


Technetium Hot Paper
How to cite: *Angew. Chem. Int. Ed.* **2022**, *61*, e202113777

International Edition: doi.org/10.1002/anie.202113777

German Edition: doi.org/10.1002/ange.202113777

Ammonium Pertechnetate in Mixtures of Trifluoromethanesulfonic Acid and Trifluoromethanesulfonic Anhydride

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Dedicated to Uwe Otto on the occasion of his retirement

Abstract: Ammonium pertechnetate reacts in mixtures of trifluoromethanesulfonic anhydride and trifluoromethanesulfonic acid under final formation of ammonium pentakis(trifluoromethanesulfonato)oxidotechnetate(V), $(\text{NH}_4)_2[\text{TcO}(\text{OTf})_5]$. The reaction proceeds only at exact concentrations and under the exclusion of air and moisture via pertechnetyl trifluoromethanesulfonate, $[\text{TcO}_3(\text{OTf})]$, and intermediate Tc^{VI} species. ^{99}Tc nuclear magnetic resonance (NMR) has been used to study the Tc^{VI} compound and electron paramagnetic resonance (EPR), ^{99}Tc NMR and X-ray absorption near-edge structure (XANES) experiments indicate the presence of the reduced technetium species. In moist air, $(\text{NH}_4)_2[\text{TcO}(\text{OTf})_5]$ slowly hydrolyses under formation of the tetrameric oxidotechnetate(V) $(\text{NH}_4)_4[\{\text{TcO}(\text{TcO}_4)_4\}] \cdot 10\text{H}_2\text{O}$. Single-crystal X-ray crystallography was used to determine the solid-state structures. Additionally, UV/Vis absorption and IR spectra as well as quantum chemical calculations confirm the identity of the species.

Introduction

Even though metal trifluoromethanesulfonates (triflates, ^-OTf) see wide applications as catalysts^[1,2] or leaving groups in both organic^[3–6] and inorganic chemistry,^[7–9] their solid-

state chemistry has not seen much attention. Homoleptic triflates are crystallographically poorly investigated, even though these weakly coordinating anions (WCAs)^[10,11] are, amongst others, widely used in organic reactions,^[12–15] and have been proposed for novel applications such as the recycling of thoria in thorium-based nuclear fuels.^[16] There may be a variety of reasons for this, as triflates generally crystallise rather poorly, and they are readily displaced by stronger donors such as water. In addition, the chemistry in anhydrous superacids (HOTf : $\text{p}K_{\text{a}(\text{H}_2\text{O})} = -14$) often demands skilled techniques such as working in flame-sealed ampoules and the use of inert gas systems with corrosion-resistant equipment. Less than 24 of homoleptic p-, f- and d-block metal triflates have been reported with structural data so far (Conquest search v. 5.42, Nov. 2020). High triflate coordination has been observed with actinides, such as in $(\text{H}_5\text{O}_2)[\text{Th}(\text{H}_2\text{O})_6(\text{OTf})_3][\text{Th}(\text{H}_2\text{O})_3(\text{OTf})_6]$ ^[17] as well as with lanthanides such as in $(\text{NO})_5[\text{Eu}(\text{OTf})_8]^{5-}$.^[18] However, high oxidation state triflates are rare.^[19,20] Of these, antimony complexes show the highest valency of +5 at the metal centre in the complexes $[\text{SbCl}_4(\text{OTf})_2]^{2+}$ ^[21] and $[\text{Sb}(\text{C}_6\text{F}_5)_4(\text{OTf})]^{2+}$.^[22] Particularly interesting in this regard is the chemistry of the group 7 metals Mn, Tc and Re, as their position in the periodic table makes them prone to unique chemistry. However, a systematic

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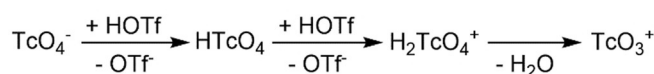
 Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under:
 <https://doi.org/10.1002/anie.202113777>.

