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Article

Technetium Fluoride Trioxide, TcO_3F, Preparation and Properties[†]

Joanna Supeł, Ulrich Abram, Adelheid Hagenbach, and Konrad Seppelt*

Institute of Chemistry, Freie Universität, D-14195 Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany

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TcO_4^- in HF solution reacts to form $Tc_3O_9F_4^-$ along with some TcO_3F. Pure TcO_3F is obtained if a mixture of HF/BiF_5 is applied. TcO_3F dimerizes in the solid state via fluoride bridges, similar to the structures of CrO_2F_2 and VOF_3. TcO_3F reacts in HF with AsF_5 or SbF_5 under formation of $TcO_2F_2^+As(Sb)F_6^-$.

Introduction

Of the three known fluoride oxides of technetium(VII), namely TcO_3F, TcO_2F_3, and $TcOF_5$, there exists the least information about the first and oldest of the three.

$TcOF_5$ has been found only recently.[1,2] It is prepared from TcO_2F_3 by reaction with KrF_2 and is a molecular species with a close to octahedral structure, as confirmed by NMR, IR, and Raman spectroscopy, a single-crystal structure determination, and local density functional calculations. It is one of the only four existing molecular oxide pentafluorides; the others are $ReOF_5$, $OsOF_5$, and IOF_5.

TcO_2F_3 was first observed in 1982,[3] and 1991.[4] The reaction of Tc_2O_7 with XeF_6 finally resulted in a preparative method, and a crystal structure is now available.[5] TcO_2F_3 is in the solid state a fluoride-bridged polymer, with distorted octahedral coordination around the Tc atoms, the two oxygen atoms being in a cis position.

TcO_3F might have been detected in the mass spectrum of Tc_2O_7/UF_4 mixtures.[6] It was first prepared in weightable amounts by fluorination of TcO_2 at 150 °C.[7] Later, it was assumed that it is formed simply by dissolving TcO_4^- in anhydrous HF,[3,8] but it has never been isolated from such solutions, although the reported vapor pressure of TcO_3F[7] should make the separation from HF readily possible.

We have become interested in TcO_3F after we obtained ReO_3F pure and solved its complicated crystal structure.[9] The latter can be described as a cis oxide and fluoride-bridged helical polymer with six-coordinated Re atoms. On the other hand, MnO_3F is monomeric and *pseudo* tetrahedral even in the solid state.[10]

The aim of this investigation is to find a simple way of preparing TcO_3F and to evaluate its crystal structure as well as some of its chemistry.

Experimental Section

Caution. *Handling anhydrous HF or compounds that produce HF upon hydrolysis requires eye and skin protection.*

Radiation Precautions. *^{99}Tc is a weak β-emitter. Manipulations of ^{99}Tc compounds are performed in a laboratory approved for the handling of such radioactive materials.*

Materials and Apparatus. Sample handling is performed using Teflon−PFA (polyperfluoroether−terafluoroethylene) tubes that are sealed at one end and equipped at the other end with a metal valve and thus connectable to a stainless steel vacuum line.

NMR spectra are recorded on a JEOL multinuclear instrument at 400 MHz for ^{1}H. ^{99}Tc spectra are recorded relative to TcO_4^- in H_2O as external standard. Raman spectra are recorded on a Bruker RFS 100 FT-Raman spectrometer.

Single crystals are handled with cooling to ~ -140 °C under nitrogen in a special device,[11] and mounted on a Bruker SMART CCD 1000 TK diffractometer using Mo Kα radiation, a graphite monochromator, a scan width of 0.3° in ω, and a measuring time of 10 s per frame. Usually each compound is measured up to $2\theta =$

[†] Dedicated to Neil Bartlett on the occasion of his 75th birthday.

* To whom correspondence should be addressed. E-mail: Seppelt@chemie.fu-berlin.de.

