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A Fluent Transition from Triiodide, I_3^-, to Tris(trifluoromethyltellurate)(1−), $[(TeCF_3)_3]^-$—A Structural Study

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Dedicated to Professor Reint Eujen on the occasion of his 60th birthday

Abstract: A complete series of compounds with the anions $[(TeCF_3)_{3-x}I_x]^-$ ($x=0$–2) had been prepared and characterised in the solid state and by NMR spectroscopic methods. Dynamic behaviour in solution can be assumed for $[(TeCF_3)_3]^-$ and $[(TeCF_3)_2I]^-$, while in the solid state all three bis(triphenylphosphoranyliden)ammonium (PNP) salts resemble structures found in triiodides. The molecular structures of $[PNP][(TeCF_3)_{3-x}I_x]^-$ ($x=0$–2) are discussed in comparison with $[PNP]I_3$, I_2, and $Te_2(CF_3)_2$. On this basis, the structures of the $[(TeCF_3)_3]^-$ and $[(TeCF_3)I_2]^-$ ions are comparable to symmetric I_3^- ions, while the $[(TeCF_3)_2I]^-$ ion resembles an asymmetric I_3^- unit.

Keywords: iodine · polyanions · structure elucidation · tellurium

Introduction

A short time after the discovery of iodine and its classification as a new element, Pelletier and Caventou synthesised strychnine triiodide in 1819. In the meantime more than 500 triiodides with different cations have been prepared and characterised by X-ray diffraction (XRD) methods[1] among dozens of higher polyiodides.[2]

As a further development of "Grimm's hydride displacement", Haas[3] presented the "para-element concept". On the background of this semi-empirical approach, $[TeCF_3]^-$ resembles I^-, $(TeCF_3)_2$ consequently I_2, and $[(TeCF_3)_3]^-$ finally I_3^-. Tellurium and iodine as neighbours in the periodic table show comparable hardness in the sense of the Pearson hard/soft acid/base (HSAB) concept.[4] While several homonuclear polytellurides, such as Te_3^{2-} and Te_3^{4-}[5–7] have been structurally characterised, examples of tri(organotellurates), $[(TeR)_3]^-$, are limited to $[(TePh)_3]^-$, which has been prepared either by reduction of diphenylditellurium (PhTeTePh) by a samarium(II) complex[8] or sodium borohydride,[9] or by addition of LiTePh to PhTeTePh.[8] The structurally characterised compounds exhibit nearly linear $[(TePh)_3]^-$ moieties in the solid state.

In this paper, we discuss the molecular structures of the "para-element" series, $[(TeCF_3)_3]^-$, $[(TeCF_3)_2I]^-$, $[(TeCF_3)I_2]^-$, and I_3^- (Table 1).

Results and Discussion

Synthesis and molecular structure of $[PNP][(TeCF_3)_3]$ (PNP = bis(triphenylphosphoranyliden)ammonium): Since $[NMe_4][TeCF_3]$ has become easily accessible,[10] some efforts have been made to use this reagent to transfer the $TeCF_3$ group onto other elements. For example, $[PNP][Au(TeCF_3)_2]$[11] was obtained from the reaction of AuCl and $[NMe_4][TeCF_3]$ followed by cation exchange with a PNP halide (PNP = bis(triphenylphosphoranyliden)ammonium). Already the molecular structure of this anion resembles the $[AuI_2]^-$ analogue,[12] suggesting similar electronic nature of both the iodide and the $[TeCF_3]^-$ group.

The $[PNP]^+$ ion was chosen as a bulky cation with significant low symmetry that appears to be predestined to form crystalline materials with quasi-linear or planar cores.[12–14]

$Te_2(CF_3)_2$ itself behaves as a weak and soft acid in solution.[15] This is demonstrated by ^{19}F NMR experiments showing significant differences in shifts and coupling constants depending on the basicity of the solvent. Formation of $[NMe_4][(TeCF_3)_3]$ is achieved by combining equimolar amounts of $Te_2(CF_3)_2$ and $[NMe_4][TeCF_3]$ at ambient tem-

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Table 1. Compilation of selected bond lengths and angles for $[(TeCF_3)_3]^-$, $[(TeCF_3)I_2]^-$, $[(TeCF_3)_2I]^-$, and related compounds.