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approach is hampered by the fact that Tc is a radioelement (^{99}Tc , β^- emitter, $t_{1/2} = 210000$ years). Although its radiological properties do not require much shielding, a radio-nuclide laboratory is needed for open handling of milligram amounts. The unique differences between the group 7 elements can be seen in the properties of their oxides in oxidation state +7. Mn_2O_7 is a shock-sensitive, violet oil that solidifies at 5.9°C with a bent structure of corner-sharing MnO_4 tetrahedra.^[23] In contrast, Tc_2O_7 is a volatile compound crystallising in thin, pale yellow, hygroscopic plates with a unique linear arrangement^[24] and Re_2O_7 is made up of regular corner-sharing ReO_4 tetrahedra which form polymeric double layers.^[25] Their corresponding acids also behave very differently from each other, as HMnO_4 is not existent, and the only material represented in the literature is known as “feste Permangansäure” (“solid permanganic acid”) with the composition $\text{Mn}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$.^[26] In contrast, concentrated HTcO_4 is dark-yellow and forms a dark-red solid upon further evaporation.^[27] A hypothetical “ HReO_4 ” does not exist and must be described as a hydrated rhenium oxide $\text{Re}_2\text{O}_7 \cdot (\text{OH}_2)_2$.^[28] In addition, the chemistry of oxocations (“metaly” ions) of oxidation states +7 or higher are limited to a few compounds, such as rare group 8 complexes of the perosmyl(VIII) trioxo dication OsO_3^{2+} or the perosmyl(VIII) dioxo tetracation OsO_2^{4+} .^[29,30] The osmyl(VII) pentacation $\text{Os}^{\text{VII}}\text{O}^{5+}$ is a rare example of a cation with an overall charge of +5.^[31] Oxo cations of ruthenium have only been known in oxidation state +6 in RuOF_4 .^[32] In contrast, rhenium forms in oxidation state +7 stable compounds with the ReO_5^{5+} ,^[31,33] ReO_2^{3+} ^[33,34] and ReO_3^+ cores. The latter has been most prominently known from organometallic complexes such as the classic methyl trioxorhenium.^[35] Its respective halide salts (F, Cl, Br), are all highly reactive and only moderately stable at ambient conditions. $[\text{ReO}_3]^+[\text{I}]^-$ cannot be isolated due to the oxidation potential of Re^{VII} .^[36,37] Of the lighter homologues, MnO_3^+ is known in the solid state, however, there is no indication that a free and unsolvated cation of this type can be generated, while the radioactive pertechnetyl cation TcO_3^+ has been made in the form of the fluoride^[38] and fluorosulfate.^[39] Inspired by the work of Seppelt, who notes that “the best candidate for a largely unsolvated MO_3^+ cation is TcO_3^+ ”, we have investigated the chemistry of NH_4TcO_4 in triflic acid (HOTf) and triflic anhydride (Tf_2O). TcO_3^+ has previously been stabilised in the 1,4,7-triazacyclononane (tacn) complex $[\text{TcO}_3(\text{tacn})]^+\text{Br}^-$.^[40] TcO_4^- also reacts in the presence of benzoyl chloride and stabilising coordinating ligands such as 1,10-phenanthroline or 2,2'-bipyridine to $[\text{TcO}_3\text{Cl}(\text{phen})]$ and $[\text{TcO}_3\text{Cl}(\text{bipy})]$, respectively.^[41] The volatile pertechnetyl fluorosulfate $[\text{TcO}_3]^+[\text{SO}_3\text{F}]^-$ has been isolated by treating KTcO_4 with fluorosulfuric acid that contained SO_3 , followed by sublimation at room temperature and cooling to -78°C .^[40] Pertechnetyl fluoride $[\text{TcO}_3]^+[\text{F}]^-$ can be isolated from a reaction of TcO_2 with F_2 or after treatment of KTcO_4 with BiF_5 and anhydrous HF followed by sublimation at -78°C .^[39,42]

Results and Discussion

In our reinvestigation of the Tc chemistry in superacids, following up on the work by Poineau et al.^[43] and Denden et al.,^[44,45] we have been able to isolate pertechnetyl triflate $[\text{TcO}_3(\text{OTf})]$ for the first time and have observed that TcO_4^- in such systems undergoes a spontaneous reduction to ammonium pentakis(trifluoromethanesulfonato)oxotechnetate(V) without the presence of an obvious reducing agent (see SI for proposed mechanism). We were interested in a more straightforward way of targeting a pertechnetyl cation with a weakly coordinating anion, and have hypothesised that the formation of the trioxotechnetium monocation may indeed follow a protonation–dehydration process as proposed by Poineau and co-workers.^[43] Using a suitable strong acid such as triflic acid with its corresponding anhydride thus results in the formation of the TcO_3^+ core (Scheme 1).^[43]



Scheme 1. Formation of TcO_3^+ in triflic acid.

In our hands, the treatment of NH_4TcO_4 (2 mg, 11 μmol , 0.693 MBq; dry, as an evaporated residue from an aqueous stock solution) with 581 μL Tf_2O and 19 μL HOTf under Ar atmosphere and subsequent heating to 60°C for 30 min yields a colourless solution. Upon cooling to room temperature this shows a tinge of purple and microcrystalline yellow $[\text{TcO}_3(\text{OTf})]$ in nearly quantitative yield according to liquid scintillation counting (LSC, see SI).

A ^{99}Tc NMR spectrum of the anhydrous reaction mixture (without any added d-solvent) shows a very narrow signal at $\delta = 209$ ppm ($\nu_{1/2} = 350$ Hz), which can be assigned to $[\text{TcO}_3(\text{OTf})]$. It shall be noted that the same signal is obtained from a reaction of NBu_4TcO_4 and neat fuming triflic acid under strictly dry conditions and also appears as a side-product when solid ammonium or alkaline pertechnetates react with HOTf without the addition of Tf_2O . When such reaction mixtures are exposed to moist air, quickly another, much broader signal can be detected at $\delta = 273$ ppm ($\nu_{1/2} = \text{approx. } 8300$ Hz). This can be assigned to the formation of a compound with lower local symmetry and/or fast ligand exchange reactions in solution.^[46] A similar spectrum is observed for a solution of pertechnetate in sulfuric acid. The spectra and more details are given in the Supporting Information. With regard to previous XAFS and spectroscopic studies,^[44,45,47,48] the species with the broad ^{99}Tc NMR signals can be assigned to pseudo-octahedral $[\text{TcO}_3(\text{OH})(\text{OH}_2)_2]$ or $[\text{TcO}_3(\text{L})(\text{OH}_2)_2]$ species ($\text{L} = \text{OTf}^-$ or HSO_4^-).

