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Hexafluoridotechnetate(IV) Revisited

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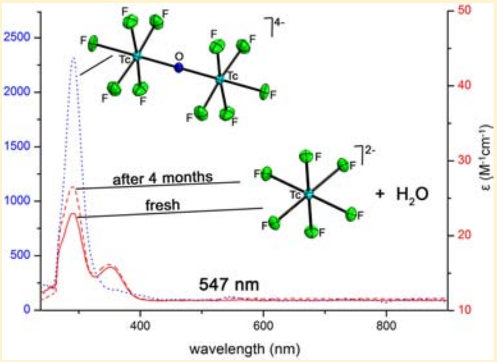
Supporting Information

ABSTRACT: Novel synthetic routes to hexafluoridotechnetate(IV) are reported, and for the first time the single-crystal X-ray structures of several $M_2[TcF_6]$ salts (M = Na, K, Rb, Cs, NH_4, and NMe_4) were determined. The ammonium and the alkaline metal salts crystallize in the trigonal space group $P\overline{3}m$, while the NMe_4^+ salt belongs to the space group $R\overline{3}$. $[TcF_6]^{2-}$ salts are widely stable in aqueous solution. In alkaline media, however, a slow hydrolysis is observed, and the first hydrolysis product, the dimeric, oxido-bridged complex $[F_5Tc{-}O{-}TcF_5]^{4-}$, could be studied structurally.



INTRODUCTION

Hexafluoridotechnetate(IV) has been known for almost 50 years, but still there are some open questions about the synthesis, structural chemistry and reactivity of this compound. Some of the previous findings are contradictory or not fully consistent, and some of the described properties may refer to impure samples. It is also surprising that up to now no exact crystallographic study on the basis of single crystal data of any $[TcF_6]^{2-}$ salt is available. The only well-documented and reliable crystallographic information refers to a powder study on $K_2[TcF_6]$,[1] while occasional reports about the sodium, rubidium, or cesium salts do not contain any information about synthesis or other details of the compounds.[2−4]

Generally, it must be stated that technetium fluorido compounds are under-represented in the chemistry of this artificial element. Most reports about technetium fluorides focus on oxido complexes of the metal in its higher oxidation states ("+5" to "+7").[5−13] Less is known only about corresponding fluorido complexes with nitridotechnetium(VI) cores,[14] or binary fluorides.[15−17] The existence of a stable technetium(IV) fluoride has been predicted recently by means of first-principles calculations, and its structure is assumed to be isomorphous to $TcCl_4$.[18]

Here, we report on novel and improved syntheses for $[TcF_6]^{2-}$ salts; single crystal structures of the ammonium, sodium, potassium, rubidium, cesium, and tetramethylammonium salts; a reinspection of some spectroscopic results; as well as the structure of a hydrolysis product.

EXPERIMENTAL SECTION

Materials. All reagents were reagent grade and used without further purification. ^{99}Tc was purchased as solid ammonium pertechnetate from Oak Ridge National Laboratory. The salt was purified by recrystallization from aqueous solutions. $K_2[TcF_6]$ was prepared from $K_2[TcBr_6]$, AgF, and HF.[19] All manipulations with HF were done in Teflon vessels (5 mL) or Teflon tubes.

Radiation Precautions. ^{99}Tc is a long-lived weak β^- emitter (E_{max} = 0.292 MeV). Normal glassware or teflon tubes provide adequate protection against the weak β radiation when milligram amounts are used. Secondary X-rays play a significant role only when larger amounts of ^{99}Tc are handled. All manipulations were done in a laboratory approved for the handling of radioactive materials.

Physical Measurements. IR spectra were measured with a Shimadzu IR Affinity-1 spectrometer between 400 and 4000 cm^{-1}. Raman spectra were recorded on a RFS 100 instrument (Bruker), and UV/vis spectra were taken on a SPECORD 40 instrument (Analytik Jena).

Tc values were determined by liquid scintillation counting. A defined amount of the technetium sample (3−5 mg) was dissolved in 5 mL of H_2O. A total of 1 mL of this solution was diluted to 5 mL. Then, samples of 50, 100, and 200 μL were each mixed with 10 mL of Rotiszint eco plus cocktail (Carl Roth, Karlsruhe, Germany) in polypropylene scintillation vials. ^{99}Tc was measured using a *HIDEX 300 SL* liquid scintillation counter. The ^{99}Tc activity was calculated using the counts of the channels 0−1000 with a counting efficiency of 100%.

