

Synthesis and Structural Characterization of Tetraalkylammonium Salts of the Weakly Coordinating Anion $[\text{Al}(\text{OTeF}_5)_4]^-$

Sofiya Kotsyuda,^[a] Anja Wiesner,^[a] Simon Steinhauer,^[a] and Sebastian Riedel*^[a]

Dedicated to Professor Dr. Thomas Klapötke on the occasion of his 60th birthday

Abstract. The weakly coordinating properties of the $[\text{Al}(\text{OTeF}_5)_4]^-$ anion were studied by the synthesis and characterization of its tetraalkylammonium salts $[\text{NAlk}_4][\text{Al}(\text{OTeF}_5)_4]$ [$\text{Alk}_4 = -(\text{CH}_3)_4, -(\text{C}_2\text{H}_5)_4, -(\text{C}_2\text{H}_5)_3\text{CH}_3, -(\text{C}_3\text{H}_7)_4, -(\text{C}_4\text{H}_9)_4$]. The one-pot synthesis includes formation of the Brønsted acid in 1,2-difluorobenzene,

$\text{H}[\text{Al}(\text{OTeF}_5)_4]_{(\text{solv.})}$, and its reaction with $[\text{NAlk}_4]\text{Cl}$ [$\text{Alk}_4 = -(\text{CH}_3)_4, -(\text{C}_2\text{H}_5)_4, -(\text{C}_2\text{H}_5)_3\text{CH}_3, -(\text{C}_3\text{H}_7)_4, -(\text{C}_4\text{H}_9)_4$] to the corresponding salts. Single crystals were obtained for $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Al}(\text{OTeF}_5)_4]$ and characterized by X-ray diffraction analysis.

Introduction

The coordinating properties of so-called weakly coordinating anions (WCAs) are nowadays usually associated with a low nucleophilicity and basicity as well as a high stability against oxidation and strong electrophiles which goes along with the delocalization of the negative charge over the large surface area.^[1] The chemistry of fluorinated WCAs has been developed about three decades ago and was typically represented by $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{AsF}_6]^-$, $[\text{SbF}_6]^-$ at the time.^[2] By introducing perfluorinated alkyl or aryl substituents like in $[\text{B}(\text{CF}_3)_4]^-$ and $[\text{B}(\text{C}_6\text{F}_5)_4]^-$, the weakly coordinating properties and stabilities towards electrophiles and oxidants could be improved.^[3,4] Another important contribution to this field are the aluminum-based anions with highly fluorinated alkoxy groups such as $[\text{Al}(\text{OR}^F)_4]^-$ [$\text{R}^F = -\text{C}(\text{CF}_3)_3, -\text{C}(\text{H})(\text{CF}_3)_2, -\text{C}(\text{CH}_3)(\text{CF}_3)_2, -\text{C}(\text{Ph})(\text{CF}_3)_2$].^[11,5–6] Due to the strong electron-withdrawing property,^[7] comparable to fluorine, and a high steric demand the pentafluoroorthotellurate ligand, $-\text{OTeF}_5$, can also form weakly coordinating anions with various central atoms: $[\text{E}(\text{OTeF}_5)_n]^-$ ($n = 4, \text{E} = \text{B}$, or $n = 6, \text{E} = \text{As}, \text{Sb}, \text{Bi}, \text{Nb}$).^[8–13] Recently, our workgroup introduced the $[\text{Al}(\text{OTeF}_5)_4]^-$ anion^[12] and demonstrated its potential for the stabilization of reactive cations by the synthesis and first structural proof of $[\text{P}_4\text{H}][\text{Al}(\text{OTeF}_5)_4]$. Due to their chemical stability, WCAs are used for the synthesis of substances for potential electrochemical applications, for example, $[\text{NR}_4][\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4]$,

or $[\text{NR}_4][\text{Al}\{\text{OC}(\text{H})(\text{CF}_3)_2\}_4]$ ($\text{R} = \text{Bu}, \text{Et}, \text{Me}$), where the most suitable are those with ionic liquids properties.^[8,9]

Herein we report about the preparation and characterization of a series of $[\text{NAlk}_4][\text{Al}(\text{OTeF}_5)_4]$ salts [$\text{Alk}_4 = -(\text{CH}_3)_4, -(\text{C}_2\text{H}_5)_4, -(\text{C}_2\text{H}_5)_3\text{CH}_3, -(\text{C}_3\text{H}_7)_4, -(\text{C}_4\text{H}_9)_4$].