If the amount of acid, the time or the temperature is increased, the formation of the purple colour becomes more and more intense at room temperature, and the yield of pertechnetyl triflate is decreased to as low as 44 % (see SI for synthetic details, UV/Vis absorption spectra and yields). As the reaction proceeds, small amounts of gas can be seen evolving. As no additional reductant was present, we propose

that in the redox reaction, molecular O₂ might form in the presence of HOTf (see video in supplement). An attempt to analyse the gas evolution in the head space of the reaction using mass spectrometry was rendered impossible due to the highly corrosive nature of the HOTf.

Interestingly, as long as purple material is present in the solution, the mixture shows thermochromic properties. Cooling to -15°C intensifies the purple colour, while heating to 100°C results in a colourless solution within less than a minute (see videos). We have not been able to fully identify the nature of the purple solution. But previous research has also noted the observation of red and/or purple compounds when experiments on pertechnetetic acid have been performed. They have been attributed to reduced species, for example, Tc^{VI} compounds.^[47–50] The purple solutions obtained during our experiments are indeed EPR-active, and indicate the presence of transient Tc^{VI} species, but with relatively low concentrations (see SI). The spectral parameters are close to those of nitridotechnetium(VI) complexes with OTf[−] ligands.^[51,52] The EPR signal disappears with the purple colour. In parallel, the purple solution shows a strong ⁹⁹Tc NMR resonance at $\delta = +209$ ppm, which correlates well with other hexacoordinate compounds containing TcO₃⁺.^[40,53,54] In addition, in some of the recorded spectra a small resonance at $\delta = -817$ ppm is visible, which could not yet be assigned unambiguously.

To fully address the varying degrees at which the pertechnetyl cation forms under synthetic conditions, we have undertaken a range of synthetic studies with varying ratios of acid to anhydride, and at different temperatures and concentrations. We can state that the exact ratio of NH₄TcO₄:HOTf:Tf₂O is paramount to the successful synthesis. While NH₄TcO₄ does not react with Tf₂O alone, varying amounts of HOTf have a strong effect on the stability of the colour of the solution (see SI for details). However, we have been able to isolate bright yellow crystals of [TcO₃(OTf)] from a purple solution after careful crystallisation at -15°C . The material is air-sensitive, but can be handled under Fomblin-Y[®] oil for several minutes without decomposition. Figure 1 shows the yellow crystals under Fomblin-Y[®] oil with residual purple mother liquor floating on top (left), and isolated crystals as seen through a microscope (right) (field of view ca. 5 mm).

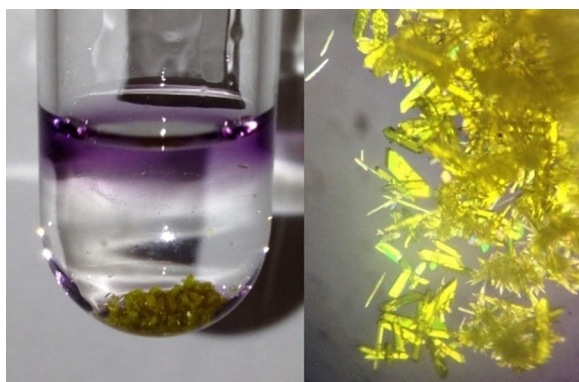


Figure 1. Yellow crystals of [TcO₃(OTf)] under Fomblin-Y[®] oil with residual purple mother liquor floating on top (left) and isolated crystals as seen through a microscope (right) (field of view ca. 5 mm).

The material was isolated easily by removing the supernatant via syringe or pipette. It was possible to dry the yellow product under vacuum and to store it for several months under Ar at room temperature. The solid-state structure (CCDC 2114965) of the material can be seen in Figure 2.

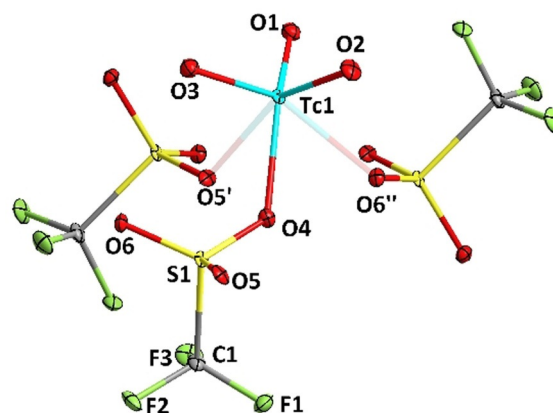


Figure 2. ORTEP representation of the coordination of [TcO₃(OTf)]. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: Tc1–O1 1.690(3), Tc1–O2 1.683(2), Tc1–O3 1.682(3), Tc1–O4 2.221(3), Tc1–O5' 2.272(2), Tc1–O6'' 2.275(2); O1–Tc1–O4 155.4(1), O1–Tc1–O2 105.5(1), O1–Tc1–O3 104.5(1), O1–Tc1–O5' 86.7(1), O1–Tc1–O6'' 88.0(1), O4–Tc1–O2 89.9(1), O4–Tc1–O3 89.4(1), O4–Tc1–O5 73.20(9), O5'–Tc1–O6'' 73.78(8).

