Hot Paper

A Rare Example of a Gallium-Based Lewis Superacid: Synthesis and Reactivity of Ga(OTeF$_5$)$_3$

Lukas Fischer,[a] Kurt F. Hoffmann,[a] and Sebastian Riedel*[a]

The Lewis superacid Ga(OTeF$_5$)$_3$ has been synthesized and characterized, revealing a monomeric structure in solution and a dimeric structure in the solid state. Isolated adducts of Ga(OTeF$_5$)$_3$ with strong and weak Lewis bases have been characterized spectroscopically as well as by single-crystal X-ray diffractometry. The Lewis acidity of this new species has been evaluated by means of different experimental and theoretical methods, which has allowed to classify it as one of only a few examples of a gallium-based Lewis superacid. The high Lewis acidity of Ga(OTeF$_5$)$_3$ was used to amplify the strength of the Brønsted acid HOTeF$_5$, leading to the protonation of diethyl ether. Furthermore, Ga(OTeF$_5$)$_3$ was utilized to access the strong oxidizing system Ga(OTeF$_5$)$_3$/Xe(OTeF$_5$)$_2$ in SO$_2$ClF, which was successfully employed in the synthesis of the dimethyl chloronium salt [Cl(CH$_3$)$_2$][Ga(OTeF$_5$)$_4$], a strong electrophilic methylation reagent.

Introduction

Lewis acids have a broad field of application as for example in organic catalysis or in the activation of small molecules.[1] Especially strong Lewis acids, the so-called Lewis superacids, have gained popularity in the last two decades, since they have successfully been utilized in the hydrosilylation of olefins,[2] Diels-Alder reactions,[3] and deoxygenation reactions,[4] among others. The most consistent definition for Lewis superacids was given by Krossing and defines them as molecular compounds with a higher fluoride ion affinity (FIA) than monomeric SbF$_5$ in the gas phase.[5] However, the FIA is not the most suitable measurement for soft Lewis acids due to the hard nature of the fluoride ion. Therefore, the definition was expanded to include strong Lewis acids with a soft nature. The hydride ion affinity (HIA) was chosen as a scale to assess the Lewis acidity of soft Lewis acids. Thus, the new subcategory of soft Lewis superacids is defined as molecular compounds with a higher HIA than B(C$_6$F$_5$)$_3$ in the gas phase.[6]

In general, group 13 elements, being electron deficient and with a vacant p orbital, are predestined for the synthesis of strong Lewis acids, with a broad number of boron- and aluminum-based Lewis superacids, which include for example B(p-CF$_3$-C$_6$F$_4$)$_3$, Al(OC(CF$_3$)$_3$)$_3$ and Al(OC(C$_6$F$_5$)$_3$)$_3$, being reported in the literature.[5–7] Focusing on the heavier elements in this group, a small number of gallium-based Lewis acids can be classified as soft Lewis superacids or are slightly under the defined threshold.[8] However, no isolated gallium-based Lewis acid reaches the criteria to be considered as a hard Lewis superacid. This is a particularly interesting observation as the Ga(III) cation is generally considered a hard Lewis acid.[9] With an overall lower electronegativity, especially compared to boron and aluminum, and the influence of the d-block contraction on the gallium atom, the Lewis acidity of gallium-based Lewis acids is affected.[10] In addition, many strong electron-withdrawing groups commonly used in the synthesis of Lewis superacids allow inter- and intra-molecular interactions between the central atom and the ligands. These interactions further decrease the Lewis acidity of the gallium atom: gallium triflate, Ga(OTf)$_3$, for example forms a polymeric structure via bridging triflate groups,[11] and in Ga(N(C$_6$F$_5$)$_2$)$_3$ multiple ortho-fluorine atoms of the ligand coordinate to the gallium center, saturating its coordination sphere.[12]
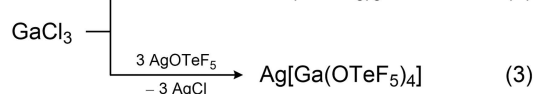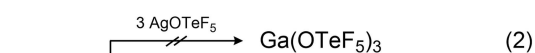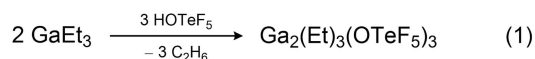
A promising building block in order to enhance the Lewis acidity of a gallium center is the pentafluoroorthotellurate group (OTeF$_5$, teflate), as it has proven to be very efficient in the synthesis of Lewis superacids due to its strong electron-withdrawing properties. The main-group element Lewis superacids E(OTeF$_5$)$_n$ (n = 3, E=B, Al; n = 5, E=As) and the transition-metal Lewis superacid Au(OTeF$_5$)$_3$ show an outstandingly high Lewis acidity,[13] with As(OTeF$_5$)$_5$ being the only literature known neutral arsenic-based Lewis superacid.[14,15] The boron compound B(OTeF$_5$)$_3$ is commonly used as a transfer reagent for the OTeF$_5$ group as it easily reacts with a range of element fluorides like XeF$_2$, SbF$_3$ or TeF$_4$ with the release of BF$_3$ to give the corresponding element teflate compounds.[15,16] The aluminum compound Al(OTeF$_5$)$_3$ and its reaction product with HOTeF$_5$, the Brønsted superacid H[Al(OTeF$_5$)$_4$]$_{solv.}$, have been used to synthesize highly reactive and unusual cations like the xenonium cation [Xe(OTeF$_5$)(NC$_5$F$_5$)]$^+$, the arenium cations [C$_6$H$_7$]$^+$ and [C$_9$H$_{13}$]$^+$, protonated white phosphorus [P$_4$H]$^+$ and the perfluorinated tritylium cation [C(C$_6$F$_5$)$_3$]$^+$.[17,18] Additionally, Al(OTeF$_5$)$_3$ was successfully utilized in the synthesis of highly Lewis acidic materials like a teflate-doped aluminum chlorofluoride (ACF).[19]