X-Ray Crystallography. The intensities for the X-ray determinations were collected on STOE IPDS 2T or Enraf Nonius CAD 4 ($K_2[TcF_6]$) instruments with Mo Kα radiation (λ = 0.71073 Å) at 200 K. Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS97 and SHELXL97.[20] Hydrogen atom positions were calculated for idealized positions and treated with the "riding model" option of SHELXL. The nitrogen atoms of the

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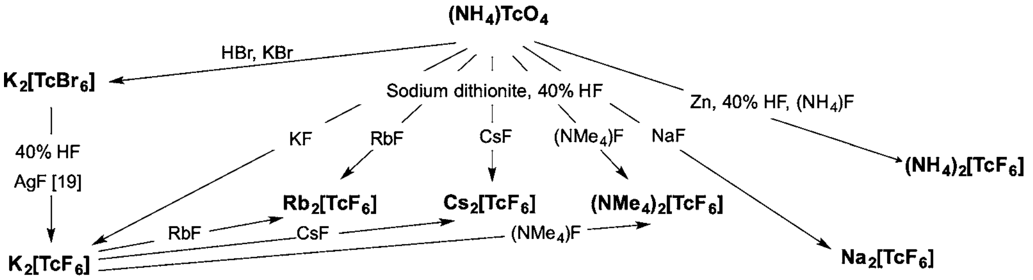
Table 1. Crystal Data and Refinement Parameters

	$(NH_4)_2[TcF_6]$	$Na_2[TcF_6]$	$K_2[TcF_6]$	$Rb_2[TcF_6]$	$Cs_2[TcF_6]$	$(NMe_4)_2[TcF_6]$	$Na(NH_4)_3[F_5TcO\text{-}TcF_5]\cdot 2(NH_4)F$
formula	F_6N_2Tc[a]	F_6Na_2Tc	F_6K_2Tc	F_6Rb_2Tc	F_6Cs_2Tc	$C_8H_{24}F_6N_2Tc$	$F_{12}N_5NaOTc_2$[a]
cryst syst	trigonal	trigonal	trigonal	trigonal	trigonal	rhombohedral	orthorhombic
space group	$P\bar{3}m$	$P\bar{3}m$	$P\bar{3}m$	$P\bar{3}m$	$P\bar{3}m$	$R\bar{3}$	*Pbam*
a (Å)	5.943(1)	5.958(1)	5.796(1)	5.949(1)	6.240(1)	9.992(1)	7.583(1)
b (Å)	5.943(1)	5.958(1)	5.796(1)	5.949(1)	6.240(1)	9.992(1)	15.350(2)
c (Å)	4.738(1)	4.757(1)	4.614(1)	4.759(1)	4.980(1)	20.039(1)	6.135(1)
V (Å^3)	144.92(5)	146.24(5)	134.22(4)	145.86(5)	167.93(5)	1108.5(2)	714.1(2)
Z	1	1	1	1	1	3	2
ρ_{calc} (g·cm^{-3})	2.750	2.929	3.590	4.359	4.725	1.619	2.479
μ (mm^{-1})	2.531	2.640	4.268	19.079	12.856	1.022	2.102
reflns collected	1366	1669	1168	1577	1871	4139	3738
reflns unique	147	173	130	173	193	666	770
data/restraints/params	147/0/12	173/0/12	130/0/13	173/0/13	193/0/13	666/0/28	770/0/62
absorption correction	integration	integration	psi scans	integration	integration	none	integration
max/min transmission	0.7873/0.4538	0.7405/0.5874	0.4734/0.3025	0.1917/0.0398	0.3900/0.0995		0.9472/0.8870
R1 [I > 2σ(I)]	0.0544	0.0819	0.0136	0.0429	0.0522	0.0481	0.0379
wR2 [I > 2σ(I)]	0.1670	0.2035	0.0285	1089	0.1267	0.1189	0.0819
GOF	1.389	1.257	1.145	1.140	1.501	1.138	1.070
CSD	425916	425915	425914	425918	425912	425917	425913

[a] The positions of the hydrogen atoms could not be determined reliably. Thus, the H atoms have not been considered during the refinement procedure.