Results and Discussion

The synthesis of the $[\text{NAlk}_4][\text{Al}(\text{OTeF}_5)_4]$ salts, where $\text{Alk}_4 = -(\text{CH}_3)_4, -(\text{C}_2\text{H}_5)_4, -(\text{C}_2\text{H}_5)_3\text{CH}_3, -(\text{C}_3\text{H}_7)_4, -(\text{C}_4\text{H}_9)_4$, includes the formation of protonated 1,2-difluorobenzene by reacting $\text{Al}(\text{C}_2\text{H}_5)_3$ with 4 equivalents of HOTeF_5 (Figure 1) as a first step.

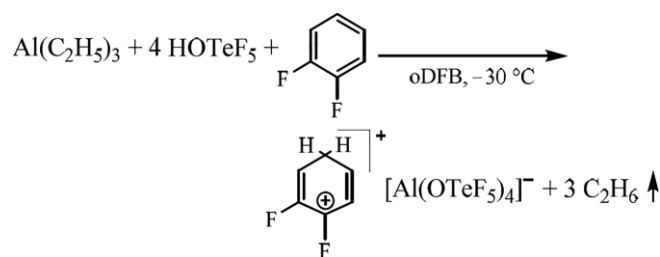


Figure 1. The formation of the Brønsted acid in 1,2-difluorobenzene.

Thereupon, the in situ formed Brønsted acid is reacted with $[\text{NAlk}_4]\text{Cl}$ [$\text{Alk}_4 = -(\text{CH}_3)_4, -(\text{C}_2\text{H}_5)_4, -(\text{C}_2\text{H}_5)_3\text{CH}_3, -(\text{C}_3\text{H}_7)_4, -(\text{C}_4\text{H}_9)_4$], added either neat or as a solution in dichloromethane, which is followed by HCl evolution (Figure 2). The synthesis of the $[\text{N}(\text{CH}_3)_4][\text{Al}(\text{OTeF}_5)_4]$ salt results in a good yield (84%), whereas the quaternary ammonium salts of the $[\text{Al}(\text{OTeF}_5)_4]^-$ anion with longer alkyl chains approach yields up to 99%, which is connected to a better solubility in 1,2-difluorobenzene of the latter ones.

In the following, the NMR spectra of $[\text{N}(\text{CH}_3)_4][\text{Al}(\text{OTeF}_5)_4]$ are discussed as a typical example of the described series. The ^{19}F NMR spectrum shows the typical AB_4 spin-spin splitting

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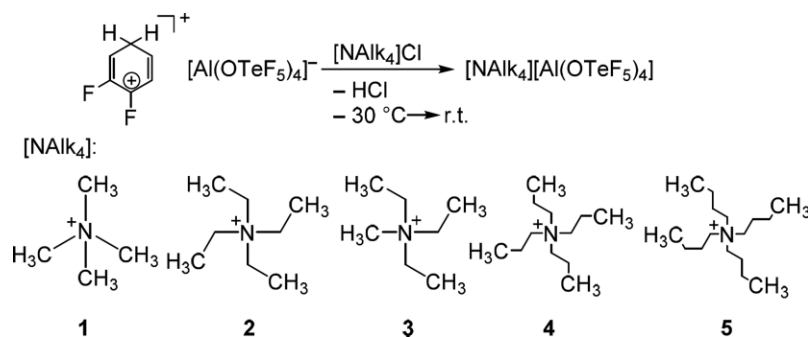


Figure 2. The formation of $[NAlk_4][Al(OTeF_5)_4]$ salts.

Table 1. Assignment of the vibrational modes of $[N(CH_3)_4][Al(OTeF_5)_4]$ (1), $[N(C_2H_5)_4][Al(OTeF_5)_4]$ (2), $[N(C_2H_5)_3CH_3][Al(OTeF_5)_4]$ (3), $[N(C_3H_7)_4][Al(OTeF_5)_4]$ (4), and $[N(C_4H_9)_4][Al(OTeF_5)_4]$ (5).

Assignment	1	2	3	4	5
$\nu(CH)$	3050 (vw)	3006 (vw)	3014 (vw)	2982 (vw)	2977 (vw)
$\nu(CH)$	–	–	–	2944 (vw)	–
$\nu(CH)$	–	–	–	2892 (vw)	2878 (vw)
$\delta(CH_3)$	1488 (m)	1488 (m)	1485 (m)	1475 (m)	1480 (m)
$\delta(CH)$	1421 (vw)	1396 (m)	1462 (m)	1386 (vw)	1466 (vw)
$\rho(CH_3)$	–	1173 (m)	1194 (vw)	–	–
$\nu_{as}(Al-O)$	925 (s)	930 (s)	928 (s)	929 (s)	928 (s)
$\nu(CN)$	838 (w)	–	811(w)	–	–
$\nu(CN)$	780 (m)	784 (w)	777 (w)	–	–
$\nu_{as}(Te-F_4)$	706 (s)	705 (s)	704 (s)	701 (s)	711(s)
$\nu_{as}(O-Te-F)$	687 (vs)	688 (vs)	688 (vs)	688 (vs)	692 (vs)
$\delta(Al-O-Te)$	567 (m)	–	–	–	–
$\nu_s(Al-O)$	540 (m)	550 (m)	550 (m)	560 (m)	550 (m)
$\delta(C-N)$	457 (m)	–	422 (m)	421 (vw)	–