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Table 1. Crystal Data

chemical formula	$K^+Tc_3O_9F_4$·1.5 TcO_3F	TcO_3F	CrO_2F_2	VOF_3	TcO_2F_3·TcO_3F	$TcO_2F_2^+SbF_6^-$·2HF	$TcO_2F_2^+$·AsF_6^-·2HF
fw	800.6	165.0	122.0	123.9	352.0	443.8	396.9
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/pm	827.2(1)	568.9(3)	565.5(3)	556.9(6)	820.1(2)	852.9(2)	512.6(3)
b/pm	1414.8(1)	506.9(3)	485.3(2)	500.7(4)	1458.3(4)	903.8(2)	810.3(6)
c/pm	2474.9(3)	930.5(5)	911.6(3)	934.1(7)	530.5(2)	1134.3(2)	1969.1(12)
β/deg	92.72(2)	93.21(1)	92.95(5)	91.32(4)	90.13(1)	108.14(1)	95.57(2)
$V/10^6$ pm^3	2893.14	267.93	249.85	260.40	634.47	830.96	813.89
T/°C	−100	−115	−120	−90	−140	−100	−100
Z	4	4	4	4	4	4	4
μ/mm^{-1}	4.62	5.18	4.40	3.67	4.42	5.06	5.96
ρ_{calcd}/g cm^{-1}	3.676	4.09	3.24	3.16	3.69	3.55	3.24
reflns							
measured	17 631	1876	8383	2207	6137	10 285	9828
independent	8261	660	1612	611	1817	2544	2377
variables	442	47	46	47	101	136	135
$2\theta_{max}$/deg	60.05	57.83	81.84	56.01	65.80	61.13	60.16
R1($I > 4\sigma(I)$)	0.036	0.061	0.023	0.026	0.045	0.013	0.038
R1	0.063	0.075	0.028	0.029	0.050	0.014	0.082
wR2(all data)	0.077	0.156	0.060	0.068	0.096	0.030	0.095

61° by 1800 frames, thus covering a full sphere. Semiempirical absorption corrections are used by equalizing symmetry-equivalent reflections (SADABS). Structures are solved and refined with the SHELDRICK programs.[12] Experimental details of the crystal structure determinations are given in Table 1. $NH_4^+TcO_4^-$ has been purchased from Oakridge NEI Laboratories. $KTcO_4$ is prepared by addition of KCl and isolation of the less-soluble precipitate. AsF_5 and SbF_5 are from laboratory stock, as is HF. AsF_5 is used as such, SbF_5 vacuum distilled twice into a −78° trap before use. HF is vacuum distilled once and kept in a stainless steel cylinder over BiF_5. BiF_5 is prepared from BiF_3 and elemental F_2 at 550 °C, as described in ref 13.

$K^+Tc_3O_9F_4^-$·1.5TcO_3F. $KTcO_4$ (30 mg) is filled into a 8 mm outer diameter PFA tube, and on a vacuum line 2 g (0.1 mol) of anhydrous HF are condensed on it. The reaction mixture is warmed to room temperature and shaken for 30−60 min. The clear yellow solution is pumped to dryness in dynamic vacuum, leaving a brown microcrystalline precipitate. Addition of more HF gives back the yellow-brown solution at 25 °C, slow cooling to −30 °C gives large, cubic-shaped brown crystals. The yield is estimated to be quantitative, based on TcO_4^-. The NH_4^+ salt can be prepared similarly, but crystals of the K^+ salt are of much better quality.

TcO_3F. An 8 mm outer diameter PFA tube is filled with 90 mg (0.3 mmol) of BiF_5 and 2.5 g (0.125 mol) of HF. Under an inert gas atmosphere and cooling to −78 °C, 30 mg (0.15 mmol) of $KTcO_4$ is added. The mixture is warmed to room temperature under shaking. Within 30 min at 25 °C the solution and solid turn yellow. In a dynamic vacuum the mixture is pumped through −78 and −196 °C cooled PFA traps. TcO_3F is collected in the −78 °C trap. Addition of 1 mL of HF and very slow cooling to −78 °C within 2 weeks affords light yellow crystal plates. The yield is estimated about 50%, mp 18.5 °C. Raman spectrum (solid, −100 °C, cm^{-1}): 943 (st), 933(st), 915(m), 466(w), 383(m), 366(m), 293(w), 228(w), 186(w), 139(w), 105(m). ^{99}Tc NMR (SO_2FCl): 48.92 ppm, $w_{1/2} = 70$ Hz (25 °C). ^{99}Tc NMR (HF) 43.1 ppm, $w_{1/2} = 225$ Hz (−80 °C), 45.1 ppm, $w_{1/2} = 27$ Hz (25 °C). ^{19}F NMR (SO_2ClF, HF): very broad signal, centered about −50 ppm.