Scheme 1. Synthetic Route for the Preparation of $[TcF_6]^{2-}$ Salts



ammonium ions were calculated without the corresponding hydrogen atoms. More details on data collections and structure calculations are contained in Table 1. Additional information on the structure determinations has been deposited with the Fachinformationszentrum Karlsruhe (Germany).

SYNTHESES

Syntheses of $M_2[TcF_6]$ Complexes by Metathesis Reactions. $K_2[TcF_6]$ (29 mg, 0.1 mmol) was dissolved in 1 mL of $HF_{(aq)}$ (40%). MF (M = Rb, Cs, NMe_4) (0.2 mmol) in 0.3 mL of $HF_{(aq)}$ was added. The solution was allowed to evaporate overnight at room temperature, which gave colorless crystals. The $M_2[TcF_6]$ complexes were separated from the other fluorides by subsequent washing with cold water and recrystallization from aqueous HF. $Rb_2[TcF_6]$ yield: (32 mg, 83%). Anal. Calcd for Rb_2TcF_6: Tc, 24.6. Found: Tc, 24.1. IR (KBr, cm^{-1}): 563 s (Tc−F). Raman (cm^{-1}): 605, 520, 249, 240 (Tc−F). $Cs_2[TcF_6]$ yield: (39 mg, 83%). Anal. Calcd for Cs_2TcF_6: Tc, 20.6. Found: Tc, 19.8. IR (KBr, cm^{-1}): 555 s (Tc−F). Raman (cm^{-1}): 598, 514, 237 (Tc−F). $(NMe_4)_2[TcF_6]$ yield: (30 mg, 83%). Anal. Calcd for $C_8N_2TcF_6$: Tc, 27.4. Found: Tc, 26.9%. IR (KBr, cm^{-1}): 3286 br, 3012 m, 2351 m, 1525 s, 1487 s, 1463 s, 1255 sh, 1236 s, 948 s, 565 s (Tc−F).

Syntheses of $M_2[TcF_6]$ Complexes Directly from Pertechnetate. (a) Solid $NH_4[TcO_4]$ (0.2 mmol, 36 mg) was dissolved in 10 mL of 40% $HF_{(aq)}$. $Na_2S_2O_4$ (0.4 mmol, 69.6 mg) in 0.2 mL of water was added. Immediately, a small amount of a pale brown residue was formed. The solution was heated on reflux for 2 h. The pale brown precipitate was filtered off, and MF (M = Na, K, Rb, Cs, NMe_4) (0.45 mmol) in 1 mL of $HF_{(aq)}$ was added. The solution was kept for slow evaporation at room temperature overnight. Colorless crystals of $M_2[TcF_6]$ together with byproducts were obtained. The byproducts were removed by washing each twice with 0.5 mL of cold water. $M_2[TcF_6]$ was recrystallized from $HF_{(aq)}$. For the isolation of the pure sodium salt, the washing/recrystallization procedure must be repeated 3−4 times in order to remove sodium fluoride completely. $Na_2[TcF_6]$ yield: 25 mg, 50%. Raman (cm^{-1}): 611, 530, 260 (Tc−F). Anal. Calcd for Na_2TcF_6: Tc, 38.2. Found: Tc, 37.6. $K_2[TcF_6]$ yield: 46 mg, 80%. Raman (cm^{-1}): 613, 525, 259, 243 (Tc−F). Anal. Calcd for K_2TcF_6: Tc, 33.9. Found: Tc, 33.1. $Rb_2[TcF_6]$ yield: 61 mg, 80%. Anal. Calcd for Rb_2TcF_6: Tc, 25.8. Found: Tc, 25.0. $Cs_2[TcF_6]$ yield: 86 mg, 90%. Anal. Calcd for Cs_2TcF_6: Tc, 20.7. Found: Tc, 20.1. $(NMe_4)_2[TcF_6]$ yield: 65 mg, 90%. Anal. Calcd for $C_8N_2TcF_6$: Tc, 27.4. Found: Tc, 26.9.