	$[(TeCF_3)_3]^-$	$[(TeCF_3)I_2]^-$	$[(TeCF_3)_2I]^-$	I_3^-	$[I_2{\cdot}I]^-$	$[I_2{\cdot}I]^-$	I_2	$(TeCF_3)_2$
d(Te–Te) [pm]	296.9(1)/298.3(1)		277.6(1)					266.9(3)
d(I–I) [pm]				289.6(1)/292.8(1)	279.1(4)/311.3(4)	275.3(1)/314.8(1)	271.5(6)	
d(Te–I) [pm]		293.7(1)/293.7(1)	323.9(1)					
∢(E-E-E) [°] (E=Te or I)	177.8(1)	178.1(1)	177.4(1)	178.8(1)	180.0(1)	170.9(1)		
ref.	this work	this work	this work	[13]	[24]	[25]	[26]	[17]

perature or below in anhydrous MeCN [Eq. (1)]. Exchange of NMe_4 to PNP gave $[PNP][(TeCF_3)_3]$ in approximately 87% yield.

$$[NMe_4][TeCF_3] + Te_2(CF_3)_2 \rightarrow [NMe_4][(TeCF_3)_3] \xrightarrow[-[NMe_4]I]{+[PNP]I} [PNP][(TeCF_3)_3] \quad (1)$$

NMR data of both the NMe_4 and PNP salts in CD_3CN are identical irrespective of the cation. Only one signal was observed for the $[(TeCF_3)_3]^-$ ion in the ^{19}F, ^{13}C and ^{125}Te NMR spectra; this result gives evidence of fast exchange reactions [Eq. (2)]. In comparison to the known equilibrium between I_3^-, I_2 and I^-, similar relations for $[(TeCF_3)_3]^-$ appear to be very probable.

$$[(TeCF_3)_3]^- \rightleftharpoons Te_2(CF_3)_2 + [TeCF_3]^- \quad (2)$$

$[PNP][(TeCF_3)_3]$ is readily soluble in nitriles, acetic acid ethyl ester, tetrahydrofuran, dichlormethane and benzene, sparingly soluble in toluene and diethyl ether, and insoluble in alkanes and water. It can be stored under water for several days without significant decomposition. In contrast, adding traces of water to a solution in acetonitrile forces the formation of TeO_2 and CF_3H.

Bis(triphenylphosphoranylidene)ammonium tris(trifluoromethyltellurate)(1−) ($[PNP][(TeCF_3)_3]$) was isolated from the reaction mixture as a red crystalline material with a visible melting point of 80–82 °C. It was identified by XRD methods and elemental analysis.

The salt crystallises in the triclinic space group $P\bar{1}$ with $a=1094.4(1)$, $b=1170.4(1)$, $c=1666.3(1)$ pm, $\alpha=82.03(1)$, $\beta=78.80(1)$, $\gamma=84.59(1)°$ and $Z=2$. The structure of the anion is depicted in Figure 1 and consists of distorted, isolated linear trimeric units (∢Te-Te-Te = 177.8(1)°) that are intercalated into a PNP framework. Shortest contacts between tellurium and hydrogen atoms of 338.8 pm are longer than the sum of van der Waals radii.[16] Te–Te bond lengths are 296.9(1) and 298.3(1) pm, respectively. These values appear to be characteristic for a Te-Te-Te arrangement in comparison with literature values.[8,9] Te–C bonds lengths of the terminal trifluoromethyltellurium groups are 213.7(7) and 214.1(5) pm, while that to the central trifluoromethyl group is significantly elongated (218.0(5) pm). The C–F bonds of the $TeCF_3$ groups show an average value of approximately 133.7 pm and differ from that of the central $TeCF_3$ unit (130.6 pm). All angles and torsion angles are close to 90 and 180°. As a consequence, the Te-Te-Te unit may be considered as a three-centre four-electron (3c-4e) bond. This is supported by the fact that both Te–Te bonds (296.9(1) and 298.3(1) pm) are significantly longer than the sum of covalent radii (274 pm). With respect to the "para-element concept",[3] $[PNP][(TeCF_3)_3]$ resembles the analogue to $[PNP]I_3$, which has been characterised by Tebbe and Krauss in 1990.[13] Comparison of these crystal structures shows evident similarities looking along the *b* axis, although the salts are not isostructural (Figure 2).