The Tc atom is coordinated pseudo-octahedrally, and the Tc=O double bond lengths (Tc1–O1 1.690(3) Å, Tc1–O2 1.683(2) Å, Tc1–O3 1.682(3) Å) are consistent with Tc^{VII} in other TcO₃⁺ complexes. The distance to one triflate oxygen atom (Tc1–O4 2.221(3) Å) is slightly shorter than to the two other triflate oxygen atoms (Tc1–O5' 2.272(2) Å and Tc1–O6'' 2.275(2) Å) coming from the neighbouring molecules.

The coordination in the solid state is represented in Figure 3. Separated layers of bridged pertechnetyl triflate units run along the crystallographic *b*- and *c*-axes. One SO₃ moiety of the triflate anion, thus, binds to one technetium atom and coordinates two other adjacent TcO₃ moieties to form a two-dimensional network.

We have attempted to obtain PXRD of this material, however, finely grained crystals of the sample are unstable on the PXRD film and decompose within five minutes. In contrast, suspending [TcO₃(OTf)] in Tf₂O gives a pale yellow suspension. After letting the material settle for five minutes, a UV/Vis absorption spectrum was measured with a distinct

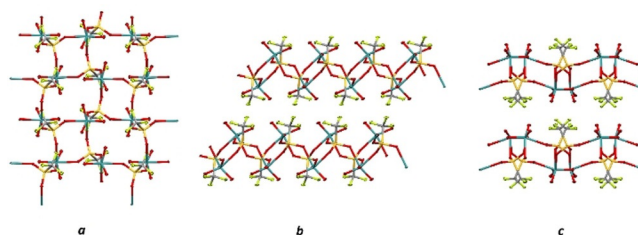


Figure 3. Crystal packing of pertechnetyl triflate [TcO₃(OTf)] in the direction of the crystallographic *a*-axis (a), *b*-axis (b) and *c*-axis (c).

absorption at 350 nm. Dissolving the material in water gives a pale yellow solution with a similar absorption spectrum. This corresponds well with quantum mechanical calculations that predict a λ_{max} at 335 and 370 nm, respectively. UV/Vis absorption spectra were calculated at the ω B2GP-PLYP/def2-TZVP/SMD//PBE-D3BJ/def2-TZVP/SMD level of theories (see SI for details).^[54–60]

From the purple solution, green needle-like crystals were grown at -15°C over the course of two weeks, which were suitable for X-ray diffraction (Figure 4).

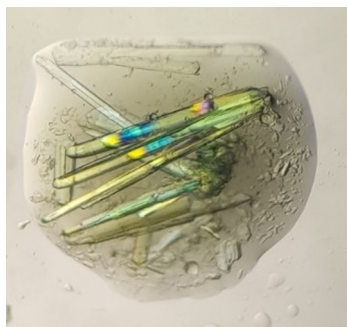


Figure 4. Green crystals of $(\text{NH}_4)_2[\text{TcO}(\text{OTf})_5]\cdot\text{HOTf}$ (field of view ca. 1 mm).

The solid state structure (CCDC 2114967) of the hitherto unknown ammonium pentakis(trifluoromethanesulfonato)-oxidotechnetate(V), $(\text{NH}_4)_2[\text{TcO}(\text{OTf})_5]$ can be seen in Figure 5. The structure consists of pseudo-octahedrally coordinated Tc atoms, with one apex occupied by an oxido ligand with a $\text{Tc}1=\text{O}1$ bond length of 1.612(2) Å, while the other five