(b) $NH_4[TcO_4]$ (0.1 mmol) was dissolved in a 0.2 mL of water. $HF_{(aq)}$ (1 mL, 40%) and 0.77 mmol of Zn dust were added carefully. The reaction mixture was heated at 50 °C for 30 min. NH_4F (0.1 mmol, 4 mg) in 0.5 mL of HF was added, and the mixture was allowed to evaporate slowly at room temperature overnight. $(NH_4)_2[TcF_6]$ was formed as colorless crystals and separated from $ZnF_2\cdot 4H_2O$ by washing with water. Yield: 12 mg, 50%. Anal. Calcd for $N_2H_8TcF_6$: Tc,

Table 2. Structural Parameters of the Hexafluoridotechnetates(IV) Studied

	$(NH_4)_2[TcF_6]$	$Na_2[TcF_6]$	$K_2[TcF_6]$	$Rb_2[TcF_6]$	$Cs_2[TcF_6]$	$(NMe_4)_2[TcF_6]$
Tc−F/Å	1.922(6)	1.895(6)	1.928(1)	1.933(3)	1.935(5)	1.929(2)
F−Tc−F/deg	87.7(2)	87.6(3)	86.93(5)	87.2(2)	87.8(2)	89.8(1)
	92.3(2)	92.4(3)	93.07(5)	92.8(2)	92.2(2)	90.2(1)
	180.0(4)	180.0(4)	180.0(1)	180.0(1)	180.0(1)	180.0(1)

34.7. Found: Tc, 33.9%. IR (KBr, cm^{-1}): 3282 br, 1616 m, 1523 m, 1415 s, 567 s (Tc−F).

Synthesis of $(NH_4)_3Na[F_5Tc{-}O{-}TcF_5]$. $(NH_4)_2[TcF_6]$ (0.1 mmol) was dissolved in $NH_{3(aq)}$ (25%) solution. The reaction mixture turned pink. NaF (0.1 mmol) was added, and the mixture was kept at room temperature for slow evaporation. Pink crystals were isolated in quantitative yield. Anal. Calcd for $N_5H_{20}ONaTc_2F_{12}$: Tc, 35.6. Found: Tc, 35.3%. IR (KBr, cm^{-1}): 3242, 1414, 913 (Tc−O), 731 (Tc−O−Tc), 555 (Tc−F). Raman: 3195 m, 1691 m, 1430 m, 1089 m, 606 s, 583 sh, 518 m, 235 s. UV/vis: λ 291 nm (ε = 2096), 547 nm (ε = 38.9).

■ RESULTS AND DISCUSSION

The first synthesis of $K_2[TcF_6]$ was done by melting $K_2[TcBr_6]$ with KHF_2, followed by an aqueous workup.[1] The procedure was in analogy with the preparation of the corresponding rhenium compound and gave a pale-pink material (a color which was also reported for some $[ReF_6]^{2-}$ salts prepared in this way).[21,22] An improved procedure was presented in 1985. It is based on the sequential treatment of $K_2[TcBr_6]$ with HF (40%) and AgF and gives $K_2[TcF_6]$ in excellent yields as a colorless solid.[19] Although the latter procedure is a little time-consuming, it remains a good choice for the synthesis of the potassium salt. Metathesis reactions with RbF, CsF, or $(NMe_4)F$ in 40% HF can be used for the isolation of the rubidium, cesium, or tetramethylammonium salts.

