_2$ ^[208]	$[\text{I}(\text{OTeF}_5)_4]^-$ ^[209]	$\text{XeF}_{(6-n)}(\text{OTeF}_5)_n$ ($n = 1-6$) ^[147,206]
			$[\text{Sb}(\text{OTeF}_5)_3]$ ^[146]	$\text{F}_5\text{TeOTeF}_5$ ^[142]	$\text{IO}(\text{OTeF}_5)_3$ ^[151]	$\text{XeOF}_{(4-n)}(\text{OTeF}_5)_n$ ($n = 1-4$) ^[147,206,207]
			$\text{SbF}_{(5-n)}(\text{OTeF}_5)_n$ ($n = 1, 2$) ^[211]	$\text{TeF}_{(4-n)}(\text{OTeF}_5)_n$ ($n = 1-4$) ^[208]	$[\text{IO}(\text{OTeF}_5)_4]^-$ ^[209]	$\text{XeO}_2\text{F}_{(2-n)}(\text{OTeF}_5)_n$ ($n = 1-2$) ^[207]
			$[\text{Sb}(\text{OTeF}_5)_6]^-$ ^[130]	$\text{TeF}_{(6-n)}(\text{OTeF}_5)_n$ ($n = 1-6$) ^[212]	$\text{IF}_{(5-n)}(\text{OTeF}_5)_n$ ($n = 1-5$) ^[151]	
			$\text{Bi}(\text{OTeF}_5)_5$ ^[130]			
			$[\text{Bi}(\text{OTeF}_5)_6]^-$ ^[130]			

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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 $\text{B}(\text{OTeF}_5)_3$, the Brønsted acid HOTeF_5 , and weakly coordinating anions (WCAs) like $[\text{Sb}(\text{OTeF}_5)_6]^-$. 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 , $\text{Ga}(\text{OSO}_2\text{CF}_3)_3$), Brønsted acids (e.g. $\text{HCl}-\text{AlCl}_3$, $\text{HBr}-\text{AlBr}_3$), and WCAs (e.g. $[\text{Al}(\text{OC}(\text{CF}_3)_3)_4]^-$, $[\text{Ga}(\text{C}_6\text{F}_5)_4]^-$) 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*

Angew. Chem. Int. Ed. **2017**, *56*, 8263–8266.

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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 $[\text{Al}(\text{OTeF}_5)_4]^-$ containing Reactive Counterions

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

Z. Anorg. Allg. Chem. **2018**, *644*, 1344–1348.

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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 $[\text{P}_4\text{H}][\text{Al}(\text{OTeF}_5)_4]$: Protonation of White Phosphorus with the Brønsted Superacid $\text{H}[\text{Al}(\text{OTeF}_5)_4]_{(\text{solv})}$

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

Chem. Sci. **2018**, *9*, 7169–7173.

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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*

Chem. Eur. J. **2019**, *accepted*.

<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
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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 $\text{Al}(\text{OTeF}_5)_3$ 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 $\text{MeCN} \rightarrow \text{Al}(\text{OTeF}_5)_3$ has been prepared. It is a promising starting material for further Lewis acid-mediated reactions.

With $\text{Al}(\text{OTeF}_5)_3$ and one additional equivalent pentafluoroorthotelluric acid, the Brønsted superacid $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ ($\text{Ar} = 1,2\text{-difluorobenzene}$) 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 $[\text{Al}(\text{OTeF}_5)_4]^-$. By this route several synthetically useful salts such as the alkali metal, silver, trityl or nitrosonium salts are accessible. The Brønsted superacid $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ has also been applied to protonate weak bases.

For this purpose, benzene or mesitylene have been treated with $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$ 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 $[\text{Al}(\text{OTeF}_5)_4]^-$. Furthermore, it was possible to protonate white phosphorus taking advantage of the non-oxidizing nature of $[\text{ArH}][\text{Al}(\text{OTeF}_5)_4]$. For the first time, the structure of the reactive $[\text{P}_4\text{H}]^+$ 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 $\text{P}-\text{H}-\text{P}$ 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 $\text{Ga}_2(\text{Et})_3(\text{OTeF}_5)_3$. This compound can be described as an oxygen-bridged dimer, however it can also be understood as a contact ion pair of $[\text{Ga}(\text{Et})_2]^+$ and the weakly coordinating anion $[\text{Ga}(\text{Et})(\text{OTeF}_5)_3]^-$. Salts of the latter and of the homoleptic anion $[\text{Ga}(\text{OTeF}_5)_4]^-$ were also successfully synthesized and characterized.