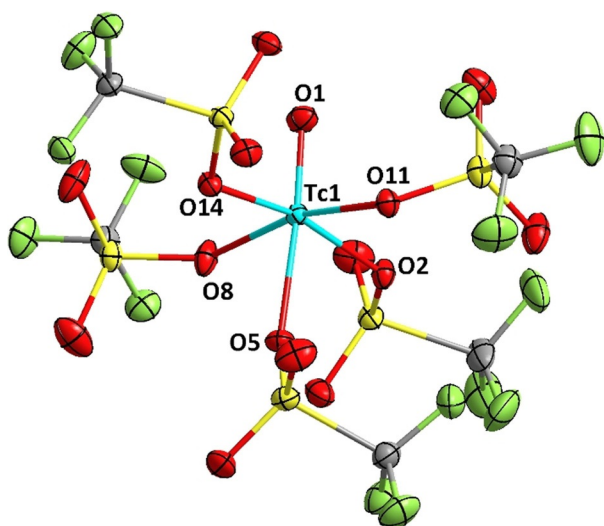


Figure 5. ORTEP representation of the $[\text{TcO}(\text{OTf})_5]^{2-}$ anion. One molecule of coordinated HOTf and the two NH_4^+ cations are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: $\text{Tc}1-\text{O}1$ 1.612(2), $\text{Tc}1-\text{O}2$ 2.010(2), $\text{Tc}1-\text{O}5$ 2.130(2), $\text{Tc}1-\text{O}8$ 2.025(2), $\text{Tc}1-\text{O}11$ 2.013(2), $\text{Tc}1-\text{O}14$ 2.046(2); $\text{O}1-\text{Tc}1-\text{O}5$ 175.66(8), $\text{O}1-\text{Tc}1-\text{O}2$ 99.85(8), $\text{O}1-\text{Tc}1-\text{O}8$ 96.10(8), $\text{O}1-\text{Tc}1-\text{O}11$ 98.40(8), $\text{O}1-\text{Tc}1-\text{O}14$ 94.98(8), $\text{O}5-\text{Tc}1-\text{O}2$ 82.70(7), $\text{O}5-\text{Tc}1-\text{O}8$ 80.48(7), $\text{O}5-\text{Tc}1-\text{O}11$ 85.11(7), $\text{O}5-\text{Tc}1-\text{O}14$ 82.65(6).

coordination sites are occupied by $\kappa^1\text{-O}$ coordinating triflate anions. The triflate *trans* to the $\text{Tc}=\text{O}$ moiety has, due to the *trans*-influence,^[61] a significantly longer bond length of 2.130(2) Å compared to the triflate groups in the equatorial positions, which range between 2.010(2)–2.046(2) Å. The $\text{O}=\text{Tc}-\text{OTf}(\textit{trans})$ axis is nearly linear (175.66(8)°), while the equatorial ligands are slightly bent downwards in an umbrella-type fashion (94.98(8)–99.85(8)°), which is the typical motif for $\text{Tc}^{\text{V}}\text{O}$ complexes. The network is held together by hydrogen bonds, most prominently those of the NH_4^+ cations, which coordinate two adjacent $[\text{TcO}(\text{OTf})_5]^{2-}$ moieties (Figure 6). Two protons of the NH_4^+ ion are connected to one equatorial OTf^- ligand and the *trans* triflate group of one $[\text{TcO}(\text{OTf})_5]^{2-}$ moiety and at the same time to an equatorial triflate group of a neighbouring $[\text{TcO}(\text{OTf})_5]^{2-}$ complex.

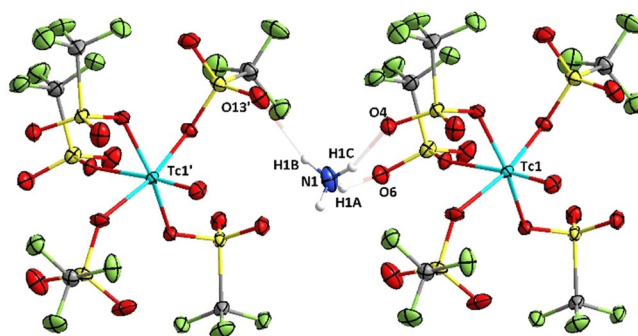


Figure 6. Hydrogen interactions of the NH_4^+ linking two adjacent $[\text{TcO}(\text{OTf})_5]^{2-}$ moieties.

A XANES spectrum of $(\text{NH}_4)_2[\text{TcO}(\text{OTf})_5]$ is in accord with the Tc + 5 oxidation state. We were also able to record a ^{99}Tc NMR spectrum of the technetium(V) complex. Expectedly, it is characterised by an extremely broad line at $\delta = 6600$ ppm ($\nu_{1/2} \approx 18$ kHz). The chemical shift and the line width are in accord with the ^{99}Tc NMR spectrum of $(\text{NBU}_4)[\text{TcOCl}_4]$, one of the few Tc^{V} complexes which have been studied by ^{99}Tc NMR before.^[62] The spectra of both compounds are shown in the SI.

$(\text{NH}_4)_2[\text{TcO}(\text{OTf})_5]$ is sensitive against moisture and exposure to air results in a slow decomposition. Hydrolysis and disproportionation finally give TcO_2 and TcO_4^- . When the hydrolysis is performed under controlled conditions, green-red dichroic crystals of $(\text{NH}_4)_4[\{\text{TcO}(\text{OTcO}_3)_4\}_4]\cdot 10\text{H}_2\text{O}$ can be isolated in approximately 30% yield. They have a melting point of about 30°C , but can be stored at lower temperature and dry conditions without decomposition. The compound consists of a central $\{\text{Tc}_4\text{O}_4\}^{12+}$ unit with four pertechnetato ligands coordinated to each of the central technetium atoms. Figure 7 shows the structure of the resulting $(\text{NH}_4)_4[\{\text{TcO}(\text{OTcO}_3)_4\}_4]$ salt (CCDC 2114966). A similar compound with the same anionic unit and four $(\text{H}_7\text{O}_3)^+$ cations has been reported very recently as the product of a not yet fully understood auto reduction of HTcO_4 .^[63]