TcO_2F_3·TcO_3F. BiF_5 (115 mg, 0.375 mmol), 2.5 g (0.125 m) of HF, and 30 mg (0.15 mmol) of $KTcO_4$ are reacted as described above. After recrystallization from HF at −78 °C, a large crop of deeply yellow colored cubes and a small amount of the light yellow platelets of TcO_3F are formed. The cube-shaped crystal are brought to the crystal structure determination.

$TcO_2F_2^+$·AsF_6^-·2HF. TcO_3F (10−20 mg), dissolved in HF, is combined with 225 mg of AsF_5 at −196 °C. The sample is warmed carefully to −10° (***caution,*** *pressure!*), and a clear yellow solution is formed. Brief warming to room temperature is followed by slow cooling to −78°. Fine, needle-shaped yellow crystals are formed. These are brought to the crystal structure determination. The compound decomposes within days even if stored at −40 °C.

$TcO_2F_2^+SbF_6^-$·2HF. A PFA U-tube is filled with 100 mg (0.46 mol) of SbF_5 and connected to the preparation setup (TcO_4^-, HF, BiF_5) of TcO_3F. The volatile TcO_3F/HF mixture is distilled into the U-tube at −78°. About half of the HF is distilled off into a −198 °C cold trap. Warming to 0 °C and cooling to −78 °C gives a large crop of yellow platelets, along with large colorless cubes that are determined as $H_3O^+SbF_6^-$ by crystallography. Raman spectrum (solid, −100 °C, cm^{-1}) 993(st), 982(m), 732(w), 710, 691, 669(st), 642(m), 586, 518, 407(m), 381, 322(m), 312(m), 285(m), 264, 240, 232(w), 201, 188, 176, 157, 122. $TcO_2F_2^+SbF_6^-$·2HF melts in part at 40 °C under evolution of HF. After pumping off the latter, a light yellow powder is obtained, with a Raman spectrum of previously published $TcO_2F_2^+SbF_6^-$:[14] Raman spectrum (solid, 25 °C, cm^{-1}): 992(st), 980(m), 748, 732, 720, 680(m), 666(st), 612(w), 550, 533, 410(m), 385, 327(m), 311(m), 290, 269, 246(m), 240, 207, 176, 130, 120.

VOF_3 (cf. ref 15[15]). V_2O_5 is fluorinated with undiluted F_2 at 475 °C in a copper tube and sublimed into a PFA tube. Single crystals are obtained by recrystallization from HF at −78 °C.

CrO_2F_2. $K_2Cr_2O_7$ is dissolved in HF under formation of a brown gas. Volatiles are condensed into a −30 °C cold PFA trap. Brown crystals appear on the cooled wall, whereas liquid HF condenses into the bottom of the tube. ^{19}F NMR (SO_2FCl, −70 °C): $\delta = 109.57$ ppm, $w_{1/2} \cong 300$ Hz. Raman spectrum (solid, −100 °C): 959 (100), 941 (70), 655 (8), 592 (10), 539 (30), 498 (15), 431 (20), 397 (15), 339 (25), 277 (40), 238 (30), 186 (25), 164 (20), 150 (15), 122 (35) cm^{-1}.