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The versatility of Al(OTeF$_5$)$_3$ sparked our interested in the heavier homologue Ga(OTeF$_5$)$_3$. Earlier work in our group already explored the access to teflate-containing gallium compounds. First attempts to synthesize Ga(OTeF$_5$)$_3$ in an analogous route to Al(OTeF$_5$)$_3$ did not yield the desired gallium Lewis acid.[20] By reacting GaEt$_3$ with HOTeF$_5$ the partially substituted product Ga$_2$(Et)$_3$(OTeF$_5$)$_3$ was obtained instead [Equation (1)]. The use of GaCl$_3$ as the starting material and reacting it with 4 equivalents of AgOTeF$_5$ led to the silver salt Ag[Ga(OTeF$_5$)$_4$] [Equation (3)], but the reaction with 3 equivalents of AgOTeF$_5$ only led to an incomplete substitution and a mixture of different species, and not to the desired Ga(OTeF$_5$)$_3$ Lewis acid.

$$2\ GaEt_3 \xrightarrow[-\ 3\ C_2H_6]{3\ HOTeF_5} Ga_2(Et)_3(OTeF_5)_3 \qquad (1)$$

$$GaCl_3 \begin{cases} \xrightarrow[]{3\ AgOTeF_5} Ga(OTeF_5)_3 & (2) \\ \xrightarrow[-\ 3\ AgCl]{3\ AgOTeF_5} Ag[Ga(OTeF_5)_4] & (3) \end{cases}$$

In this work we present the synthesis and characterization of the Lewis acid Ga(OTeF$_5$)$_3$ by reaction of GaCl$_3$ and ClOTeF$_5$, as well as adducts of this compound with different Lewis bases. The Lewis acidity of Ga(OTeF$_5$)$_3$ is assessed by means of established experimental and theoretical methods and its use in superacidic and strong oxidizing systems leading to reactive cations is demonstrated.

Results and Discussion

Synthesis and Characterization of Ga(OTeF$_5$)$_3$

As stated in the introduction, the use of the common teflate-transfer reagents (HOTeF$_5$, AgOTeF$_5$) for the synthesis of Ga(OTeF$_5$)$_3$ was not successful. In search of a suitable combination of a teflate-transfer reagent and an easily accessible gallium precursor to synthesize Ga(OTeF$_5$)$_3$, we turned to the strong oxidizer ClOTeF$_5$.[21] This effective teflate-transfer reagent was already used in the past for the synthesis of various main-group and transition-metal teflate compounds[15,22] and was also most recently applied in the successful synthesis of the first homoleptic nickel, cobalt and manganese teflate anions [M(OTeF$_5$)$_4$]$^{2-}$ (M=Ni, Co, Mn) and [Mn(OTeF$_5$)$_5$]$^{2-}$, the gold Lewis superacid Au(OTeF$_5$)$_3$ and the corresponding anion [Au(OTeF$_5$)$_4$]$^-$.[13,23]

As the hypochlorite ClOTeF$_5$ is mainly used in reactions with main-group and transition-metal chlorides, the driving force being the release of gaseous Cl$_2$, we investigated its reactivity towards GaCl$_3$. It was found that the solvent-free reaction of GaCl$_3$ and 3 equivalents of ClOTeF$_5$ quantitatively yields the desired Lewis acid Ga(OTeF$_5$)$_3$ **1** [Equation (4)].

$$GaCl_3 \xrightarrow[-\ 3\ Cl_2]{3\ ClOTeF_5} \underset{\textbf{1}}{Ga(OTeF_5)_3} \qquad (4)$$
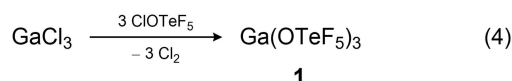
Upon condensing liquid ClOTeF$_5$ onto GaCl$_3$ and subsequent warming to −30°C, a suspension is formed and the release of chlorine gas is observed. Warming the reaction mixture to room temperature and removing all volatile compounds *in vacuo* resulted in compound **1** as a fine colorless moisture-sensitive powder in gram scale. Under inert conditions, the product is stable up to 120°C, as determined by TGA measurement (SI Figure S24).