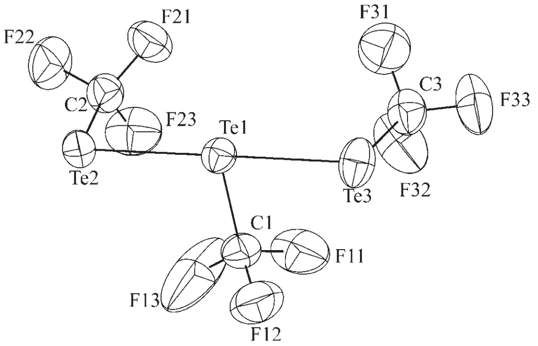

Figure 1. Molecular structure of the tris(trifluoromethyltellurate)(1−) anion. Interatomic distances [pm], angles [°] and torsion-angles [°]: Te1–Te2 296.9(1), Te1–Te3 298.3(1), Te1–C1 218.0(5), Te2–C2 214.1(5), Te3–C3 213.7(7), C–F in CF_3 groups 122.7(8)–137.9(7); Te2-Te1-Te3 177.8(1), Te1-Te2-C2 97.0(1), Te1-Te3-C3 94.0(1), Te2-Te1-C1 91.9(1), Te3-Te1-C1 89.1(1), F-C-F in central CF_3 group 95.6(4)–112.9(6), F-C-F in terminal CF_3 groups 104.3(5)–106.6(5); C2-Te2-Te1-C1 −89.3(2), C1-Te1-Te3-C3 86.7(2).

With respect to the parent molecule and ion, $Te_2(CF_3)_2$ and $[TeCF_3]^-$, the Te–C bond length of the central $TeCF_3$ unit (218.0(5) pm) matches nearly exactly the value determined for $Te_2(CF_3)_2$ (218.6(6) and 217.5(6) pm),[17] while those of the terminal $TeCF_3$ moieties (213.7(7) and 214.1(5) pm) are slightly elongated in comparison with those of the $TeCF_3$ anion.[18] The Te–Te bonds of 296.9(1) and 298.3(1) pm are significantly longer than in $Te_2(CF_3)_2$ (266.9(3) pm),[17] which might be interpreted in terms of a 3c-4e bond in this pseudotrigonal-bipyramidal anion (AB_2CE_2 structure). These results reveal that in the solid state the $[(TeCF_3)_3]^-$ ion is best described as trifluoromethyl[bis{trifluoromethyltellurato(0)}]tellurate(II), $[CF_3Te^{II}(Te^0CF_3)_2]^-$, while on the basis of NMR experiments (−80 °C to room temperature) a dynamic behaviour, that is, equivalence of all $TeCF_3$ units, must be assumed.

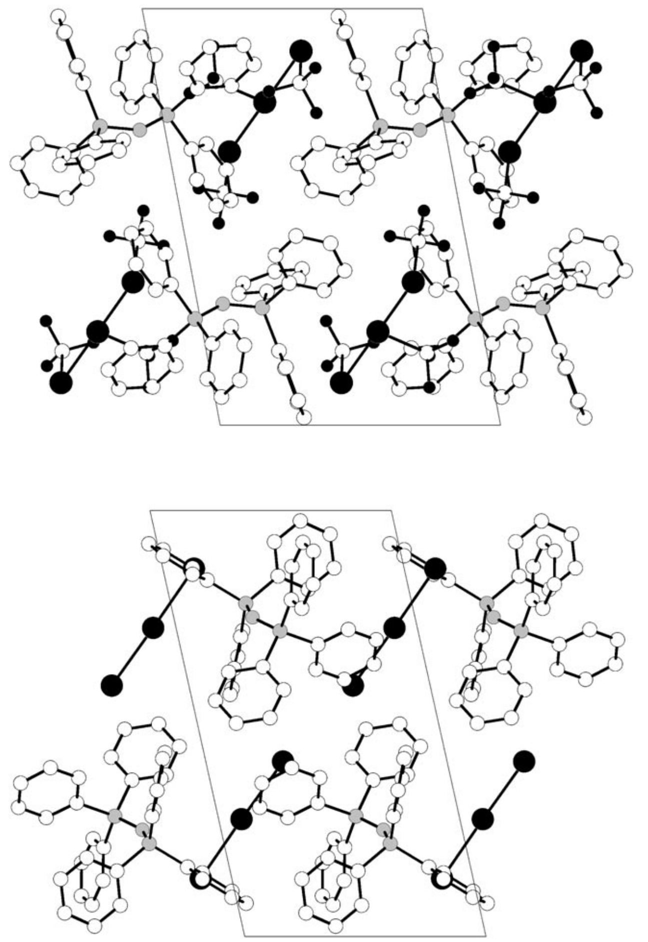

Figure 2. View on the unit cells of [PNP][$(TeCF_3)_3$] (top) and [PNP]I_3[13] (bottom) along the *b* axes. Hydrogen atoms have been omitted for clarity.