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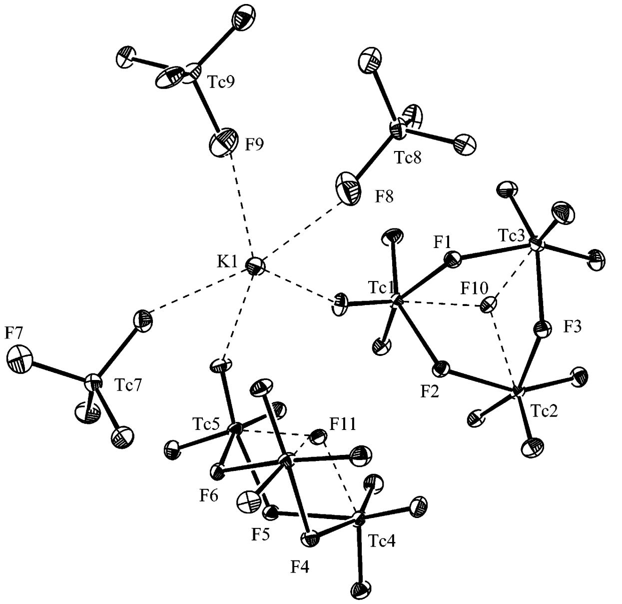

Figure 1. Asymmetric unit of $K^+Tc_3O_9F_4^-\cdot 1.5TcO_3F$. For clarity, the second K^+ ion (K2) is omitted. Ortep representation, 50% probability ellipsoids.

Table 2. Selected Bond Lengths (pm) and Angles (deg)

	$K^+Tc_3O_9F_4^-\cdot 1.5TcO_3F$
	$Tc_3O_9F_4^-$ Unit
Tc═O	167.3−169.1(4)
Tc−F	209.7−225.9(3)
O═Tc═O	103.3−106.0(2)
Tc−F−Tc	102.9−114.6(1)
$K^+\cdots F$	269.6−284(4)
$K^+\cdots O$	281.2−321.4(4)
	TcO_3F Unit
Tc═O	168.7−175.4(4)
Tc−F	175.1−176.1(4)
O═Tc═O	108.2−111.3(2)
F−Tc═O	108.1−111.3(2)
	TcO_3F
Tc═O	167.4−173.8(1)
Tc−F	203.9, 213.3(1)
Tc···O	228.2(1)
O═Tc═O	103.2−105.4(4)
F−Tc−F	69.5(3)
	CrO_2F_2
Cr═O	157.4, 157.6(1)
Cr−F	181.7, 186.7, 209.4(1)
Cr···F	222.9(1)
O═Cr═O	103.87(5)
F−Cr−F	73.21, 83.64, 152.51(4)
	VOF_3
V═O	155.1(2)
V−F	171.3, 178.9, 192.0, 197.2(2)
V···F	229.4(2)
F−V−F	72.9, 87.0, 91.6, 101.4, 153.6, 156.6(8)
	$TcO_2F_3\cdot TcO_3F$
	TcO_2F_3 Chain
Tc═O	164.6, 165.6(5)
Tc−F	183.5, 184.8, 207.5, 209.3(4)
O═Tc═O	101.6(3)
F−Tc−F	80.2−81.1(3), 154.6
	TcO_3F
Tc═O	167.8−170.6(6)
Tc−F	181.7(5)
O═Tc═O	107.0−108.7(3)
	$TcO_2F_2^+SbF_6^-\cdot 2HF$
Tc═O	164.8, 165.0(1)
Tc−F	181.7, 182.4(1)
Tc···F	221.0, 222.4(1)
O═Tc═O	103.16(6)
F−Tc−F	146.73(4)
F···Tc···F	77.30(4)
Sb−F	185.8−188.8, 195.6(1)
F···(H)−F	241.5(2)
	$TcO_2F_2^+AsF_6^-\cdot 2HF$
Tc═O	163.9, 164.5(4)
Tc−F	181.5, 181.8(4)
Tc···F	220.6, 223.3(4)
O═Tc═O	102.5(2)
F−Tc−F	145.9(2)
F···Tc···F	79.0(2)
As−F	169.5−173.0, 181.3(4)
F···(H)−F	249.4(5)

Results

The present legal restrictions of handling radioactive, volatile Tc compounds call for a simple, one-step procedure at room temperature. Therefore, the original preparation from TcO_2 and F_2 at 150 °C was not taken into consideration. We can show that by dissolving $K^+TcO_4^-$ in anhydrous HF no TcO_3F in appreciable amounts can be obtained, although it is obviously present in solution.[3,8] From such solutions large yellow crystals can be obtained, which according to their crystal structure are $K^+Tc_3O_9F_4^-\cdot 1.5TcO_3F$, see Figure 1 and Tables 1 and 2.