The ^{19}F NMR spectrum of compound **1** in a strongly coordinating solvent like acetonitrile shows a well-defined AB$_4$ pattern with chemical shifts of −32.7 ppm (F$_A$) and −43.6 ppm (4 F$_B$) and coupling constants of $^2J_{F\text{-}F}=176$ Hz, $^1J_{Te\text{-}F(A)}=3086$ Hz, and $^1J_{Te\text{-}F(B)}=3488$ Hz (SI Figure S3). However, the nucleophilic acetonitrile easily coordinates to the gallium center, saturates the electron deficit and therefore drastically lowers the Lewis acidity of the system, as it was already shown for Al(OTeF$_5$)$_3$.[24] Conventional solvents with a low nucleophilicity like pentane or toluene are unsuitable for compound **1**, as they do not dissolve the Lewis acid. Halogenated weakly nucleophilic solvents like CH$_2$Cl$_2$ or fluorobenzene are partially suitable, as **1** slowly decomposes in them at room temperature. The best results in terms of solubility and stability were obtained using the rather unconventional weakly nucleophilic solvent SO$_2$ClF: it readily dissolves compound **1** even at low temperatures down to −90°C, while also no decomposition of **1** is observed at room temperature. The ^{19}F NMR spectrum of Ga(OTeF$_5$)$_3$ in SO$_2$ClF shows a collapsed AB$_4$ pattern for the OTeF$_5$ group (Figure 1). The chemical shift and the coupling constants were determined by simulation to be at −41.5 ppm (F$_A$) and −43.2 ppm (4 F$_B$) with coupling constants of $^2J_{F\text{-}F}=187$ Hz, $^1J_{Te\text{-}F(A)}=3450$ Hz, and $^1J_{Te\text{-}F(B)}=3500$ Hz. The ^{19}F NMR spectra of **1** in acetonitrile and SO$_2$ClF both show only one chemically equivalent teflate group, which indicates that the Lewis acid is monomeric in solution.

Quantum-chemical calculations suggest that **1** forms the solvent adduct Ga(SO$_2$ClF)$_2$(OTeF$_5$)$_3$ with SO$_2$ClF, as shown in Figure 2. However, in the absence of a solvent, the IR spectrum of the pure solid compound **1** indicates a dimeric structure, in
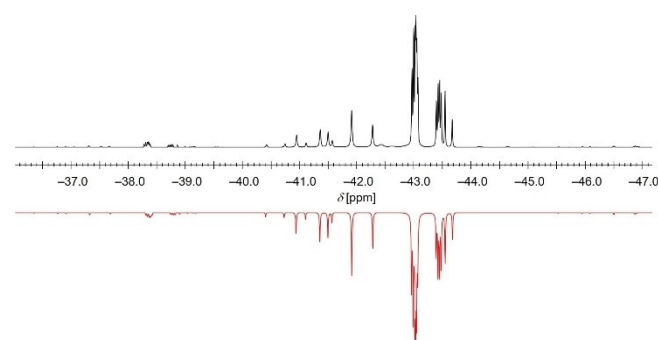

Figure 1. ^{19}F NMR spectrum of Ga(OTeF$_5$)$_3$ **1** in SO$_2$ClF (top: experimental (376 MHz, 25°C), bottom: simulated).

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$$[Ga(OTeF_5)_3]_2 \quad \xrightarrow[\Delta_R H^0 = -19.5 \text{ kJ mol}^{-1}]{+ 4 \text{ SO}_2\text{ClF}} \quad 2 \text{ Ga(SO}_2\text{ClF)}_2(\text{OTeF}_5)_3$$
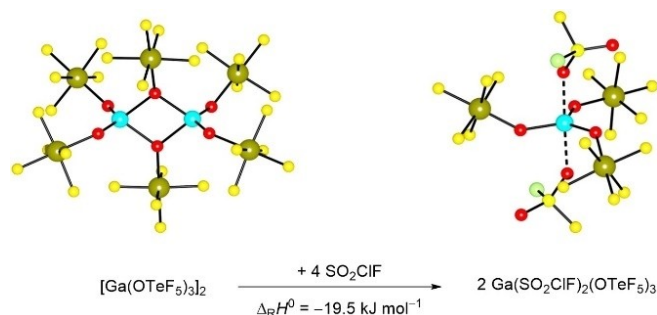
Figure 2. Calculated solvation energy of the dimer $[Ga(OTeF_5)_3]_2$ in SO_2ClF (B3LYP/def2-TZVPP).