pattern that arises from resonances of the axial F_A and the four equatorial F_B fluorine nuclei which are split into a pseudo-quintet at -38.7 ppm (F_A) and a pseudo-doublet at -45.9 ppm (F_B) by a $^2J(^{19}F, ^{19}F)$ coupling constant of 188 Hz. Moreover, the ^{125}Te satellites with coupling constants of $^2J(^{125}Te, ^{19}F_A) = 3342$ Hz and $^2J(^{125}Te, ^{19}F_B) = 3473$ Hz are observed. The ^{27}Al NMR spectrum depicts a resonance at $\delta = 46.8$ ppm with ^{125}Te satellites of the isotopologues $[Al(O^{125}TeF_5)(OTeF_5)_3]^-$ and $[Al(O^{125}TeF_5)_2(OTeF_5)_2]^-$ with a $^2J(^{125}Te, ^{27}Al)$ coupling constant of 72 Hz. The 1H NMR spectra show the characteristic resonances for the respective $[NAlk_4]^+$ cation.

The IR spectra of $[NAlk_4][Al(OTeF_5)_4]$ depict the expected vibrational bands for $[Al(OTeF_5)_4]^-$ as well as for the corresponding cations and are in agreement with the literature (see Table 1).^{114–151} Mass spectra of all salts show the typical fragmentation patterns of $[NAlk_4]^+$ and of $[Al(OTeF_5)_4]^-$ ionic species (see Experimental Section). For this homologous series of salts, a transition from classical salts ($[N(CH_3)_4][Al(OTeF_5)_4]$ and $[N(C_2H_5)_4][Al(OTeF_5)_4]$) to ionic liquids ($[N(C_2H_5)_3CH_3][Al(OTeF_5)_4]$, $[N(C_3H_7)_4][Al(OTeF_5)_4]$ and $[N(C_4H_9)_4][Al(OTeF_5)_4]$) with the extension of the alkyl chain is observed (see Table 2). As it is reported in the literature,¹¹³ the use of asymmetric cations can result in the lowering of the melting points of the respective salts, which can be observed for $[N(C_2H_5)_3CH_3][Al(OTeF_5)_4]$, whose melting point is drastically lower than that of $[N(C_2H_5)_4][Al(OTeF_5)_4]$. The salts $[N(CH_3)_4][Al(OTeF_5)_4]$ and $[N(C_2H_5)_4][Al(OTeF_5)_4]$ exhibit

higher thermal stability than $[N(C_3H_7)_4][Al(OTeF_5)_4]$ and $[N(C_4H_9)_4][Al(OTeF_5)_4]$ and can be shortly handled on air without change in the mass and state of matter. In case of $[N(C_3H_7)_4][Al(OTeF_5)_4]$ and $[N(C_4H_9)_4][Al(OTeF_5)_4]$ salts, we observed an immediate increase in the mass and change from solid to a liquid state while weighting on air, which might be due to absorption of moisture from air.

Table 2. Decomposition temperatures T_d and melting points T_m of the synthesized salts.

	Compound	T_d / C	T_m / C
1	$[N(CH_3)_4][Al(OTeF_5)_4]$	235	190
2	$[N(C_2H_5)_4][Al(OTeF_5)_4]$	215	135
3	$[N(C_2H_5)_3CH_3][Al(OTeF_5)_4]$	185	72
4	$[N(C_3H_7)_4][Al(OTeF_5)_4]$	210	98
5	$[N(C_4H_9)_4][Al(OTeF_5)_4]$	182	58

Single crystals of $[N(C_4H_9)_4][Al(OTeF_5)_4]$ suitable for an X-ray diffraction analysis were obtained by slow cooling of a solution in a mixture of *n*-pentane, dichloromethane, and chloroform (3:1:1) to -25 °C. The salt $[N(C_4H_9)_4][Al(OTeF_5)_4]$ crystallizes in the tetragonal space group $I\bar{4}2d$ (see Figure 3). The crystal structure of $[N(C_4H_9)_4][Al(OTeF_5)_4]$ consists of well isolated $[N(C_4H_9)_4]^+$ cations and $[Al(OTeF_5)_4]^-$ anions. The central atom of the anion exhibits a distorted tetrahedral environment with the bond angle $(Al-O-Te) = 139.2(4)–146.8(4)^\circ$ being nearly as distorted as in the $Cs[Al(OTeF_5)_4]$ salt $(Al-O-Te) = 136.4(2)–149.3(3)^\circ$.¹¹⁶ Like the anion, the $[N(C_4H_9)_4]^+$ cation

also shows a disorder and features a C5–N1–C1 angle of 106.0(4)°. $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$ was crystallized as well; however, since the crystal is highly disordered, it is shown in the Supporting Information.