The structure can be described as a heterocubane of Tc and F atoms, where one corner Tc atom is missing. The three oxygen atoms complete the distorted octahedral coordination around the Tc atom. This cluster is considered as the reaction product of three TcO_3F molecules with one F^-. Interestingly, there are TcO_3F molecules also in the lattice as molecules. They are connected to the cluster Tc atoms via very long contacts of the fluorine atoms (∼360−390 pm). The K^+ ions are coordinated to the oxygen atoms of the clusters and to the TcO_3F molecules with typical distances of 260−290 pm.

This structure explains why TcO_3F, although present in solution, cannot simply be freed out of the solution or the solid compound: The TcO_3F is kept in the solid state by intermolecular interactions to K^+ and F^- so that its vapor pressure is severely lowered as compared to pure TcO_3F. Not even by heating to ca. 80 °C under vacuum is any TcO_3F released. If the excess of HF is simply pumped off, the formation reaction of TcO_3F can turn back to the starting compound.

$$TcO_4^- + 3\,HF \rightleftharpoons TcO_3F + H_3O^+ + 2\,F^-$$

Once this had been established, the preparation of TcO_3F is possible if the K^+ and H_3O^+ ions are taken out of the equilibrium. This is done by adding the nonvolatile Lewis acid BiF_5 that forms very stable $K^+BiF_6^-$ and $H_3O^+BiF_6^-$ salts. BiF_5 has to be added in a stoichiometrical amount, excess drives the fluorination reaction further to known TcO_2F_3.

$$TcO_4^- + 2BiF_5 + 3HF \rightarrow BiF_6^- + H_3O^+BiF_6^- + TcO_3F$$

$$TcO_4^- + 3BiF_5 + 6HF \rightarrow BiF_6^- + 2H_3O^+BiF_6^- + TcO_2F_3$$

If BiF_5 is applied in amounts between 1:2 and 1:3, then the co-crystallizate $TcO_2F_3\cdot TcO_3F$ is formed, see below.

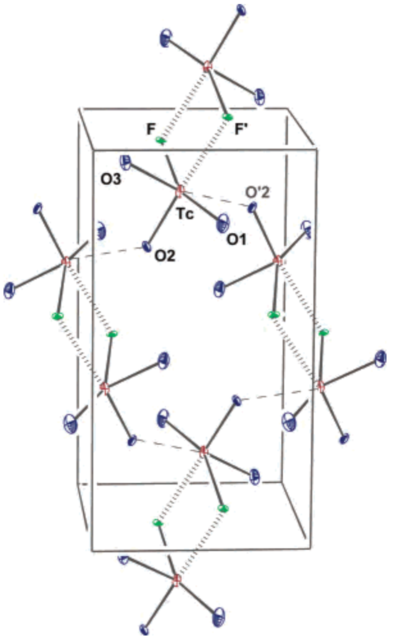

Figure 2. Structure of TcO_3F in the solid state, 50% probability ellipsoids. Shown is one (extended) unit cell. TcO_3F is a dimer via two slightly asymmetric fluoride bridges with one additional long contact to a neighboring oxygen atom. The structures of CrO_2F_2 and VOF_3 are very similar, except that one (CrO_2F_2) and two (VOF_3) oxygen atoms are replaced by fluorine atoms. In these structures, the weak interaction between the dimeric units is therefore also a fluoride bridge. Bond lengths and angles are listed in Table 2.