which two gallium atoms are connected through two bridging teflate groups. The experimentally obtained IR spectrum of **1** and the calculated spectrum of the dimeric Lewis superacid $[Ga(OTeF_5)_3]_2$ are in good agreement (SI Figure S21). The ring vibration of the four-membered gallium-oxygen ring of the dimer is observed at 582 cm^{-1}. Quantum-chemical calculations further support the presence of a dimeric structure in the solid state, since this dimerization process is energetically favored by -88.0 kJ mol^{-1} (B3LYP/def2-TZVPP). Thus the gallium compound $Ga(OTeF_5)_3$ and the analogous aluminum Lewis superacid $Al(OTeF_5)_3$ share the same structural motifs as a solvent coordinated monomer in solution and a dimer in the solid state.[24]

The high Lewis acidity of $Ga(OTeF_5)_3$ allows the formation of adducts with even weak nucleophilic bases as for example pentafluoropyridine NC_5F_5. By addition of an excess of NC_5F_5 to a CH_2Cl_2 solution of $Ga(OTeF_5)_3$ and cooling the solution to $-40\,°C$, single crystals suitable for X-ray diffraction analysis were obtained. $Ga(NC_5F_5)(OTeF_5)_3$ **2** crystallizes in the monoclinic space group $P2_1/c$. The gallium atom is coordinated by three oxygen atoms and the nitrogen atom of the pentafluoropyridine in a distorted tetrahedron, which becomes evident from the O–Ga–O and N–Ga–O angles ranging from 100.04(6)° to 116.19(7)° (Figure 3). The geometry index τ_4 for **2** is calculated to be 0.93, with 1 being the value for a perfect tetrahedron.[25]

The ^{19}F NMR spectrum of compound **2** shows the AB$_4$ pattern of the OTeF$_5$ group at -41.7 ppm (F$_A$) and -43.0 ppm (4 F$_B$) (SI Figure S1). The signals of the fluorine atoms of the coordinated pentafluoropyridine are shifted to the low field (F$_o = -86.9$ ppm, F$_m = -158.3$ ppm, F$_p = -120.3$ ppm) compared to uncoordinated NC_5F_5 (F$_o = -88.2$ ppm, F$_m = -162.2$ ppm, F$_p = -134.8$ ppm). This low field shift has already been described when a strong electron withdrawing moiety is attached to the nitrogen atom.[18,26] The two NMR active gallium isotopes ^{69}Ga and ^{71}Ga can be utilized for the NMR spectroscopic analysis of the gallium center. The higher sensitivity of the ^{71}Ga nucleus compared to the ^{69}Ga nucleus makes the ^{71}Ga NMR spectroscopy the preferred method. Unfortunately, the signal of the Lewis superacid **1** in the ^{71}Ga NMR spectrum is too broad to be observed. However, upon coordination of NC_5F_5, a broad signal (FWHM = 672 Hz) is detected at 122 ppm (SI Figure S2). This is in agreement with the sharp signal (FWHM = 65) observed in
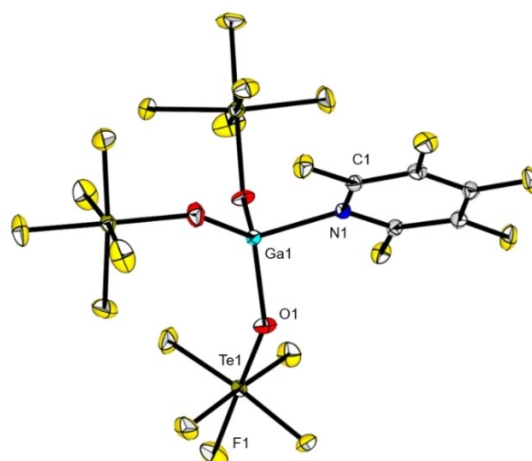

Figure 3. Molecular structure of **2** in the solid state. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and bond angles [°]: Ga1–O1 180.91(19), Ga1–O2 179.6(2), Ga1–O3 181.57(19), Ga1–N1 200.9(2), O1–Ga1–O2 112.87(10), O1–Ga1–O3 112.87(9), O1–Ga1–N1 100.13(9), O2–Ga1–O3 116.07(9), O2–Ga1–N1 106.57(9), O3–Ga1–N1 106.62(9). For crystallographic details see Supporting Information.

the ^{71}Ga NMR spectrum at 120 ppm for the gallate anion $[Ga(OTeF_5)_4]^-$, in which the gallium atom is also four-fold coordinated in a distorted tetrahedral geometry.

Evaluation of the Lewis Acidity of Ga(OTeF$_5$)$_3$

To assess the Lewis acidity of **1**, experimental and theoretical methods were used. First, the Lewis acidity was experimentally determined by the evaluation of the ν(CN) stretching vibration of the corresponding acetonitrile adduct in the IR spectrum. The acetonitrile adduct $Ga(CD_3CN)(OTeF_5)_3$ **3a** was obtained by dissolving **1** in CD_3CN and removing the solvent afterwards *in vacuo*. Deuterated acetonitrile was used to avoid the Fermi resonance which occurs when using CH_3CN.[6] The ν(CN) stretching vibration of the acetonitrile adduct **3a** (2326 cm^{-1}) is shifted by 68 cm^{-1} compared to that of free CD_3CN (2258 cm^{-1}). This shift is in the range of other Lewis superacids like $Al(OTeF_5)_3$ (2328 cm^{-1}), with a shift of 70 cm^{-1}, or SbF_5 (2324 cm^{-1}), with a shift of 66 cm^{-1} (Table 1).