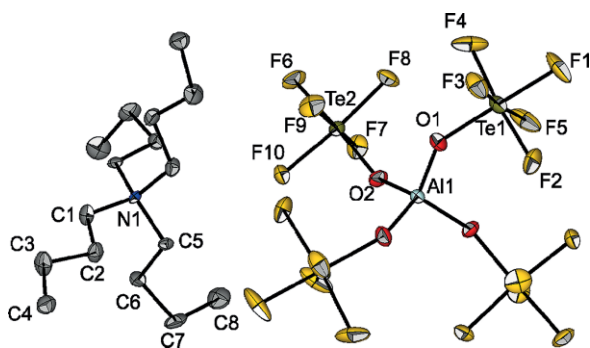


Figure 3. Molecular structure of $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Al}(\text{OTeF}_5)_4]$ in the solid state with thermal ellipsoids shown at the 50% probability level. Hydrogens are omitted for clarity. Selected bond lengths in pm: Al1–O1 173.7(6), Te1–F1 183.1(6), Te1–F2 183.3(5), Te1–F3 181.7(5), Te1–F4 182.6(5), Te1–F5 183.1(5), Te1–O1 181.4(6), Te2–F6 183.0(5), Te2–F7 181.5(5), Te2–F8 182.4(5), Te2–F9 182.6(5), Te2–F10 183.2(5), N1–C1 151.6(9), C1–C2 150.6(11), C2–C3 150.0(12), C3–C4 150.7(11), N1–C5 152.1(9), C5–C6 150.7(11), C6–C7 154.0(11), C7–C8 152.1(12).

Conclusions

Herein we reported on the facile one-pot syntheses and characterization of the tetraalkylammonium salts of the weakly coordinating $[\text{Al}(\text{OTeF}_5)_4]^-$ anion. The salts $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$ and $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Al}(\text{OTeF}_5)_4]$ were additionally characterized by single-crystal X-ray diffraction analysis. The melting points of the obtained salts showed the transition from classical salts to formal ionic liquids by either increasing the length of the alkyl chains or by the use of asymmetric cations.

Experimental Section

All reactions were carried out under inert conditions using standard Schlenk techniques. Glass vessels were greased with Teflon III. All solid materials and triethylaluminum ($\text{Al}(\text{C}_2\text{H}_5)_3$, 93%) were handled inside a glove box with an atmosphere of dry argon ($\text{O}_2 < 0.5$ ppm, $\text{H}_2\text{O} < 0.5$ ppm). The tetraalkylammonium chlorides $[\text{NAlk}_4]\text{Cl}$ [$\text{Alk}_4 = -\text{CH}_3, -\text{C}_2\text{H}_5, -(\text{C}_2\text{H}_5)_3\text{CH}_3, -\text{C}_3\text{H}_7, -\text{C}_4\text{H}_9$] were dried under vacuum and heating up to 100 °C over 24 h prior to use. The pentafluoroorthotelluric acid was synthesized as reported in the literature.^[17] All solvents were dried either with CaH_2 or with Sicapent® before use. Elemental analysis was performed with an Elementar vario EL III. Double determination was performed to ensure homogeneous samples. IR spectra were collected on a Bruker ALPHA FTIR spectrometer equipped with a diamond ATR attachment in an argon-filled glove box. NMR spectra were recorded on either a JEOL 400 MHz ECS or ECZ-R spectrometer. Reported chemical shifts are referenced to the Ξ values given in IUPAC recommendations of 2008^[18] using the ^2H signal of the deuterated solvent as internal reference. For external locking $[\text{D}_6]\text{acetone}$ was flame sealed in a glass capillary and the lock oscillator frequency was adjusted to give $\delta(^1\text{H}) = 7.26$ ppm for a CHCl_3 sample locked on the capillary. Chemical shifts and coupling constants of strongly coupled spin systems are given

as simulated in g NMR spectroscopy.^[19] Mass spectra were measured on an Advion Compact mass spectrometer expression L with a quadrupole mass filter. Samples were inserted directly using a Hamilton syringe and measured with ESI in acetonitrile. Crystal structures were obtained on a Bruker D8 Venture diffractometer with a PHOTON 100 CMOS area detector using $\text{Mo-}K_\alpha$ radiation. Single crystals were coated with a perfluoroether oil at -25 °C and selected in a nitrogen atmosphere. Using Olex2,^[20] the structures were solved with the ShelXT^[21] structure solution program by intrinsic phasing and refined with the ShelXL^[22] refinement package using least-squares minimization. The melting point and decomposition temperature of crystalline samples were determined on a Stuart Melting Point Apparatus SMP30.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1951182 ($[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$) and CCDC-1971655 ($[\text{N}(\text{C}_4\text{H}_9)_4][\text{Al}(\text{OTeF}_5)_4]$) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>).