Synthesis and molecular structure of [PNP][$(TeCF_3)I_2$]: [PNP][$(TeCF_3)I_2$] has been isolated in excellent yield (88 %) after oxidation of tetramethylammonium trifluoromethyltellurate(0) with elemental iodine and cation exchange in a similar manner as conducted for the aryl derivatives $[TePhI_2]^-$[19] and $[Te(2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2)I_2]^-$[20] [Eq. (3)].

$$[NMe_4][TeCF_3] + I_2 \rightarrow [NMe_4][(TeCF_3)I_2] \xrightarrow[-[NMe_4]]{+[PNP]I} [PNP][(TeCF_3)I_2] \quad (3)$$

[PNP][$(TeCF_3)I_2$] is a red crystalline solid with a visible melting point of 155 °C. It has been identified by XRD measurements, elemental analysis and NMR spectroscopy.

As described above for [PNP][$(TeCF_3)_3$], the anions are intercalated into a PNP framework without significant cation–anion contacts. Weak secondary Te–I contacts (385.8(1) pm) around a centre of inversion build up dimeric square-planar units. The Te–C bond length (220.5(3) pm) does not significantly deviate from that in $[(TeCF_3)_3]^-$, and the Te–I bond length of 293.7(1) pm does not significantly deviate from those in the related anions, $[TePhI_2]^-$[19] and $[Te(2,4,6\text{-}i\text{-}Pr_3\text{-}C_6H_2)I_2]^-$.[20] Secondary Te–I contacts are significantly longer, but are in agreement with values reported for the dimer of (1,3-diethyl-1,3-dihydro-4,5-dimethyl-2*H*-imidazol-2-ylidene)diiodotellurium(II)[21] and for $[TeI_2(\mu\text{-}I)_2TeI_2]^{2-}$.[22] A similar dimeric motif is also found in the anion structure of $[Te(CF_3)_2(\mu\text{-}Cl)_2Te(CF_3)_2]^{2-}$.[23] Taking into account all bond lengths and angles, the anion is best described as trifluoromethyldiiodotellurate(II), $[(TeCF_3)I_2]^-$ (Figure 3).

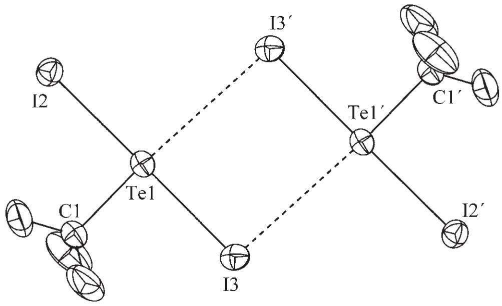

Figure 3. Molecular structure of the dimeric trifluoromethyldiiodotellurate(II) anion. Interatomic distances [pm], angles [°]: Te1–I2 293.7(1), Te1–I3 293.7(1), Te1–I3′ 385.8(1), Te1–C1 220.5(3), C–F in CF_3 group 131.4(5), 132.0(4) and 132.4(4); I2-Te1-I3 178.1(1), I2-Te1-C1 91.4(9), I3-Te1-C1 88.1(8), F-C-F in CF_3 group 104.1(3)–106.4(3).

Synthesis and molecular structure of [PNP][$(TeCF_3)_2I$]: In a similar manner as the base $[TeCF_3]^-$ adds to $Te_2(CF_3)_2$, the iodide also undergoes a similar reaction [Eq. (4)].

$$[PNP]I + Te_2(CF_3)_2 \rightarrow [PNP][(TeCF_3)_2I] \quad (4)$$

[PNP][$(TeCF_3)_2I$] is formed selectively upon mixing a solution of [PNP]I in MeCN and a 10 % excess of $Te_2(CF_3)_2$. Orange to red crystals of [PNP][$(TeCF_3)_2I$] were grown on storing a saturated solution overnight at −30 °C. The salt (84 % yield) has a visible melting point of 125 °C. The composition of [PNP][$(TeCF_3)_2I$] was elucidated by XRD analysis; ^{19}F, ^{13}C and ^{125}Te NMR spectra; and elemental analysis. NMR spectra show in all cases only one signal, making a dynamic behaviour in solution very probable. Additionally, the reaction of equimolar amounts of [NMe_4][$(TeCF_3)_3$] and [NMe_4][$(TeCF_3)I_2$] in MeCN selectively yielded [NMe_4][$(TeCF_3)_2I$].