Table 1. Experimental evaluation of the Lewis acidity of the group 13 Lewis acids E(OTeF$_5$)$_3$ (E = B, Al, Ga) by evaluation of the ν(CN) stretching vibration (L = CD$_3$CN) and the modified GB method (L = Ph$_3$PO).

Compound	ν(CN) stretching vibration		modified GB method	
	ν (CN) cm^{-1}	$\Delta\nu$ (CN) cm^{-1}	$\delta(^{31}P)$ ppm	$\Delta\delta(^{31}P)$ ppm
CD$_3$CN	2258	–	–	–
Ph$_3$PO	–	–	27.1	–
GaL(OTeF$_5$)$_3$	2326	68	53.5	26.4
AlL(OTeF$_5$)$_3$	2328	70	50.2	23.1
BL(OTeF$_5$)$_3$	2361	103	51.5	24.4

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For further evaluation of the Lewis acidity, a modified version of the Gutmann-Beckett method was performed. In the standard method, the signal shift $\Delta\delta(^{31}P)$ in the ^{31}P NMR spectrum of triethylphosphine oxide Et_3PO and the corresponding Lewis acid adduct is compared, with a higher low field shift indicating a higher Lewis acidity.[27] For the modified version, the bulkier triphenylphosphine oxide Ph_3PO is used instead, which shows consistent trends with the original method for the signal shift $\Delta\delta(^{31}P)$.[28] The change of the phosphine oxide was necessary due to the multiple coordination of Et_3PO to **1**, leading to several signals in the ^{31}P NMR spectrum. The bulkier Ph_3PO forms exclusively the 1:1 complex $Ga(OPPh_3)(OTeF_5)_3$ **4a**, giving only one signal in the ^{31}P NMR spectrum at 53.5 ppm and therefore a signal shift of 26.4 ppm. For comparison, the corresponding adducts of the lighter group 13 teflate Lewis superacids, $Al(OPPh_3)(OTeF_5)_3$ **4b** and $B(OPPh_3)(OTeF_5)_3$ **4c**, were also prepared. The signal shifts in the aluminum compound **4b** ($\Delta\delta(^{31}P) = 23.1$ ppm) and the boron compound **4c** ($\Delta\delta(^{31}P) = 24.4$ ppm) are similar to the observed shifts for the gallium compound **4a** (Table 1). This indicates similar Lewis acidities for all three $E(OTeF_5)_3$ compounds (E=B, Al, Ga).

Single-crystals of the compounds **4a–4c** were obtained from their respective CH_2Cl_2 solutions, which were layered with *n*-pentane and cooled to $-40\,°C$. Their molecular structures in the solid state could be determined by X-ray diffractometry and are shown in Figure 4. Selected interatomic distances and angles are provided in Table 2. The heavier homologues **4a** and **4b** with gallium and aluminum as the Lewis acidic center are structurally comparable and do not exhibit any significant differences in the E–O4 and P–O4 bond lengths and the E–O4–P bond angles. However, compound **4c** has due to the smaller size of the boron atom a significantly shorter E–O4 bond compared to **4a** and **4b**. The resulting short distance between the boron and the phosphorus atom in **4c** leads to an increased torsion angle $O_{teflate}$–E–P–C, as the bulky ligands sterically interfere with each other, leading to the more staggered structure found for **4c** (Figure 4, bottom).