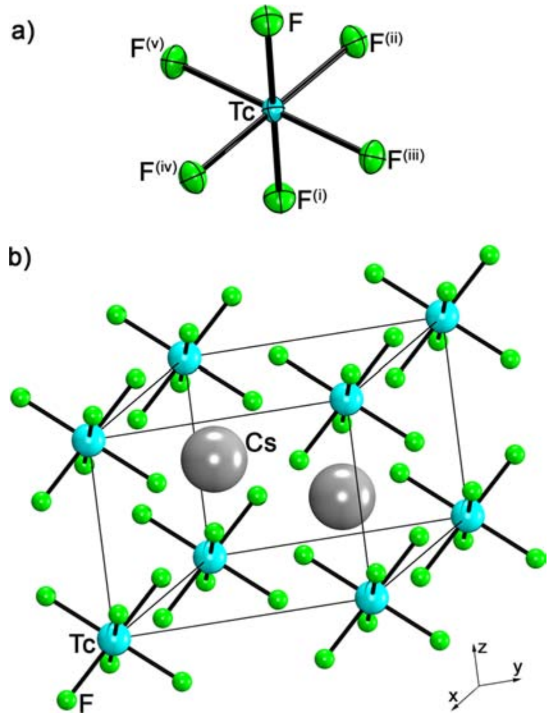


Figure 1. (a) Ellipsoid representation of the $[TcF_6]^{2-}$ anion in $Cs_2[TcF_6]$ (symmetry operators: (i) $-x, -y, -z$, (ii) $-y, x + y, -z$, (iii) $-y, x - y, z$, (iv) $y, x, -z$, (v) $-y, -x, z$) and (b) unit cell plot.

A faster and direct synthesis for the alkaline and tetramethylammonium salts of $[TcF_6]^{2-}$ has now been developed with the reduction of ammonium pertechnetate by sodium dithionite in refluxing aqueous HF. The products deposit from the reaction mixtures upon concentration and can readily be purified from alkaline fluorides by subsequent washing with a small amount of water and recrystallization from aqueous HF. For the synthesis of the readily soluble $(NH_4)_2[TcF_6]$, zinc dust was used as a reducing agent in a similar reaction. A complete overview of the synthetic routes is given in Scheme 1.

Freshly prepared samples of the $M_2[TcF_6]$ salts are completely colorless. The previously described pale pink color could not be detected visually or in the UV/vis spectra of the compounds. They show the reported intense absorptions at 291 nm (ε 2.5) and 352 nm (ε = 16.2), but no band in the range between 300 and 600 nm. Aqueous solutions of $K_2[TcF_6]$ slowly change color and appear pale pink after a period of several weeks. This process is accelerated in alkaline media. It goes along with a slight increase of the absorption around 290 nm and a decrease of that at 350 nm. Additionally, a weak absorption appears around 550 nm. This band is consistent with an absorption, which is observed in the spectrum of a hydrolysis product of $[TcF_6]^{2-}$ (*vide infra*). Thus, the reported pink color is not directly related with hexafluoridotechnetate, but with ongoing hydrolysis in (alkaline) aqueous media. This conclusion is supported by the discussion in an early report about the rhenium analogue $[ReF_6]^{2-}$, where a pink color was only observed in samples which come from the fusion of KHF_2 and $K_2[ReBr_6]$ with subsequent aqueous workup, but not for $K_2[ReF_6]$, which results from gas phase reactions between the same precursor and absolute HF.[22]

Single crystals of $M_2[TcF_6]$ salts (M = Na, K, Rb, Cs, NH_4, and NMe_4) were grown by the slow evaporation of solutions in 40% HF. The ammonium and the alkaline metal salts crystallize in the trigonal space group $P\bar{3}m$, while the tetramethylammonium salt is rhombohedral. Selected structural parameters are summarized in Table 2. The technetium atoms are located on the origins of the trigonal cells. This results in six symmetry-related fluorido ligands, which show Tc−F bond lengths between 1.895(5) and 1.935(5) Å. Figure 1 shows structure plots of the cesium salt as representative for the structures of the $M_2[TcF_6]$ salts (M = NH_4, Na, K, Rb, Cs). They crystallize isostructural to $K_2[ReF_6]$, the only hexafluoridorhenate(IV), which has to the best of our knowledge been studied by a single-crystal X-ray diffraction study.[23] The octahedra formed by the $[TcF_6]^{2-}$ anions are compressed along the crystallographic z axis, which lowers the local symmetry of the ion.