Synthesis of $[\text{N}(\text{CH}_3)_4][\text{Al}(\text{OTeF}_5)_4]$: A sample of $\text{Al}(\text{C}_2\text{H}_5)_3$ (60 mg, 0.53 mmol, 1 equiv.) was dissolved in 5 mL of 1,2-difluorobenzene. The solution was degassed and HOTeF_5 (508 mg, 2.1 mmol, 4 equiv.) was condensed onto it at -196 °C. A bubbler was added and the reaction mixture was warmed up to -30 °C, giving rise to a yellow solution. Solid $[\text{N}(\text{CH}_3)_4]\text{Cl}$ (58 mg, 0.53 mmol, 1 equiv.) was added to the reaction mixture through a funnel, and the mixture was slowly warmed to room temperature. After stirring for 24 h, all volatile parts of the reaction mixture were removed under reduced pressure and the residue was washed with a 1:1 mixture of dichloromethane and 1,2-difluorobenzene. $[\text{N}(\text{CH}_3)_4][\text{Al}(\text{OTeF}_5)_4]$ was obtained as a colorless powder (84%, 465 mg, 0.44 mmol). **EA:** $\text{C}_4\text{H}_{12}\text{NAlO}_4\text{Te}_4\text{F}_{20}$ (1055.49 $\text{g}\cdot\text{mol}^{-1}$): C 4.857 (calcd. 4.55); H 1.256 (calcd. 1.14); N 1.292 (calcd. 1.32)%. **^1H NMR** (401 MHz, CD_2Cl_2 , 22 °C): $\delta = 2.95$ [s, CH_3] ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2 , 22 °C): $\delta = -38.7$ [m, 1F_A , $^2J(^{19}\text{F}, ^{19}\text{F}) = 189$, $^1J(^{19}\text{F}_A, ^{125}\text{Te}) = 3348$ Hz], -45.7 [m, 4F_B , $^1J(^{125}\text{Te}, ^{19}\text{F}_B) = 3465$ Hz] ppm. **^{27}Al NMR** (104 MHz, CD_2Cl_2 , 22 °C): $\delta = -47.5$ [s, 75% $[\text{Al}(\text{OTeF}_5)_4]^-$; d, 22.5% $[\text{Al}(\text{OTeF}_5)_3(\text{O}^{125}\text{TeF}_5)]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 73$ Hz; t, 2.5% $[\text{Al}(\text{OTeF}_5)_2(\text{O}^{125}\text{TeF}_5)_2]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 71$ Hz] ppm. **ESI-MS** (3.5 kV): m/z (%) negative: 225 (20) $[\text{TeF}_5]^-$, 241 (100) $[\text{OTeF}_5]^-$, 479 (1) $[\text{H}(\text{OTeF}_5)_2]^-$, 763 (2) $[\text{Al}(\text{OTeF}_5)_3\text{F}]^-$, 983 (1) $[\text{Al}(\text{OTeF}_5)_4]^-$; positive: 74.2 (100) $[\text{N}(\text{CH}_3)_4]^+$. **IR** (ATR, 25 °C): $\tilde{\nu} = 3050$ [ν_{w} , $\nu(\text{CH})$], 1488 [m, $\delta(\text{CH}_3)$], 1421 [ν_{w} , $\delta(\text{CH})$], 925 [s, $\nu_{\text{as}}(\text{Al}-\text{O})$], 838 [w, $\nu(\text{CN})$], 780 [w, $\nu(\text{CN})$], 706 [s, $\nu_{\text{as}}(\text{Te}-\text{F}_4)$], 687 [vs, $\nu_{\text{as}}(\text{O}-\text{Te}-\text{F})$], 567 [m, $\delta(\text{Al}-\text{O}-\text{Te})$], 540 [m, $\nu_{\text{s}}(\text{Al}-\text{O})$], 457 [m, $\delta(\text{C}-\text{N})$] cm^{-1} .