The P–O4 bond length in **4c** is increased by about 3 pm compared to **4a** and **4b**. As a result of the strong electron-withdrawing properties of the Lewis superacids, the P–O4 bond length is elongated in all three structures by up to 10 pm compared to free Ph_3PO (P–O = 146(1) pm).[29] In addition to the experimental evaluation of the Lewis acidity of **1**, the fluoride (FIA), chloride (CIA) and hydride (HIA) ion affinities were calculated by quantum-chemical methods and compared to other literature-known strong gallium Lewis acids and structur-
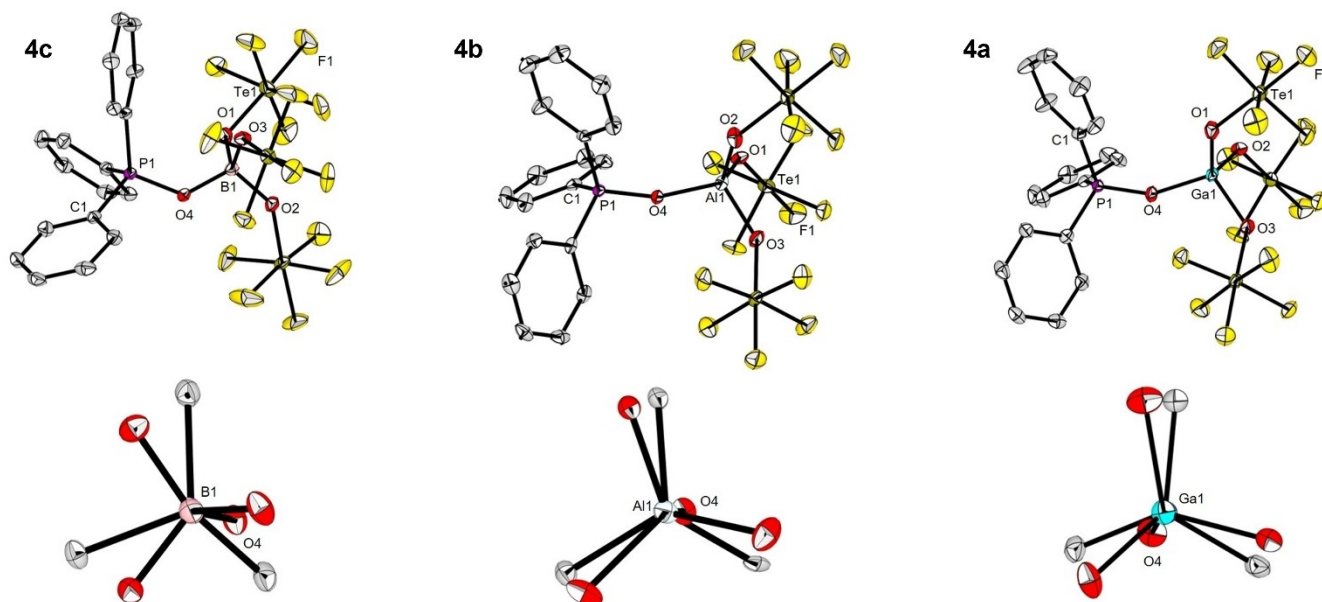

Figure 4. Top: Molecular structures of **4a–4c** in the solid state. Displacement ellipsoids set at 50% probability. H atoms are omitted for clarity. Bottom: Molecular structures of **4a–4c** viewed along the E–P vector (E=B, Al, Ga). Only the direct environment of E and P is shown for clarity. For crystallographic details and structural parameters see Supporting Information.

Table 2. Selected interatomic distances [pm] and angles [°] for **4a–4c**.			
	$Ga(OPPh_3)(OTeF_5)_3$ **4a**	$Al(OPPh_3)(OTeF_5)_3$ **4b**	$B(OPPh_3)(OTeF_5)_3$ **4c**
E–O4	180.9(3)	172.9(4)	147.9(4)
E–O$_{teflate}$	181.9(3)–182.3(3)	173.5(4)–174.4(4)	145.2(4)–147.0(4)
P–O4	153.5(3)	153.3(4)	156.0(2)
E–O4–P	153.61(18)	161.1(3)	129.28(18)
O$_{teflate}$–E–P–C	14.73(15)–20.32(17)	13.01(23)–17.51(26)	31.43(19)–44.55(35)

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ally similar group 13 Lewis superacids (Table 3). The FIA, CIA and HIA were chosen to give a multidimensional overview for the comparison of the Lewis acidity, including both hard and soft acidity.[8,30] For comparison, compound **1** was calculated as the hypothetical monomer and as the dimer, which is formed in the solid state (see above). In addition, since SO_2ClF has been shown to be the ideal solvent for **1**, the ion affinities for the solvent adduct $Ga(SO_2ClF)_2(OTeF_5)_3$ were calculated as well (Table 3). Regarding the FIA, not only the molecular compound **1**, but also the dimer and the SO_2ClF adduct all significantly exceed that of SbF_5, which allows to classify **1** as a hard Lewis superacid (see Table 3). To our best knowledge, this classification makes **1** the only literature-known example of an isolated hard gallium Lewis superacid. The calculated FIA value of **1** places it below the structurally similar aluminum Lewis superacid $Al(OTeF_5)_3$, yet above the boron Lewis superacid $B(OTeF_5)_3$. Due to the softer nature of the gallium atom compared to boron and aluminum, the CIA and HIA values were calculated to showcase the outstanding acidity of **1**, outclassing $Al(OTeF_5)_3$ and $B(OTeF_5)_3$ in these categories. With a HIA value of 590 kJ mol^{-1} (BP86/def-SV(P))/637 kJ mol^{-1} (B3LYP/def2-TZVPP), the threshold for soft Lewis superacidity is significantly exceeded by 122 kJ mol^{-1}/164 kJ mol^{-1}, respectively.[6]