5 Publications and Conference Contributions

Publication List

- [1] **A. Wiesner**, L. Fischer, S. Steinhauer, H. Beckers, S. Riedel,
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 $[\text{Ga}(\text{OTeF}_5)_4]^-$.
Chem. Eur. J. **2019**, *accepted*.
<https://doi.org/10.1002/chem.201901651>
- [2] **A. Wiesner**, S. Steinhauer, H. Beckers, C. Müller, S. Riedel,
 $[\text{P}_4\text{H}]^+[\text{Al}(\text{OTeF}_5)_4]^-$: Protonation of White Phosphorus with the Brønsted
Superacid $\text{H}[\text{Al}(\text{OTeF}_5)_4]_{(\text{solv})}$.
Chem. Sci. **2018**, *9*, 7169-7173.
<https://doi.org/10.1039/c8sc03023e>
- [3] K. F. Hoffmann, **A. Wiesner**, N. Subat, S. Steinhauer, S. Riedel,
Salts of the Weakly Coordinating Anion $[\text{Al}(\text{OTeF}_5)_4]^-$ containing Reactive
Counterions.
Z. Anorg. Allg. Chem. **2018**, *644*, 1344-1348.
<https://doi.org/10.1002/zaac.201800174>
- [4] M. A. Ellwanger, C. v. Randow, S. Steinhauer, Y. Zhou, **A. Wiesner**,
H. Beckers, T. Braun, S. Riedel
Tuning the Lewis acidity of difluorido gold(III) complexes: the synthesis of
 $[\text{AuClF}_2(\text{SIMes})]$ and $[\text{AuF}_2(\text{OTeF}_5)(\text{SIMes})]$.
Chem. Commun., **2018**, *54*, 9301-9304.
<https://doi.org/10.1039/c8cc05233f>

- [5] **A. Wiesner**, T. W. Gries, S. Steinhauer, H. Beckers, S. Riedel,
Superacids Based on Pentafluorooorthotellurate Derivatives of Aluminum.
Angew. Chem. Int. Ed. **2017**, *56*, 8263–8266.
<https://doi.org/10.1002/anie.201702807>
- [6] M. A. Ellwanger, S. Steinhauer, P. Golz, H. Beckers, **A. Wiesner**,
B. Braun-Cula, T. Braun, S. Riedel,
Taming the High Reactivity of Gold(III) Fluoride. Fluorido Gold(III)
Complexes with N-Based Ligands.
Chem. Eur. J. **2017** *23*, 13501–13509.
<https://doi.org/10.1002/chem.201702663>
- [7] K. Sonnenberg, P. Pröhm, S. Steinhauer, **A. Wiesner**, C. Müller, S. Riedel,
Formation and Characterization of $[\text{BrC}(\text{NMe}_2)_2][\text{Br}_3]$ and $[\text{BrC}(\text{NMe}_2)_2]_2[\text{Br}_8]$
in Ionic Liquids.
Z. anorg. allg. Chem. **2017**, *643*, 101–105.
<https://doi.org/10.1002/zaac.201600337>
- [8] R. Brückner, P. Pröhm, **A. Wiesner**, S. Steinhauer, C. Müller, S. Riedel,
Structural Proof for the First Dianion of a Polychloride: Investigation of $[\text{Cl}_8]^{2-}$.
Angew. Chem. Int. Ed. **2016**, *55*, 10904–10908.
<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 pentafluororthotellurate based compounds.

Conference Contributions – Poster Presentations

- [1] **A. Wiesner**, K. F. Hoffmann, T. W. Gries, S. Steinhauer, H. Beckers,
C. Müller, S. Riedel,
22nd International Symposium on Fluorine Chemistry, **2018**, Oxford, UK.
The weakly coordinating anion $[\text{Al}(\text{OTeF}_5)_4]^-$ - Stabilization of elusive
cations and Brønsted superacids.
- [2] **A. Wiesner**, T. W. Gries, S. Riedel,
255th ACS National Meeting and Exposition, **2018**, New Orleans, USA.
 $[\text{Al}(\text{OTeF}_5)_4]^-$ - A Novel Weakly Coordinating Anion.
- [3] **A. Wiesner**, T. W. Gries, S. Riedel,
GDCh-Wissenschaftsforum Chemie, **2017**, Berlin, Germany.
 $[\text{Al}(\text{OTeF}_5)_4]^-$ - A Novel Weakly Coordinating Anion.
- [4] **A. Wiesner**, K. Hoffmann, L. Conrad, S. Riedel,
18. Vortragstagung der Wöhler-Vereinigung, **2016**, Berlin, Germany.
Investigation of New Pentafluororthotellurate Derivatives of Aluminum.
- [5] **A. Wiesner**, K. Hoffmann, L. Conrad, S. Riedel,
18th European Symposium on Fluorine Chemistry, **2016**, Kiev, Ukraine.
New Aluminum Pentafluororthotellurates.