Synthesis of $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$: The synthesis was analogous to the one of $[\text{N}(\text{CH}_3)_4][\text{Al}(\text{OTeF}_5)_4]$ except for the addition of $[\text{N}(\text{C}_2\text{H}_5)_4]\text{Cl}$, which was prior to that dissolved in 2 mL of dichloromethane and added dropwise to the reaction mixture with a syringe. $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$ was obtained as a colorless powder (99%, 577 mg, 0.52 mmol). **EA:** $\text{C}_8\text{H}_{20}\text{NAlO}_4\text{Te}_4\text{F}_{20}$ (1111.60 $\text{g}\cdot\text{mol}^{-1}$): C 8.77 (calcd. 8.64); H 1.835 (calcd. 1.81); N 1.205 (calcd. 1.26)%. **^1H NMR** (401 MHz, CD_2Cl_2 , 22 °C): $\delta = 3.14$ [q, 8 H, CH_2 , $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz]; 1.30 [t, 12 H, CH_3 , $^3J(^1\text{H}, ^1\text{H}) = 7.3$, $^3J(^1\text{H}, ^{14}\text{N}) = 1.9$ Hz] ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2 , 22 °C): $\delta = -38.8$ [m, 1F_A , $^2J(^{19}\text{F}, ^{19}\text{F}) = 188$, $^1J(^{125}\text{Te}, ^{19}\text{F}_A) = 3342$ Hz], -45.7 [m, 4F_B , $^1J(^{125}\text{Te}, ^{19}\text{F}_B) = 3473$ Hz] ppm. **^{27}Al NMR** (104 MHz, CD_2Cl_2 , 22 °C): $\delta = 46.66$ [s, 75% $[\text{Al}(\text{OTeF}_5)_4]^-$; d, 22.5% $[\text{Al}(\text{OTeF}_5)_3(\text{O}^{125}\text{TeF}_5)]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 72$ Hz; t, 2.5% $[\text{Al}(\text{OTeF}_5)_2(\text{O}^{125}\text{TeF}_5)_2]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 71$ Hz] ppm. **ESI-MS** (3.5 kV): m/z (%) negative: 241 (100) $[\text{OTeF}_5]^-$, 479 (15) $[\text{H}(\text{OTeF}_5)_2]^-$, 763 (3) $[\text{Al}(\text{OTeF}_5)_3\text{F}]^-$, 981 (4) $[\text{Al}(\text{OTeF}_5)_4]^-$; positive: 130 (100) $[\text{N}(\text{C}_2\text{H}_5)_4]^+$. **IR** (ATR, 25 °C): $\tilde{\nu} = 3006$ [ν_{w} , $\delta(\text{CH})$], 1488 [m, $\delta(\text{CH})$],

1396 [m, $\delta(\text{CH})$], 1173 [m, $\rho(\text{CH}_3)$], 930 [s, $\nu_{\text{as}}(\text{Al-O})$], 784 [w, $\nu(\text{C-N})$], 705 [s, $\nu_{\text{as}}(\text{Te-F}_4)$], 688 [vs, $\nu_{\text{as}}(\text{O-Te-F})$], 550 [m, $\nu_{\text{s}}(\text{Al-O})$] cm^{-1} .

Synthesis of $[\text{N}(\text{C}_2\text{H}_5)_3\text{CH}_3][\text{Al}(\text{OTeF}_5)_4]$: The synthesis was analogous to the one of $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$. $[\text{N}(\text{C}_2\text{H}_5)_3\text{CH}_3][\text{Al}(\text{OTeF}_5)_4]$ was obtained as a colorless powder (99%, 580 mg, 0.52 mmol). **EA:** $\text{C}_{7.5}\text{H}_{18}\text{NAlO}_4\text{Te}_4\text{F}_{20}$ (1097.57 $\text{g}\cdot\text{mol}^{-1}$): C 7.974 (calcd. 7.66); H 1.695 (calcd. 1.65); N 1.285 (calcd. 1.27)%. **^1H NMR** (401 MHz, CD_2Cl_2 , 22 °C): $\delta = 3.18$ [q, 8 H, CH_2 , $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz], 2.83 [s, 3 H, CH_3], 1.53 [tt, 9 H, CH_3 , $^3J(^1\text{H}, ^1\text{H}) = 7.3$, $^3J(^1\text{H}, ^{14}\text{N}) = 1.9$ Hz] ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2 , 22 °C): $\delta = -40.8$ [m, 1 F_A , $^2J(^{19}\text{F}, ^{19}\text{F}) = 189$, $^1J(^{125}\text{Te}, ^{19}\text{F}_A) = 3354$ Hz], -48.8 [m, 4 F_B , $^1J(^{125}\text{Te}, ^{19}\text{F}_B) = 3461$ Hz] ppm. **^{27}Al NMR** (104 MHz, CD_2Cl_2 , 22 °C): $\delta = 46.8$ [s, 75%, $[\text{Al}(\text{OTeF}_5)_4]^-$]; d, 22.5% $[\text{Al}(\text{OTeF}_5)_3(\text{O}^{125}\text{TeF}_5)]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 72$ Hz; t, 2.5% $[\text{Al}(\text{OTeF}_5)_2(\text{O}^{125}\text{TeF}_5)_2]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 71$ Hz] ppm. **ESI-MS** (3.5 kV): m/z (%) negative: 241 (100) $[\text{OTeF}_5]^-$, 763 (4) $[\text{Al}(\text{OTeF}_5)_3\text{F}]^-$, 981 (5) $[\text{Al}(\text{OTeF}_5)_4]^-$; positive: 116.2 (100) $[\text{N}(\text{C}_2\text{H}_5)_3\text{CH}_3]^+$. **IR** (ATR, 25 °C): $\tilde{\nu} = 3014$ [vw, $\nu(\text{CH})$], 1485 [m, $\delta(\text{CH}_3)$], 1462 [m, $\delta(\text{CH})$], 1194 [m, $\rho(\text{CH}_3)$], 928 [vs, $\nu_{\text{as}}(\text{Al-O})$], 811 [w, $\nu(\text{CN})$], 777 [w, $\nu(\text{CN})$], 704 [s, $\nu_{\text{as}}(\text{Te-F}_4)$], 688 [vs, $\nu_{\text{as}}(\text{O-Te-F})$], 550 [m, $\nu_{\text{s}}(\text{Al-O})$], 422 [m, $\delta(\text{CN})$] cm^{-1} .