Reactivity of Ga(OTeF$_5$)$_3$

The combination of Lewis acids and Brønsted acids leads to an increased Brønsted acidity as for example in HF/SbF_5 and HSO_3F/SbF_5. With this type of acidic systems in mind, we decided to study the use of **1** in combination with Brønsted acids. The reaction of **1** and $HOTeF_5$ with diethyl ether OEt_2 in SO_2ClF led to the oxonium salt $[H(OEt_2)_2][Ga(OEt_2)_2(OTeF_5)_4]$ **5** [Equation (5)].
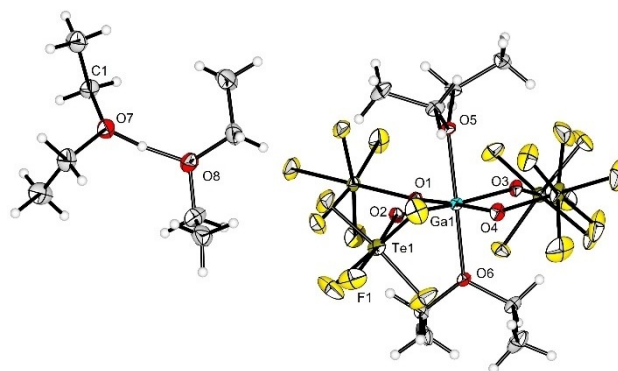

Figure 5. Section of the molecular structure of the oxonium salt **5** in the solid state. Displacement ellipsoids set at 50% probability. Selected bond lengths [pm] and angles [°]: Ga1–O1 194.1(3), Ga1–O2 193.7(3), Ga1–O3 192.4(3), Ga1–O4 193.4(3), Ga1–O5 203.5(3), Ga1–O6 202.8(3), O1–Ga1–O3 176.18(12), O2–Ga1–O4 176.12(12), O5–Ga1–O6 179.28(12). For crystallographic details see Supporting Information.

$$Ga(OTeF_5)_3 \xrightarrow[\substack{SO_2ClF \\ -40\,°C}]{\substack{1.\ HOTeF_5 \\ 2.\ OEt_2}} [H(OEt_2)_2][Ga(OEt_2)_2(OTeF_5)_4] \quad (5)$$

1   **5**
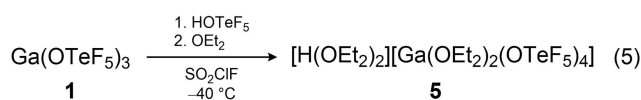
This type of protonated ethers have previously been described in the literature as the reaction product of HX (X=Cl, Br) with an alkali salt of a weakly coordinating anion like $[B(3,5-(CF_3)_2C_6H_3)_4]^-$, $[Al(OC(CF_3)_3)_4]^-$ or $[CHB_{11}H_5Cl_6]^-$ in OEt_2 or the direct protonation of OEt_2 with a Brønsted superacid like $[C_6H_7][CB_{11}H_6Cl_6]$.[32] Single-crystals of the oxonium salt **5** suitable for X-ray diffraction could be obtained by cooling a CH_2Cl_2 solution of **5** to −80 °C. The molecular structure of **5** in the solid state is shown in Figure 5. The oxonium salt **5** crystallizes in the triclinic space group $P\bar{1}$. The acidic proton in the oxonium cation connects two OEt_2 moieties through a hydrogen bond, forming the $[H(OEt_2)_2]^+$ cation. The gallium atom in the anion is

Table 3. Calculated fluoride (FIA), chloride (CIA) and hydride (HIA) ion affinities for selected Lewis acids. The ion affinities were calculated using Me$_3$SiX (X=F, Cl, H) as anchor point.[8,30]
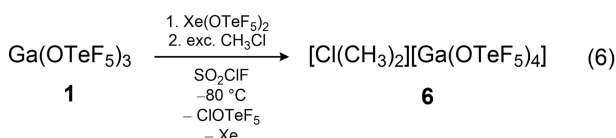
Compound	FIA [kJ mol^{-1}]		CIA [kJ mol^{-1}]		HIA [kJ mol^{-1}]	
	BP86/def-SV(P)	B3LYP/def2-TZVPP	BP86/def-SV(P)	B3LYP/def2-TZVPP	BP86/def-SV(P)	B3LYP/def2-TZVPP
Ga(OTeF$_5$)$_3$	559	591	404	541	590	637
[Ga(OTeF$_5$)$_3$]$_2$[a]	532	547	376	497	563	593
Ga(SO$_2$ClF)$_2$(OTeF$_5$)$_3$	545	538	389	488	576	583
Al(OTeF$_5$)$_3$	591	637	380	520	513	563
B(OTeF$_5$)$_3$	550	508	315	371	525	497
Ga(C$_2$F$_5$)$_3$[b]	477	503	328	364	476	523
Ga(C$_6$F$_5$)$_3$	449	455	295	311	446	468
GaCl$_3$	432	439	284	300	432	454
SbF$_5$[c]	488	499	–	–	–	–
B(C$_6$F$_5$)$_3$[d]	–	–	–	–	468	473

[a] Reported values are given per monomeric unit. [b] Not isolable as the free monomer. Only adducts reported.[31] [c] Threshold for hard Lewis superacids.[30] [d] Threshold for soft Lewis superacids.[6]