The cesium ions are located in a way that they have three groups of fluorides with distances of 3.119(6) Å (three of such), 3.156(1) Å (six of such), and 3.260(5) Å (three of such) for coordination. This well resembles the situation in the $K_2[GeF_6]$ structural type, where an approximate 9 + 3 situation

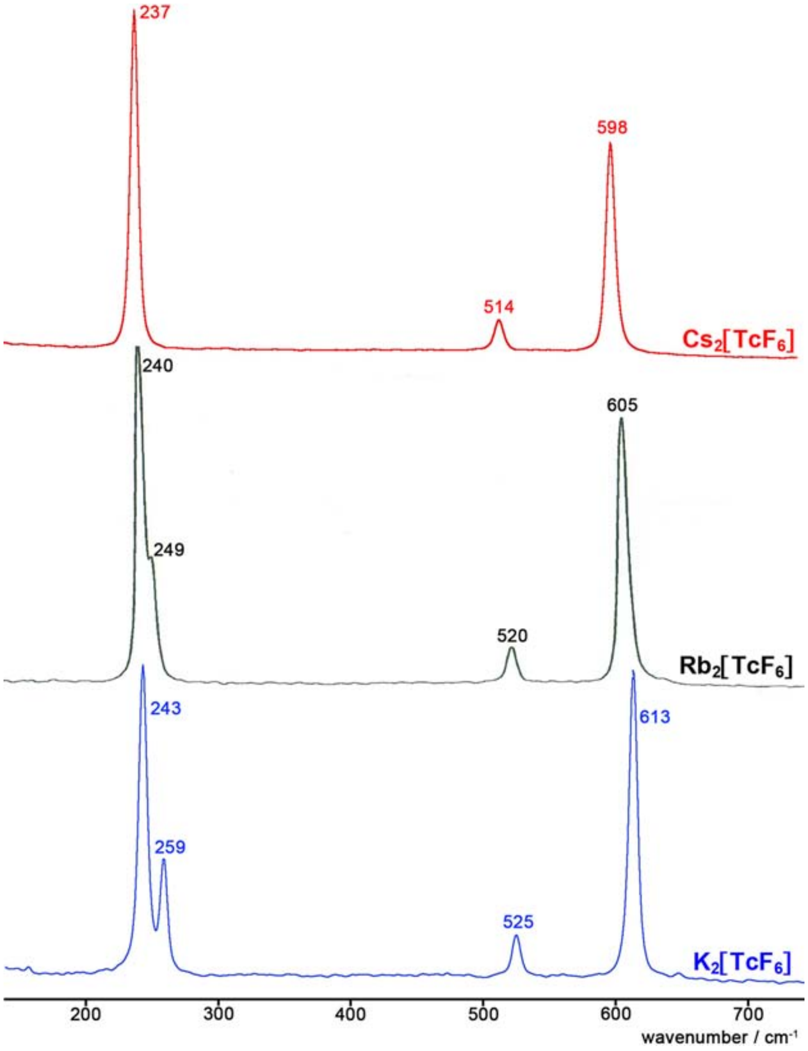


Figure 2. Raman spectra of $K_2[TcF_6]$, $Rb_2[TcF_6]$, and $Cs_2[TcF_6]$.

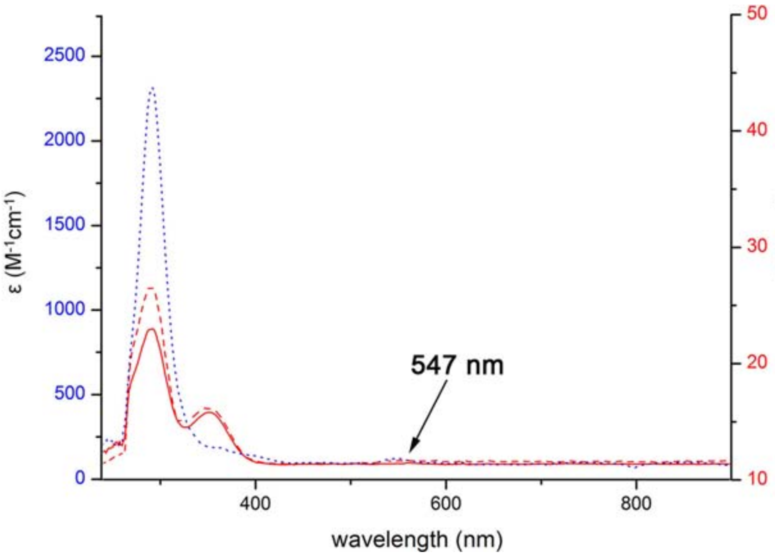


Figure 3. UV/vis spectra of $K_2[TcF_6]$ immediately after dissolution in water (red solid line) and after 4 months (red dotted line) and of $(NH_4)_3Na[F_5Tc{-}O{-}TcF_5]$ (blue line).

has been found.[24] The same bonding mode is also found for the NH_4^+, Na^+, K^+, and Rb^+ salts.