By contrast in the solid state, positions of the atoms are fixed. The anion formed is a dimer (Figure 4) with two iodine bridges generated by a centre of inversion. In comparison with the anion structures described above, the Te–C bond length (221.2(4) pm) of the central $TeCF_3$ moiety is in good agreement with values measured for the others. On the other hand, differences in Te–I bond length (elongation by about 30 pm) and Te–Te bond length (shortening by about 16 pm) suggest differences in the electronic natures of the three anion structures. The short Te–C contact of the terminal group (214.3(4) pm) suggests a $TeCF_3$ moiety, but on the other hand the shorter Te–Te contact (277.6(1) pm)

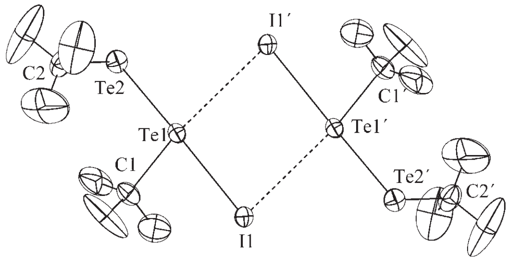

Figure 4. Molecular structure of the dimeric trifluoromethyl(trifluoromethyltellurato(0))iodotellurate(II). Interatomic distances [pm], angles [°] and torsion-angles [°]: Te1−Te2 277.6(1), Te1−I1 323.9(1), Te1−I1′ 353.6(1), Te1−C1 221.2(4), Te2−C2 214.3(4), C−F in central CF_3 group 128.0(6), 131.8(4) and 133.8(4), C−F in terminal CF_3 group 126,9(6), 128.7(6) and 132.5(7); Te2-Te1-I1 177.4(1), I1-Te1-C1 87.0(1), Te1-Te2-C2 96.1(1), F-C-F in central CF_3 group 101.5(3)-108.0(4), F-C-F in terminal CF_3 group 100.3(4)–109.7(4), C1-Te1-Te2-C2 −77.2(1).

implies relations close to a two centre-two-electron (2c-2e) bond as found in $Te_2(CF_3)_2$ (266.9(3) pm).[17] Additionally the elongation of the Te−I bond (323.9(1) pm) relative to that in $[(TeCF_3)I_2]^-$ (293.7(1) pm) indicates that $[(TeCF_3)_2I]^-$ might be regarded as an adduct of $Te_2(CF_3)_2$ and iodide. Comparable iodine–iodide contacts (311.3(4),[24] 314.8(1) pm[25]) have been found in asymmetric triiodides. The second Te−I contact of 353.6(1) pm is closer than in the ion $\{[(TeCF_3)I_2]_2\}^{2-}$ ion, but should be attributed to packing effects.

Conclusion

A complete series of anions following the "para-element concept" has been synthesised. We could show that $[(TeCF_3)_3]^-$ is really related to the triiodide anion and also $[(TeCF_3)I_2]^-$ shows comparable features. The structure of $[(TeCF_3)_2I]^-$ resembles "asymmetric" I_3^-.[24,25] Due to the too high oxidation potential of positive iodine, the missing link, that is $[I(TeCF_3)_2]^-$, could not yet be prepared. All in all, proposals made by Haas[3] are supported unambiguously by these experimental data (Table 1).

Experimental Section

General: All experiments were carried out in a dry nitrogen atmosphere in carefully dried reaction vessels by using Schlenk techniques. Solvents were purified by common methods.[27] [PNP]I,[28] $Te_2(CF_3)_2$[29] and $[NMe_4][TeCF_3]$[10] were synthesised according to literature procedures. NMR spectra were recorded on a Bruker spectrometer Avance 400 at +10°C in CD_3CN; frequencies (external standards): ^{13}C 100.6 MHz (TMS), ^{19}F 376.5 MHz (CCl_3F), ^{125}Te 126.2 MHz (Me_2Te); positive shifts denote downfield resonances. ^{13}C NMR data of the $[PNP]^+$ ion matched with previously published values.[30]

Bis(triphenylphosphoranyliden)ammonium tris(trifluoromethyltellurate)(1−): $[NMe_4][TeCF_3]$ (0.29 g, 1.07 mmol) was added in one portion to a solution of $Te_2(CF_3)_2$ (0.42 g, 1.07 mmol) in acetonitrile (20 mL) at room temperature. The mixture was stirred for about 5 min and [PNP]I (0.71 g, 1.07 mmol) was added to the solution. The precipitate was filtered off and the filtrate was concentrated in vacuo at room temperature to one third. The solution was placed at −30°C. Red crystals suitable for XRD measurement were collected in 86.9% yield (1.05 g). Elemental analysis calcd (%) for $C_{39}H_{30}F_9NP_2Te_3$ (1128.41): C 41.51, H 2.68, N 1.24, F 15.15; found: C 42.63, H 2.67, N 1.26, F 13.64; m.p. 80–82°C (glass capillary), 88°C onset of decomposition; ^{19}F NMR (376.4 MHz, CD_3CN, 10°C, CCl_3F): $\delta = -17.8$ ppm (s, $^2J(^{125}Te,^{19}F) = 227.4$ Hz, $^2J(^{123}Te,^{19}F) = 188.7$ Hz); ^{13}C NMR (100.6 MHz, CD_3CN, 10°C, TMS): 94.3 ppm (q, $^1J(^{19}F,^{13}C) = 355$ Hz, $^1J(^{125}Te,^{13}C) = 610$ Hz); ^{125}Te NMR (126.4 MHz, CD_3CN, 10°C, Me_2Te): 684 ppm (br q, $^2J(^{19}F,^{125}Te) \approx 227$ Hz).