$(\text{NH}_4)_4[\{\text{TcO}(\text{OTcO}_3)_4\}_4]$ partially dissolves in HOTf. The orange-red solution displays very broad ^{99}Tc NMR signals

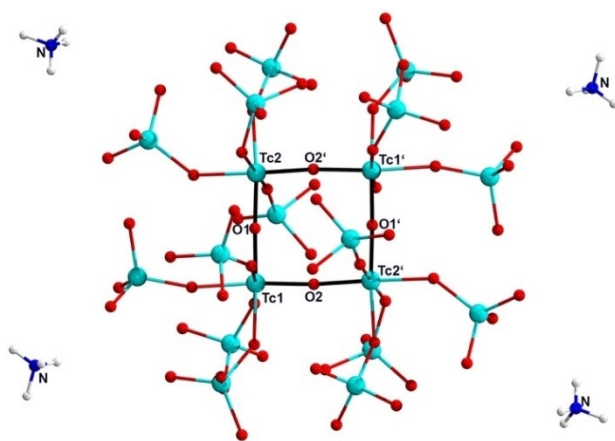


Figure 7. ORTEP representation of $(\text{NH}_4)_4\{[\text{TcO}(\text{OTfO}_3)_4]\}_4$. A ball and stick model has been chosen for clarity, an ellipsoid plot is depicted in the SI. Selected bond lengths [Å] and angles [°]: Tc1–O1 1.804(7), Tc1–O2 1.822(8), Tc2–O1 1.822(7), Tc2–O2' 1.805(8); Tc1–O1–Tc2 177.8(5) Tc1–O2–Tc2' 172.6(5).

($\nu_{1/2}$ approximately 50 kHz) in the region between those of $[\text{TcOCl}_4]^-$ ($\delta = 4950$ ppm) and $[\text{TcO}(\text{OTf})_5]^{2-}$ ($\delta = 6600$ ppm) together with a broadened pertechnetate signal ($\nu_{1/2} = 400$ Hz), see SI.

Denden et al. have investigated the reduction of technetium(VII) in triflic acid under α irradiation at a dose rate of 66 ± 7 kGy h⁻¹.^[45] Under these conditions, they observe higher reaction kinetics between 4 and 8 M HOTf, while forming the same Tc^V oxopolymeric species as without irradiation.^[44] At higher concentrations (> 11 M) they observe the formation of a yellow solution, which is attributed to $[\text{Tc}^{\text{VII}}\text{O}_3(\text{H}_2\text{O})_2(\text{OH})]$.^[43] They further describe the formation of a green solution upon irradiation, with UV/Vis absorptions at 400 and 750 nm, assigning this to a reduced species comparable to $[\text{Tc}^{\text{VO}}(\text{HSO}_4)_2(\text{OH})(\text{H}_2\text{O})_2]$. The authors hypothesise that the reduction is due to thermal decomposition and hydrolysis processes, caused by the exothermic hydration reaction of triflic acid in water. Using XAFS and DFT, they further identified $[\text{Tc}^{\text{VO}}(\text{OTf})_2(\text{OH})(\text{H}_2\text{O})]$ to be the most probable compound to form, but no crystal structure was determined at that point. We consider that behaviour very similar to our observations. It is remarkable that the amount of energy deposited due to the α irradiation is comparable to the energy provided by heating the sample by 90 K as applied during our experiment (see SI for details).

Interestingly, an attempt to isolate the $[\text{TcO}(\text{OTf})_5]^{2-}$ moiety from the Tc^V precursor $(\text{NBu}_4)[\text{TcOCl}_4]$ ^[64] by simply dissolving it in triflic acid did not yield the desired product but resulted in a blue solution that quickly decomposed.

Conclusion

We have identified a straightforward reaction pathway to synthesise pertechnetyl triflate in near-quantitative yield from NH_4TcO_4 without needing to use sublimation techniques or any unusual or hazardous precursors. The material crystallises as yellow crystals or microcrystals from triflic anhydride upon

addition of triflic acid at 60 °C and can be readily isolated by syringing off the mother liquor. UV/Vis absorption and LSC spectra show that the exact concentration, ratio and temperature are imperative for the successful synthesis. Pertechnetyl triflate may thus become a versatile starting material for future investigations on high-valency pertechnetyl compounds. From these solutions, pentakis(triflate)-oxidotechnetate(V) salts form spontaneously without addition of a reducing agent, indicating that a spontaneous auto reduction of pertechnetate is possible in nuclear waste materials.