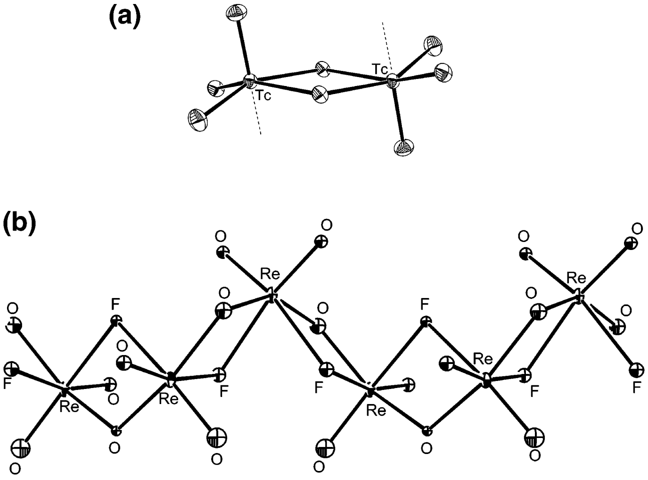

Figure 3. Comparison of the dimeric double fluorine bridged TcO_3F (a) with polymeric oxygen- and fluorine-bridged ReO_3F (b).

Once reacted, TcO_3F and HF can be pumped together out of the reaction mixtures, and yellow plates of crystalline TcO_3F are formed upon cooling to −78 °C.

The crystal structure, as shown in Figure 2 and Table 2, proves it to be a dimer in the solid state, which means that the Tc atoms are five-coordinate. Upon closer inspection of the packing, a contact between the technetium atom and one oxygen atom of an adjacent molecule is observed, raising the coordination number to six. The crystal structures of TcO_3F is therefore very different from monomeric MnO_3F and polymeric ReO_3F[9]. The structure of TcO_3F and ReO_3F is shown in Figure 3, while MnO_3F is a molecular species in all physical states.

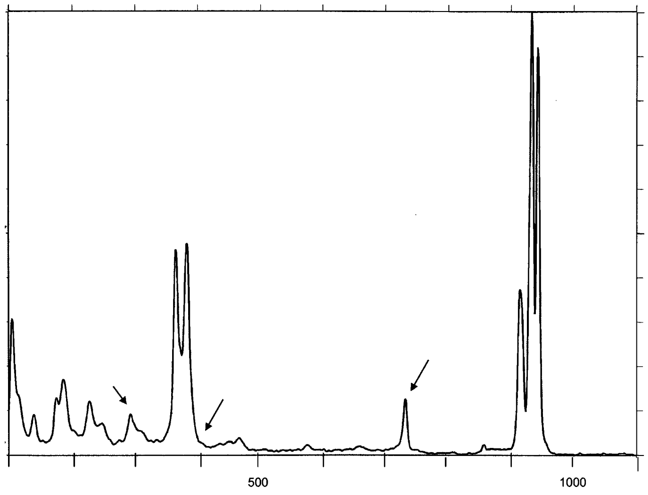

Figure 4. Raman spectrum of $(TcO_3F)_2$, solid, −100 °C. Arrows indicate location and intensity of Raman lines of the PFA container.

Surprisingly we found that there exist two other oxide fluorides with structures that are very much like that of TcO_3F, namely CrO_2F_2 and VOF_3. The structure of VOF_3 has been determined before,[15] although with low precision. As far as we know, the solid state of CrO_2F_2 has not been described before. Our structure determinations are also shown in Figure 2.[6] Lattice constants of VOF_3, CrO_2F_2, and TcO_3F are very similar, and all three belong to the same space group $P2_1/c$. In the sequence VOF_3, CrO_2F_2, and TcO_3F, all intermolecular forces within the dimeric units are getting weaker, see Table 2. So TcO_3F is closest to a molecule in the solid state, VOF_3 is a polymer, and CrO_2F_2 lies somewhere in between.

The dimeric form of TcO_3F is also visible in the Raman spectrum of the solid, see Figure 4. The existence of three Tc═O stretching vibrations above 900 cm^{-1} is in accord with the low symmetry around the Tc atom, whereas the Tc−F stretching vibrations cannot be located with certainty in contrast to monomeric TcO_3F (696 cm^{-1}, m).[8]

The weak dimer of TcO_3F can easily be broken up into a monomer if other coordinating materials are present, as has been shown already with the existence of $Tc_3O_9F_4^-\cdot TcO_3F$.

The mixed compound $TcO_2F_3\cdot TcO_3F$, which is formed when excess BiF_5 is used in the formation reaction of TcO_3F, is a $(TcO_2F_3)_n$ polymer, very much like pure TcO_2F_3, and along its chain, TcO_3F molecules are attached, see Figure 5.