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coordinated by four teflate groups in the equatorial plane and two molecules of OEt_2 in the *trans* axial positions of a distorted octahedral geometry. This octahedral coordination motif of the anion has also been reported for the silver salt $[Ag(thf)_6][Ga(thf)_2(OTeF_5)_4]$.[20]

The high Lewis acidity of **1** can further be used to access the strong oxidizing system $Ga(OTeF_5)_3/Xe(OTeF_5)_2$ in SO_2ClF. In this room-temperature stable system, $Ga(OTeF_5)_3$ and $Xe(OTeF_5)_2$ interact with each other, allowing the teflate groups to rapidly exchange between the two compounds. This can be observed in the ^{19}F NMR spectrum at room temperature, as it only shows one sharp AB_4 pattern for the teflate groups, indicating that the gallium-based Lewis superacid does not abstract a teflate group from the $Xe(OTeF_5)_2$ but rather an exchange equilibrium occurs. However, cooling the solution to $-80\,°C$ leads to a significant broadening of the AB_4 pattern, while further cooling to below $-110\,°C$ results in the splitting of the signal into two separate AB_4 patterns with a ratio of 2:3. The two new signals can be assigned to the noninteracting solvated $Ga(OTeF_5)_3$ and $Xe(OTeF_5)_2$ (SI Figure 20).

The oxidizing power of the new $Ga(OTeF_5)_3/Xe(OTeF_5)_2$ system can be utilized in the synthesis of dialkyl chloronium cations. The synthesis of this highly reactive chloronium cations using the oxidation of chloroalkanes has previously been performed using the ionic aluminate- and antimonate-based xenonium salts $[Xe(OTeF_5)][E(OTeF_5)_n]$ ($E=Al$, $n=4$; $E=Sb$, $n=6$).[33] Upon the addition of an excess of chloromethane to the $Ga(OTeF_5)_3/Xe(OTeF_5)_2$ system, the chlorine atom in MeCl is instantaneously oxidized even at $-80\,°C$, generating a methyl cation *in situ*, which reacts with another equivalent of MeCl to form the chloronium salt $[Cl(CH_3)_2][Ga(OTeF_5)_4]$ **6** [Equation (6)]. After removing all volatiles from the reaction mixture under reduced pressure the pure product could be obtained as a colorless solid with a yield of 94%. The IR spectrum of **6** is in good agreement with literature-known dimethyl chloronium salts.[34,35]

$$Ga(OTeF_5)_3 \xrightarrow[\substack{-80\,°C \\ -ClOTeF_5 \\ -Xe}]{\substack{1.\ Xe(OTeF_5)_2 \\ 2.\ exc.\ CH_3Cl \\ SO_2ClF}} [Cl(CH_3)_2][Ga(OTeF_5)_4] \qquad (6)$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{6}$$

The ^1H NMR spectrum of **6** shows a singlet at 5.75 ppm ($^1J_{H-C}=162$ Hz) that is assigned to the methyl groups of the $[Cl(CH_3)_2]^+$ cation. In addition, in the $^1H,^{13}C$ HMBC spectrum a cross-signal can be observed due to a $^3J_{H-C}$ coupling. The ^{19}F and ^{71}Ga NMR spectra of **6** show the characteristic signals of the $[Ga(OTeF_5)_4]^-$ anion.[20] Dimethyl chloronium salts are highly electrophilic methylation reagents that are able to alkylate a broad variety of weakly nucleophilic substrates.[34,36]

Conclusions

We report on the rare example of an isolable molecular gallium-based soft and hard Lewis superacid $Ga(OTeF_5)_3$ **1**, which is synthesized quantitatively and on a gram scale in an easy and solvent-free process by means of a reaction of $GaCl_3$ with $ClOTeF_5$. Compound **1** was characterized by spectroscopic methods and quantum-chemical calculations, indicating a monomeric structure in solution and a dimeric structure in the solid state. The Lewis acidity of **1** has been assessed experimentally and theoretically by standard methods and compared to other strong Lewis acids. The calculated FIA and HIA values of **1** significantly exceed the thresholds for hard and soft Lewis superacidity. The high Lewis acidity of **1** has been used to increase the Brønsted acidity of $HOTeF_5$ for the successful synthesis of the oxonium salt $[H(OEt_2)_2][Ga(OEt_2)_2(OTeF_5)_4]$ **5**. Furthermore, it was shown that **1** is able to form a strong oxidizing system with $Xe(OTeF_5)_2$ in SO_2ClF, which allows the synthesis of the powerful methylation reagent $[Cl(CH_3)_2][Ga(OTeF_5)_4]$ **6**. With the versatile use of **1** in super-acidic and highly oxidizing systems we have demonstrated that the synthesis of reactive cations stabilized by the weakly coordinating anion $[Ga(OTeF_5)_4]^-$ is possible and will be further explored in the future.

Supporting Information Summary

The authors have cited additional references within the Supporting Information.[37–46]

Deposition Numbers 2380924 (for **2**), 2380925 (for **4a**), 2165789 (for **4b**), 2380922 (for **4c**) and 2380923 (for **5**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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