Bis(triphenylphosphoranyliden)ammonium trifluoromethyldiiodotellurate(II) $[PNP][(TeCF_3)I_2]$: Iodine (2.82 g, 11.11 mmol) dissolved in acetonitrile (60 mL) was added in small portions to a well stirred solution of $[NMe_4][TeCF_3]$ (3.00 g, 11.08 mmol) in acetonitrile (60 mL), at −30°C. A yellow-orange solid precipitated after adding half of the amount of iodine, but re-dissolved on addition of the second half. The stirring was continued for one hour, while the mixture was allowed to warm up to room temperature. All volatile compounds were condensed off in vacuo. Elemental analysis calcd (%) for $[NMe_4][(TeCF_3)I_2]$ $C_5H_{12}F_3I_2NTe$ (524.56): C 11.45, H 2.31, N 2.67; found: C 12.04, H 2.25, N 2.81; ^{19}F NMR (376.4 MHz, CD_3CN, 10°C, CCl_3F): $\delta = -22.6$ ppm (s, $^2J(^{125}Te,^{19}F) = 264.2$ Hz, $^1J(^{13}C,^{19}F) = 360.4$ Hz).

To a well stirred solution of the crude product (0.65 g, 1.24 mmol) in acetonitrile (2 mL), [PNP]I (0.83 g, 1.24 mmol) was added in one portion at room temperature. The precipitate was filtered, the remaining red solution was concentrated to one third and placed at −30°C. Red crystals suitable for XRD measurement were collected in 87.9% yield (1.08 g) relative to [PNP]I. Elemental analysis calcd (%) for $[PNP][(TeCF_3)I_2]$ $C_{37}H_{30}F_3NI_2P_2Te$ (988.99): C 44.94, H 3.06, N 1.42; found: C 45.75, H 3.23, N 1.55; m.p. 155°C (glass capillary); ^{19}F NMR (376.4 MHz, CD_3CN, 10°C, CCl_3F): $\delta = -23.8$ ppm (s, $^2J(^{125}Te,^{19}F) = 264.1$ Hz); ^{13}C NMR (100.6 MHz, CD_3CN, 10°C, TMS): 84.6 ppm (q, $^1J(^{19}F,^{13}C) = 354$ Hz, $^1J(^{125}Te,^{13}C) = 598$ Hz); ^{125}Te NMR (126.4 MHz, CD_3CN, 10°C, Me_2Te): 963 ppm (br).

Bis(triphenylphosphoranyliden)ammonium trifluoromethyl{trifluoromethyltellurato(0)}iodotellurate(II): [PNP]I (1.00 g, 1.50 mmol) in acetonitrile (15 mL) was added in one portion to a solution of $Te_2(CF_3)_2$ (0.65 g, 1.65 mmol) in acetonitrile (5 mL) at room temperature. The yellow solution directly turned pale orange. The mixture was stirred for about 5 min and finally concentrated to one third in vacuo at room temperature. Storage over night at −30°C gave orange to red crystals in 84.3% yield (1.50 g relative to [PNP]I) suitable for XRD measurement. Elemental analysis calcd (%) for $C_{38}H_{30}F_6NIP_2Te_2$ (1058.70): C 43.11, H 2.86, N 1.32, F 10.77; found: C 42.92, H 2.91, N 1.46, F 11.43; m.p. 125°C (glass capillary); 129°C onset of decomposition; ^{19}F NMR (376.4 MHz, CD_3CN, 10°C, CCl_3F): $\delta = -26.4$ ppm (s, $^2J(^{125}Te,^{19}F) = 161.0$ Hz, $^2J(^{123}Te,^{19}F) = 133.9$ Hz, $^1J(^{13}C,^{19}F) = 356.2$ Hz); ^{13}C NMR (100.6 MHz, CD_3CN, 10°C, TMS): 91.1 ppm (q, $^1J(^{19}F,^{13}C) = 358$ Hz); ^{125}Te NMR (126.4 MHz, CD_3CN, 10°C, Me_2Te): 736 ppm (br q, $^2J\ (^{19}F,^{125}Te) \approx 160$ Hz).