Synthesis of $[\text{N}(\text{C}_3\text{H}_7)_4][\text{Al}(\text{OTeF}_5)_4]$: The synthesis was analogous to the one of $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$. $[\text{N}(\text{C}_3\text{H}_7)_4][\text{Al}(\text{OTeF}_5)_4]$ was obtained as a colorless powder (99%, 600 mg, 0.52 mmol). **EA:** $\text{C}_{12}\text{H}_{28}\text{NAlO}_4\text{Te}_4\text{F}_{20}$ (1167.70 $\text{g}\cdot\text{mol}^{-1}$): C 12.45 (calcd. 12.34); H 2.421 (calcd. 2.41); N 1.125 (calcd. 1.19)%. **^1H NMR** (401 MHz, CD_2Cl_2 , 22 °C): $\delta = 2.89$ [m, 8 H, CH_2], 1.53 [m, 8 H, CH_2 , $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz], 0.88 [m, 12 H, CH_3 , $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz] ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2 , 22 °C): $\delta = -37.6$ [m, 1 F_A , $^2J(^{19}\text{F}, ^{19}\text{F}) = 189$, $^1J(^{125}\text{Te}, ^{19}\text{F}_A) = 3346$ Hz], -45.0 [m, 4 F_B , $^1J(^{125}\text{Te}, ^{19}\text{F}_B) = 3471$ Hz] ppm. **^{27}Al NMR** (104 MHz, CD_2Cl_2 , 22 °C): $\delta = 47.5$ [s, 75% $[\text{Al}(\text{OTeF}_5)_4]^-$]; d, 22.5% $[\text{Al}(\text{OTeF}_5)_3(\text{O}^{125}\text{TeF}_5)]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 73$ Hz; t, 2.5% $[\text{Al}(\text{OTeF}_5)_2(\text{O}^{125}\text{TeF}_5)_2]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 71$ Hz] ppm. **ESI-MS** (3.5 kV): m/z (%) negative: 241 (100) $[\text{OTeF}_5]^-$, 479 (5) $[\text{H}(\text{O-TeF}_5)_2]^-$, 763 (4) $[\text{Al}(\text{OTeF}_5)_3\text{F}]^-$, 981 (1) $[\text{Al}(\text{OTeF}_5)_4]^-$; positive: 186 (100) $[\text{N}(\text{C}_3\text{H}_7)_4]^+$. **IR** (ATR, 25 °C): $\tilde{\nu} = 2982$ [vw, $\nu(\text{CH})$], 2944 [vw, $\nu(\text{CH})$], 2892 [vw, $\nu(\text{CH})$], 1475 [m, $\delta(\text{CH}_3)$], 1386 [vw, $\delta(\text{CH})$], 929 [vs, $\nu_{\text{as}}(\text{Al-O})$], 701 [s, $\nu_{\text{as}}(\text{Te-F}_4)$], 688 [vs, $\nu_{\text{as}}(\text{O-Te-F})$], 560 [m, $\nu_{\text{s}}(\text{Al-O})$], 421 [vw, $\delta(\text{CN})$] cm^{-1} .