The lowering of the symmetry of the coordination polyhedra of $[TcF_6]^{2-}$ from O_h to D_{3d} is well reflected by the vibrational

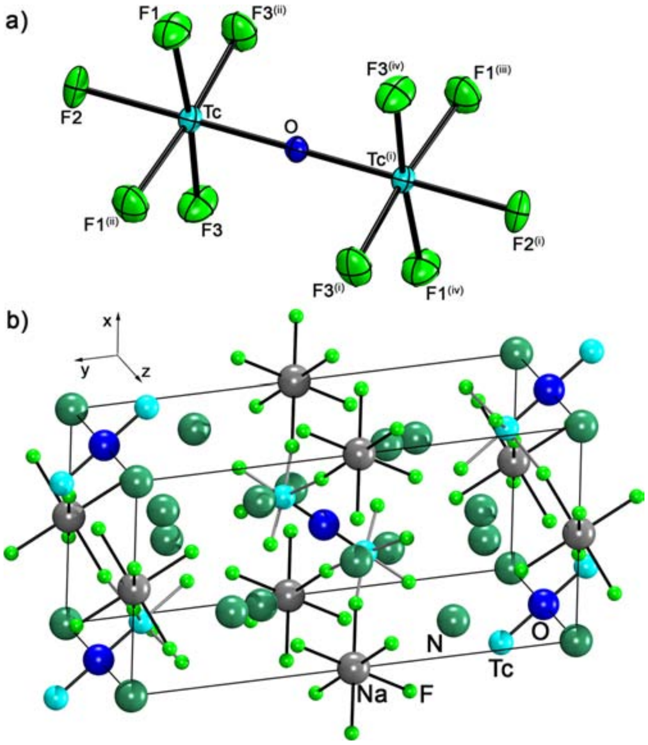


Figure 4. (a) Ellipsoid representation of the $[F_5Tc{-}O{-}TcF_5]^{4-}$ anion. Symmetry operators: (i) $-x, 2-y, z$, (ii) $x, y, 1-z$, (iii) $-x, 2-y, -z$, (iv) $-x, 2-y, 1-z$. (b) Unit cell of $Na(NH_4)_3[F_5TcOTcF_5]\cdot 2(NH_4)F$.

spectra of the compounds. This is demonstrated by the Raman spectra of $K_2[TcF_6]$, $Rb_2[TcF_6]$, and $Cs_2[TcF_6]$. The following irreducible representations apply to the point symmetry D_{3d}: $\Gamma = 2A_{1g} + A_{1u} + 2A_{2u} + 2E_g + 3E_u$, whereas the A_{1g} and E_g vibrations are Raman-active. In the case of O_h symmetry, the Raman spectrum exhibits three bands of the symmetry species A_{1g}, E_g, and F_{2g}. When the symmetry is lowered to D_{3d}, the F_{2g} band is split into two Raman-active bands of the symmetry species A_{1g} and E_g. Depending on the degree of symmetry lowering this splitting of the F_{2g} bending mode can be observed in the Raman spectra.

In the Raman spectrum of $K_2[TcF_6]$, we clearly observe two bands in the region of the Tc−F stretching vibrations (613 and 525 cm^{-1}, A_{1g}, E_g) and two bands in the region of the bending modes (259 and 243 cm^{-1} $F_{2g} \rightarrow A_{1g}, E_g$). Due to the different degree of symmetry lowering (see also the angles given in Table 2), the splitting of the F_{2g} band decreases continuously from $K_2[TcF_6]$ to $Cs_2[TcF_6]$, where it can finally no more be resolved in the experimental spectrum (Figure 2). Additionally, the minor differences of the Tc−F bond strengths are reflected by the Raman spectra. The Tc−F bond lengths slightly increase from $K_2[TcF_6]$ to $Cs_2[TcF_6]$, which leads to the expected shifts of the Raman bands to lower frequencies.