Single-crystal structure determination: The intensity data were collected on an imaging-plate diffractometer (IPDS II, Stoe & Cie) with $Mo_{K\alpha}$ radiation ($\lambda = 71.073$ pm, graphite monochromator) at 130 K. The structures were solved by direct methods and refined by full-matrix least-squares methods on F^2. The H atoms were placed in idealised positions and constrained to ride on their parent atom. The last cycles of refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms and isotropic thermal parameters for all of the hydrogen atoms. A numerical absorption correction was applied after optimisation of the crystal shape.[31–34]

Crystal data for bis(triphenylphosphoranylidene)ammonium tris(trifluoromethyltellurate)(1−): $C_{36}H_{30}F_9NP_2Te_3$, triclinic space group $P\bar{1}$, $a = 1094.4(1)$, $b = 1170.4(1)$, $c = 1666.3(1)$ pm, $\alpha = 82.03(1)$, $\beta = 78.80(1)$, $\gamma = 84.59(1)°$, $V = 2068.3(2) \times 10^6$ pm³, $Z = 2$, $\mu = 2.248$ mm^{-1}, $F(000) = 1076$, $R_{int} = 0.0577$, collected/unique/observed $[I_0 > 2\sigma(I_0)]$ data = 32553/11444/7920, $R1/wR2$ (all data) = 0.0662/0.1536, $R1/wR2$ $[I_0 > 2\sigma(I_0)] = 0.0493/0.1440$, max/min electron density = $1.82/-1.06 \times 10^{-6}$ e pm^{-3}. CCDC-283546 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for bis(triphenylphosphoranylidene)ammonium diiodotrifluoromethyltellurate(II): $C_{37}H_{30}F_3NI_2P_2Te$, monoclinic space group $P2_1/c$, $a=1143.2(1)$, $b=1844.2(1)$, $c=1805.2(1)$ pm, $\beta=108.05(1)°$, $V=3616.2(3)\times10^6$ pm^3, $Z=4$, $\mu=2.661$ mm^{-1}, F(000)$\,=1896$, $R_{int}=0.0513$, collected/unique/observed $[I_0>2\sigma(I_0)]$ data$\,=48215/7937/6600$, $R1/wR2$ (all data)$\,=0.0337/0.0647$, $R1/wR2$ $[I_0>2\sigma(I_0)]=0.0259/0.0627$, max/min electron density$\,=0.59/-1.00\times10^{-6}$ e pm^{-3}. CCDC-283547 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for bis(triphenylphosphoranylidene)ammonium trifluoromethyl{trifluoromethyltellurate(0)}iodotellurate(II): $C_{38}H_{30}F_6NIP_2Te_2$, triclinic space group $P\bar{1}$, $a=1053.3(1)$, $b=1310.5(1)$, $c=1542.5(1)$ pm, $\alpha=68.87(1)$, $\beta=89.08(1)$, $\gamma=83.26(1)°$, $V=1969.7(2)\times10^6$ pm^3, $Z=2$, $\mu=2.402$ mm^{-1}, F(000)$\,=1012$, $R_{int}=0.0284$, collected/unique/observed $[I_0>2\sigma(I_0)]$ data$\,=24520/8560/7408$, $R1/wR2$ (all data)$\,=0.0346/0.0719$, $R1/wR2$ $[I_0>2\sigma(I_0)]=0.0290/0.0686$, max/min electron density$\,=1.23/-1.02\times10^{-6}$ e pm^{-3}. CCDC-283545 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] P. H. Svensson, L. Kloo, *Chem. Rev.* **2003**, *103*, 1649–1684.
[2] Cambridge Structural Database System, Database V. 5.14, **1997**.
[3] a) A. Haas, *Chem.-Ztg.* **1982**, *106*, 239–248; b) A. Haas, *Pure Appl. Chem.* **1991**, *63*, 1577–1590.
[4] R. G. Pearson, *J. Am. Chem. Soc.* **1963**, *85*, 3533–3539.
[5] A. Cisar, J. D. Corbett, *Inorg. Chem.* **1977**, *16*, 632–635.
[6] M. G. Kanatzidis, *Angew. Chem.* **1995**, *107*, 2281–2283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2109–2111.
[7] Q. Liu, N. Goldberg, R. Hoffmann, *Chem. Eur. J.* **1996**, *2*, 390–397.