TcO_3F could be a precursor to the TcO_3^+ cation, if the F atom is taken away as F^- by a strong Lewis acid. It has been assumed before that in $TcO_4^-/HF/AsF_5$ solutions the ^{99}Tc NMR signal at 160.7 ppm is due to TcO_3^+. Also the solvated ion $TcO_3^+\cdot L$ has very recently been prepared, L = triazacyclononane.[17]

Of interest here would be a very weakly solvated, almost free TcO_3^+ cation, which is expected to have a high electron affinity. Reaction of TcO_3F and AsF_5 or SbF_5 in anhydrous HF could be a simple mode of obtaining TcO_3^+. This, however, is not the case. In both reactions, only the

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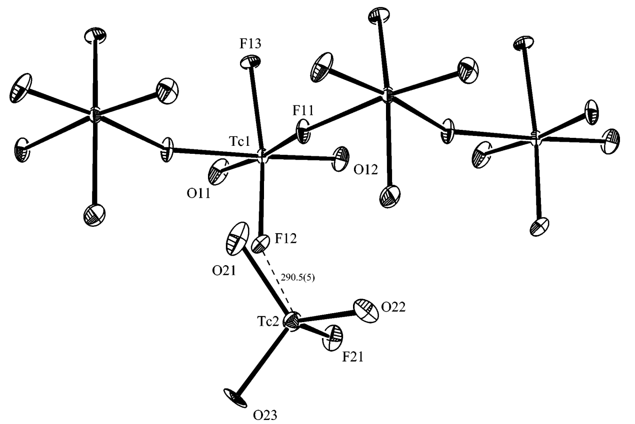

Figure 5. Co-crystallizate $TcO_2F_3 \cdot TcO_3F$. 50% probability ellipsoids. Shown is the polymeric chain of TcO_2F_3 with one loosely contacted TcO_3F molecule, distance in pm.

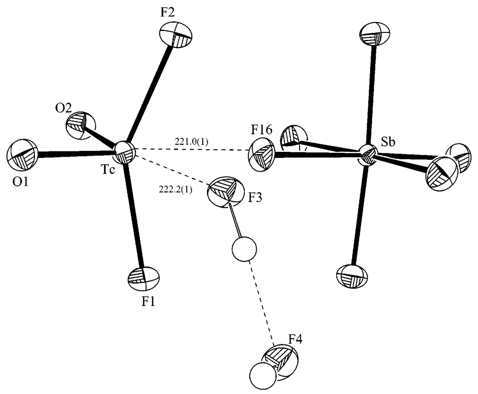

Figure 6. Zwitterionic unit $TcO_2F_2^+SbF_6^- \cdot 2HF$, 50% probability ellipsoids (except H atoms), distances in pm.

technetium-containing product $TcO_2F_2^+As(Sb)F_6^- \cdot 2HF$ is obtained, besides some $H_3O^+(As,Sb)F_6^-$. These materials can easily be distinguished after crystallization: the $TcO_2F_2^+$ salts are yellow prisms, the H_3O^+ salts are large, colorless cubes. The two $TcO_2F_2^+$ cations in both salts are virtually identical, see Figure 6. The bisphenoidal shape of the $TcO_2F_2^+$ is similar to the structure in $TcO_2F_2^+SbF_6^-$,[14] including two further contacts, here one to $SbF_6^-(AsF_6^-)$ and one to the $(HF)_2$ unit, so that the technetium atoms gain a (distorted) octahedral coordination. $TcO_2F_2^+AsF_6^- \cdot 2HF$ decomposes slowly even at −40 °C, whereas crystals of $TcO_2F_2^+ \cdot SbF_6^- \cdot 2HF$ are stable to about −30 °C. Above this temperature, HF is liberated, leaving $TcO_2F_2^+ \cdot SbF_6^-$ as a beige powder. The loss of HF can be observed in the Raman spectrum: The final product shows exactly the previously published spectrum of $TcO_2F_2^+SbF_6^-$.[14]

In summary, we do not state that a largely uncoordinated TcO_3^+ cation could not exist, but it would need a different approach, most likely the presence of HF should be avoided.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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