Acknowledgements

MZ sincerely thanks Lars Hemmersbach and Prof. Dr. Hans-Günther Schmalz for attempting to measure the O₂ evolution using their MS equipment and essentially ruining it with the highly corrosive triflic acid. MB thanks the Fonds der Chemischen Industrie and the Regional Computing Centre of the University of Cologne (RRZK) for providing computing time on the DFG-funded (Funding number: INST 216/512/1FUGG) High Performance Computing (HPC) system CHEOPS as well as for their support. The authors acknowledge the KIT synchrotron light source and the Institute for Beam Physics and Technology (KIT-IBPT) for operation of the Karlsruhe Research Accelerator (KARA). AH and AK thank Prof. Dr. Bernd Neumaier, Department of Chemistry, Division of Nuclear Chemistry, Cologne University Clinics, Institute of Radiochemistry, and Forschungszentrum Jülich for financial support. Open Access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: anhydride · pertechnetate · reduction · super acid · trifluoromethanesulfonic acid

- [1] K. Ishihara, M. Kubota, H. Kurihara, H. Yamamoto, *J. Am. Chem. Soc.* **1995**, *117*, 4413–4414.
- [2] L. Coulombel, M. Rajzmann, J.-M. Pons, S. Olivero, E. Duñach, *Chem. Eur. J.* **2006**, *12*, 6356–6365.
- [3] P. J. Stang, M. Hanack, L. R. Subramanian, *Synthesis* **1982**, 85–126.
- [4] D. L. Comins, A. Dehghani, *Tetrahedron Lett.* **1992**, *33*, 6299–6302.
- [5] T. Gramstad, R. N. Haszeldine, *J. Chem. Soc.* **1957**, 4069–4079.
- [6] B. Dhakal, L. Bohé, D. Crich, *J. Org. Chem.* **2017**, *82*, 9263–9269.
- [7] D. Veghini, H. Berke, *Inorg. Chem.* **1996**, *35*, 4770–4778.
- [8] S. Schlecht, J. Magull, D. Fenske, K. Dehnicke, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1994–1995; *Angew. Chem.* **1997**, *109*, 2087–2089.
- [9] J. Bonnamour, C. Bolm, *Org. Lett.* **2011**, *13*, 2012–2014.
- [10] I. Krossing, *Chem. Eur. J.* **2001**, *7*, 490–502.
- [11] A. Martens, P. Weis, M. C. Krummer, M. Kreuzer, A. Meierhöfer, S. C. Meier, J. Bohnenberger, H. Scherer, I. Riddlestone, I. Krossing, *Chem. Sci.* **2018**, *9*, 7058–7068.