The Raman spectra are completely consistent with single crystal analysis data. Thus, a D_{4h} symmetry of alkaline metal hexafluoridotechnetates(IV) as was suggested in a previous paper can be excluded.[4]

In contrast to the other hexahalogenidotechnetates(IV),[25] $[TcX_6]^{2-}$ (X = Cl, Br, I), the $[TcF_6]^{2-}$ salts possess a remarkable stability in water. In accordance with previous reports, they can be recrystallized from distilled water without noticeable decomposition.[1,19] A long-time experiment, however, shows that the UV absorptions undergo a marked change in their intensity as has been described above (Figure 3). Simultaneously, the solutions appear to become pink. This behavior can be understood by a gradual hydrolysis of hexafluoridotechnetate(IV), the rate of which is increased in slightly alkaline solutions. A pink solid, which contains the first hydrolysis product of $(NH_4)_2[TcF_6]$ could finally be isolated from a reaction with aqueous ammonia (25%).

Figure 3 shows the UV/vis spectrum of this compound with absorptions at 290 nm ($\varepsilon = 2096$) and 547 nm ($\varepsilon = 38.9$). It is highly probable that the spectral changes in aqueous solutions of $[TcF_6]^{2-}$ in the long-time experiment discussed above can be explained by the slow formation of this decomposition product, which could be assigned to a composition of $[F_5Tc{-}O{-}TcF_5]^{4-}$. The structure of the anion has been confirmed by an X-ray structure analysis on $(NH_4)_3Na[F_5Tc{-}O{-}TcF_5]\cdot 2(NH_4)F$.[20]

Figure 4a shows an ellipsoid representation of the complex anion together with a unit cell plot. Selected bond lengths and angles are given in Table 3. A linear oxido bridge connects two $\{TcF_5\}^-$ subunits in the complex anion. The bonding situation in the obtained $\{Tc^{IV}{-}O{-}Tc^{IV}\}^{6+}$ core is characterized by a considerable electron donation from the p_x and p_y orbitals of the oxygen atom to d_π orbitals of the metal ions. This is mainly indicated by the relatively short Tc−O−Tc bonds of 1.852(1) Å, which is in the range between typical Tc−O single and double bonds,[25] and the O−Tc−F(*cis*) angles of 92.8(1) and 92.9(1)°, which are due to the steric strain induced by the partial double bonds.

The formation of μ-O compounds during a stepwise hydrolysis of halogenido compounds of technetium(IV) is not without precedent and has been described before for $[Tc^{IV}Cl_4(solv)_2]$ compounds (solv = acetonitrile, DMSO, and H_2O).[26,27] The structures of the neutral dimers obtained are very similar to that of the $[F_5Tc{-}O{-}TcF_5]^{4-}$ anion. The fact that $[F_5Tc{-}O{-}TcF_5]^{4-}$ readily crystallizes after the addition of NaF as a mixed NH_4^+/Na^+ salt can be understood by the role which the sodium ions play in the formation of the solid state structure: they connect the complex anions by the formation of stable $\{NaF_6\}$ octahedra (see Figure 4b).

CONCLUSIONS

In conclusion, the present article describes various routes for the preparation of $[TcF_6]^{2-}$ salts with different cations and presents the first single-crystal X-ray diffraction studies on a

Table 3. Selected Bond Lengths/Å and Angles/deg in $(NH_4)_3Na[F_5Tc{-}O{-}TcF_5]\cdot 2NH_4)F^a$

Tc−O	1.852(1)	Tc−F1	1.928(3)	TcF2	1.577(5)
Tc−F3	1.947(3)	Na···F3	2.359(3)	Na···F4	2.228(6)
O−Tc−F1	92.9(1)	O−Tc−F2	179.5(2)		
O−Tc−F3	92.8(1)	Tc−O−Tc′	180		

[a] Symmetry operation: (′) $3-x, -y+2, -z+1$.

series of such compounds. On the basis of the exact crystal structures and the structural characterization of a hydrolysis product, some of the hitherto unclear and controversially discussed properties such as color and spectroscopic data could be settled. The results may contribute to a better understanding of the still not completely understood structural chemistry of hexafluoridometallates, and the ready availability of a number of $[TcF_6]^{2-}$ salts may make them interesting as precursors in the further development of synthetic chemistry of the still less explored oxidation state "+4" of this radioactive element.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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

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Notes

The authors declare no competing financial interest.

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