[8] A. C. Hillier, S.-Y. Liu, A. Sella, M. R. J. Elsegood, *Angew. Chem.* **1999**, *111*, 2918–2920; *Angew. Chem. Int. Ed.* **1999**, *38*, 2745–2747.
[9] D. Witthaut, K. Kirschbaum, O. Conrad, D. M. Giolando, *Organometallics* **2000**, *19*, 5238–5240.
[10] W. Tyrra, N. V. Kirij, D. Naumann, Yu. L. Yagupolskii, *J. Fluorine Chem.* **2004**, *125*, 1437–1440.
[11] N. V. Kirij, W. Tyrra, D. Naumann, Yu. L. Yagupolskii, I. Pantenburg, M. Schäfer, *J. Fluorine Chem.* **2004**, *125*, 1933–1938.
[12] a) G. Helgesson, S. Jagner, *Acta Chem. Scand. A* **1987**, *41*, 556–561; b) P. Braunstein, A. Müller, H. Bögge, *Inorg. Chem.* **1986**, *25*, 2104–2106.
[13] K.-F. Tebbe, N. Krauss, *Acta Crystallogr. Sect. C* **1990**, *46*, 878–880.
[14] For example: a) W. Tyrra, D. Naumann, *J. Fluorine Chem.* **2004**, *125*, 823–830; b) S. Aboulkacem, W. Tyrra, I. Pantenburg, *J. Chem. Crystallogr.* in press; c) W. Tyrra, S. Aboulkacem, I. Pantenburg, *J. Organomet. Chem.* in press; d) D. Naumann, W. Tyrra, S. Quadt, S. Buslei, I. Pantenburg, M. Schäfer, *Z. Anorg. Allg. Chem.* **2005**, *631*, 2733–2737.
[15] a) W. Dukat, Ph.D. Dissertation, University of Dortmund, **1986**; b) J. Kischkewitz, Ph.D. Dissertation, University of Dortmund **1986**.
[16] a) A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451; b) S. C. Nyburg, C. H. Faerman, *Acta Crystallogr. Sect. B* **1985**, *41*, 274–279.
[17] W. Dukat, F. Gall, C. Meyer, D. Mootz, D. Naumann, G. Nowicki, K. Schulz, *Z. Anorg. Allg. Chem.* **1996**, *622*, 617–621.
[18] W. Tyrra, D. Naumann, H. Pohl, I. Pantenburg, *Z. Anorg. Allg. Chem.* **2003**, *625*, 1039–1043.
[19] S. Hauge, O. Vikane, *Acta Chem. Scand. A* **1983**, *37*, 723–728.
[20] W. W. DuMont, H. U. Meyer, S. Kubiniok, S. Pohl, W. Saak, *Chem. Ber.* **1992**, *125*, 761–766.
[21] N. Kuhn, T. Kratz, G. Henkel, *Z. Naturforsch. B* **1996**, *51*, 295–297.
[22] M. Fujiwara, N. Tajima, T. Imakubo, M. Tamura, R. Kato, *J. Solid State Chem.* **2002**, *168*, 396–407.
[23] N. V. Kirij, Yu. L. Yagupolskii, N. Maggiarosa, W. Tyrra, D. Naumann, *J. Fluorine Chem.* **2001**, *112*, 213–218.
[24] G. H. Cheesman, A. J. T. Finney, *Acta Crystallogr. Sect. B* **1970**, *26*, 904–906.
[25] I. Pantenburg, *Z. Kristallogr. Suppl.* **2005**, *22*, 174.
[26] F. van Bolhuis, P. B. Koster, T. Migchelsen, *Acta Crystallogr.* **1967**, *23*, 90–91.
[27] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, **1988**, 3rd ed., Pergamon, Oxford.
[28] J. K. Ruff, W. J. Schlientz, *Inorg. Synth.* **1974**, *15*, 84–96.
[29] J. Kischkewitz, D. Naumann, *Z. Anorg. Allg. Chem.* **1987**, *547*, 167–172.
[30] Z.-H. Choi, W. Tyrra, A. Adam, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1287–1292.
[31] SIR-92 A program for crystal structure solution: A. Altomare, G. Cascarano, C. Giacovazzo, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.
[32] G. M. Sheldrick, SHELXL-97, Programs for Crystal Structure Analysis, University of Göttingen, Göttingen (Germany) **1997**.
[33] X-RED 1.22, Stoe Data Reduction Program (C) **2001** Stoe & Cie GmbH Darmstadt.
[34] X-Shape 1.06, Crystal Optimisation for Numerical Absorption Correction (C) **1999** STOE & Cie GmbH Darmstadt.

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