- [12] S. Kobayashi, *Eur. J. Org. Chem.* **1999**, 15–27.
- [13] S. Kobayashi, M. Sugiura, H. Kitagawa, W. W.-L. Lam, *Chem. Rev.* **2002**, *102*, 2227–2302.
- [14] R. D. Howells, J. D. Mc Cown, *Chem. Rev.* **1977**, *77*, 69–92.
- [15] J. Keskiäli, A. Parviainen, K. Lagerblom, T. Repo, *RSC Adv.* **2018**, *8*, 15111–15118.
- [16] S. Cagno, L. Gijsemans, V. Tyrpekl, T. Cardinaels, M. Verwerft, K. Binnemans, *J. Sustain. Metall.* **2017**, *3*, 659–667.
- [17] N. Torapava, I. Persson, L. Eriksson, D. Lundberg, *Inorg. Chem.* **2009**, *48*, 11712–11723.
- [18] J. Bruns, S. Krüger, M. Adlung, C. Wickleder, O. Niehaus, R. Pöttgen, T. Klüner, J. Kräuter, M. S. Wickleder, *Chem. Eur. J.* **2015**, *21*, 12389–12395.
- [19] K. Neuschulz, M. Penning, L. Groß, T. Klüner, M. S. Wickleder, *Dalton Trans.* **2012**, *41*, 4685–4691.
- [20] C. Logemann, T. Klüner, M. S. Wickleder, *Z. Anorg. Allg. Chem.* **2013**, *639*, 485–492.
- [21] A. Burchardt, K.-W. Klinkhammer, G. Lang, M. Lauster, A. Rihm, A. Schmidt, *Main Group Met. Chem.* **1998**, *21*, 543–552.
- [22] B. Pan, F. P. Gabbaï, *J. Am. Chem. Soc.* **2014**, *136*, 9564–9567.
- [23] A. Simon, R. Dronskowski, B. Krebs, B. Hettich, *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 139–140; *Angew. Chem.* **1987**, *99*, 160–161.
- [24] B. Krebs, *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 381–382; *Angew. Chem.* **1969**, *81*, 395–395.
- [25] B. Krebs, A. Mueller, H. H. Beyer, *Inorg. Chem.* **1969**, *8*, 436–443.
- [26] B. Krebs, K.-D. Hasse, *Z. Naturforsch. B* **1973**, *28*, 218–219.
- [27] C. Soderquist, J. Weaver, H. Cho, B. McNamara, S. Sinkov, J. McCloy, *Inorg. Chem.* **2019**, *58*, 14015–14023.
- [28] H. Beyer, O. Glemser, B. Krebs, G. Wagner, *Z. Anorg. Allg. Chem.* **1970**, *376*, 87–100.
- [29] R. Bougon, B. Buu, K. Seppelt, *Chem. Ber.* **1993**, *126*, 1331–1336.
- [30] M. A. Hepworth, P. L. Robinson, *J. Inorg. Nucl. Chem.* **1957**, *4*, 24–29.
- [31] J. H. Holloway, H. Selig, H. H. Claassen, *J. Chem. Phys.* **1971**, *54*, 4305–4311.
- [32] H. Shorafa, K. Seppelt, *Z. Anorg. Allg. Chem.* **2007**, *633*, 543–547.
- [33] E. E. Aynsley, R. D. Peacock, P. L. Robinson, *J. Chem. Soc.* **1950**, 1622–1624.
- [34] R. D. Peacock, *J. Chem. Soc.* **1955**, 602–603.
- [35] W. A. Herrmann, P. Kiprof, K. Rypdal, J. Tremmel, R. Blom, R. Alberto, J. Behm, R. W. Albach, H. Bock, *J. Am. Chem. Soc.* **1991**, *113*, 6527–6537.
- [36] C. C. Romão, F. E. Kühn, W. A. Herrmann, *Chem. Rev.* **1997**, *97*, 3197–3246.
- [37] A. Engelbrecht, A. V. Grosse, *J. Am. Chem. Soc.* **1954**, *76*, 2042–2045.
- [38] J. Supel, U. Abram, A. Hagenbach, K. Seppelt, *Inorg. Chem.* **2007**, *46*, 5591–5595.
- [39] J. Supel, A. Hagenbach, U. Abram, K. Seppelt, *Z. Anorg. Allg. Chem.* **2008**, *634*, 646–648.
- [40] H. Braband, U. Abram, *Inorg. Chem.* **2006**, *45*, 6589–6591.
- [41] Y. Tooyama, H. Braband, B. Spingler, U. Abram, R. Alberto, *Inorg. Chem.* **2008**, *47*, 257–264.
- [42] H. Selig, J. G. Malm, *J. Inorg. Nucl. Chem.* **1963**, *25*, 349–351.
- [43] F. Poineau, P. F. Weck, K. German, A. Maruk, G. Kirakosyan, W. Lukens, D. B. Rego, A. P. Sattelberger, K. R. Czerwinski, *Dalton Trans.* **2010**, *39*, 8616–8619.
- [44] I. Denden, R. Essehli, M. Fattahi, *J. Radioanal. Nucl. Chem.* **2013**, *296*, 149–155.
- [45] I. Denden, J. Roques, F. Poineau, P. L. Solari, M. L. Schlegel, G. Blain, M. Fattahi, *Radiochim. Acta* **2017**, *105*, 135–140.
- [46] A. D. Bain, G. J. Duns, *Can. J. Chem.* **1996**, *74*, 819–824.
- [47] G. E. Boyd, J. W. Cobble, C. M. Nelson, W. T. Smith, *J. Am. Chem. Soc.* **1952**, *74*, 556–557.
- [48] C. L. Rulfs, R. A. Pacer, R. F. Hirsch, *J. Inorg. Nucl. Chem.* **1967**, *29*, 681–691.
- [49] B. C. Childs, K. V. Lawler, H. Braband, D. S. Mast, L. Bigler, U. Stalder, D. R. Peterson, A. Jansen, P. M. Forster, K. R. Czerwinski, R. Alberto, A. P. Sattelberger, F. Poineau, *Eur. J. Inorg. Chem.* **2018**, 1137–1144.
- [50] K. V. Lawler, B. C. Childs, K. R. Czerwinski, A. P. Sattelberger, F. Poineau, P. M. Forster, *Chem. Commun.* **2018**, *54*, 1261–1264.
- [51] J. Baldas in *Technetium and Rhenium Their Chemistry and Its Applications* (Eds.: K. Yoshihara, T. Omori), Springer, Berlin, **1996**, pp. 37–76.
- [52] U. Abram, R. Kirmse, *Radiochim. Acta* **1993**, *63*, 139–144.
- [53] K. J. Franklin, C. J. L. Lock, B. G. Sayer, G. J. Schrobilgen, *J. Am. Chem. Soc.* **1982**, *104*, 5303–5306.
- [54] J. A. Thomas, A. Davison, *Inorg. Chem.* **1992**, *31*, 1976–1978.
- [55] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396.
- [56] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.
- [57] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- [58] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.
- [59] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.
- [60] L. Goerigk, M. Casanova-Paéz, *Aust. J. Chem.* **2021**, *74*, 3–15.
- [61] B. J. Coe, S. J. Glenwright, *Coord. Chem. Rev.* **2000**, *203*, 5–80.
- [62] L. A. O’Connell, R. M. Pearlstein, A. Davison, J. R. Thornback, J. F. Kronauge, A. G. Jones, *Inorg. Chim. Acta* **1989**, *161*, 39–43.
- [63] K. E. German, A. M. Fedoseev, M. S. Grigoriev, G. A. Kirakosyan, T. Dumas, C. Den Auwer, P. Moisy, K. V. Lawler, P. M. Forster, F. Poineau, *Chem. Eur. J.* **2021**, *27*, 13624–13631.
- [64] A. Davison, H. S. Trop, B. V. Depamphilis, A. G. Jones, R. W. Thomas, S. S. Jurisson, *Inorganic Syntheses*, Wiley, Hoboken, **1982**, pp. 160–162.

Manuscript received: October 11, 2021

Accepted manuscript online: November 9, 2021

Version of record online: December 3, 2021