Synthesis of $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Al}(\text{OTeF}_5)_4]$: The synthesis was comparable to the one of $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$. $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Al}(\text{OTeF}_5)_4]$ was obtained as a colorless powder (99%, 635 mg, 0.52 mmol). **EA:** $\text{C}_{12}\text{H}_{28}\text{NAlO}_4\text{Te}_4\text{F}_{20}$ (1223.84 $\text{g}\cdot\text{mol}^{-1}$): C 16.19 (calcd. 15.7); H 3.024 (calcd. 2.96); N 1.00 (calcd. 1.14)%. **^1H NMR** (401 MHz, CD_2Cl_2 , 22 °C): $\delta = 3.94$ [m, 8 H, CH_2], 1.47 [m, 8 H, CH_2 , $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz], 1.25 [m, 8 H, CH_2 , $^2J(^1\text{H}, ^{14}\text{N}) = 7.4$ Hz], 0.88 [m, 12 H, CH_3 , $^3J(^1\text{H}, ^1\text{H}) = 7.3$ Hz] ppm. **^{19}F NMR** (377 MHz, CD_2Cl_2 , 22 °C): $\delta = -38.8$ [m, 1 F_A , $^2J(^{19}\text{F}, ^{19}\text{F}) = 189$, $^1J(^{125}\text{Te}, ^{19}\text{F}_A) = 3354$ Hz], -46.4 [m, 4 F_B , $^1J(^{125}\text{Te}, ^{19}\text{F}_B) = 3461$ Hz] ppm. **^{27}Al NMR** (104 MHz CD_2Cl_2 , 22 °C): $\delta = 47.5$ [s, 75% $[\text{Al}(\text{OTeF}_5)_4]^-$]; d, 22.5% $[\text{Al}(\text{OTeF}_5)_3(\text{O}^{125}\text{TeF}_5)]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 73$ Hz; t, 2.5% $[\text{Al}(\text{OTeF}_5)_2(\text{O}^{125}\text{TeF}_5)_2]^-$, $^2J(^{27}\text{Al}, ^{125}\text{Te}) = 71$ Hz] ppm. **ESI-MS** (3.5 kV): m/z (%) negative: 241 (100) $[\text{OTeF}_5]^-$, 479 (4) $[\text{H}(\text{OTeF}_5)_2]^-$, 763 (8) $[\text{Al}(\text{OTeF}_5)_3\text{F}]^-$, 981 (8) $[\text{Al}(\text{OTeF}_5)_4]^-$; positive: 242 (100) $[\text{N}(\text{C}_4\text{H}_9)_4]^+$. **IR** (ATR, 25 °C): $\tilde{\nu} = 2977$ [vw, $\nu(\text{CH})$], 2878 [vw, $\nu(\text{CH})$], 1480 [m, $\delta(\text{CH}_3)$], 1466 [vw, $\delta(\text{CH})$], 928 [s, $\nu_{\text{as}}(\text{Al-O})$], 711 [s, $\nu_{\text{as}}(\text{Te-F}_4)$], 692 [vs, $\nu_{\text{as}}(\text{O-Te-F})$], 550 [m, $\nu_{\text{s}}(\text{Al-O})$] cm^{-1} .

Crystallographic Data on $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Al}(\text{OTeF}_5)_4]$: M = 1223.84 $\text{g}\cdot\text{mol}^{-1}$; tetragonal, space group $I4_2d$ (no. 122), $a =$

14.4368(5) Å, $b = 14.4368(5)$ Å, $c = 34.2821(19)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 7145.1(6)$ Å³, $Z = 8$, $T = 100$ K, $\mu(\text{Mo-K}\alpha) = 3.387$ mm^{-1} , $\rho_{\text{calc}} = 2.275$ $\text{g}\cdot\text{cm}^{-3}$, 15715 reflections measured ($4.546^\circ \leq 2\theta \leq 52.796^\circ$), 3641 unique ($R_{\text{int}} = 0.0633$, $R_{\text{sigma}} = 0.0483$), which were used in all calculations. The final R_1 [$I > 2\sigma(I)$] was 0.0355 and wR_2 was 0.0644 (all data).

Supporting Information (see footnote on the first page of this article): The quaternary ammonia salts of WCA were characterized by ESI-MS, IR, ^1H , ^{19}F , ^{27}Al NMR, as well as via elemental analysis. Additionally, X-ray data for the $[\text{N}(\text{C}_2\text{H}_5)_4][\text{Al}(\text{OTeF}_5)_4]$ and $[\text{N}(\text{C}_4\text{H}_9)_4][\text{Al}(\text{OTeF}_5)_4]$ are presented.

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Keywords: Brønsted acid; Pentafluoroorthotellurates; Superacidic systems; Tellurium; Weakly coordinating anion

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