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Synthesis and Structure of Technetium Trichloride

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Abstract: Technetium trichloride has been synthesized by reaction of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $\text{HCl}(\text{g})$ at 300 °C. The mechanism of formation mimics the one described earlier in the literature for rhenium. $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ [$P\bar{1}$; $a = 6.0303(12)$ Å, $b = 6.5098(13)$ Å, $c = 8.3072(16)$ Å, $\alpha = 112.082(2)^\circ$, $\beta = 96.667(3)^\circ$, $\gamma = 108.792(3)^\circ$; $\text{Tc}-\text{Tc} = 2.150(1)$ Å] is formed as an intermediate in the reaction at 100 °C. Technetium trichloride is formed above 250 °C and is isostructural with its rhenium homologue. The structure consists of Tc_3Cl_9 clusters [$R\bar{3}m$; $a = b = 10.1035(19)$ Å, $c = 20.120(8)$ Å], and the $\text{Tc}-\text{Tc}$ separation is 2.444(1) Å. Calculations on TcX_3 ($X = \text{Cl}, \text{Br}$) have confirmed the stability of TcCl_3 and suggest the existence of a polymorph of TcBr_3 with the ReBr_3 structure.

Binary transition-metal halides exhibit a rich chemistry, and the study of their structure, bonding, and physical properties permits a better understanding of the physicochemical trends across the periodic table. For the binary chlorides, approximately 60 compounds are known, and in these, the metals exhibit valences ranging from I to VI.¹ The higher-valence chlorides are accessible for the early second- and third-row metals and adopt molecular octahedral (MCl_6 ; $M = \text{W}, \text{Re}$) and edge-sharing bioctahedral (M_2Cl_{10} ; $M = \text{Nb}, \text{Ta}, \text{Mo}, \text{W}, \text{Re}$) structures.¹ Extended structures and/or cluster compounds are encountered for the lower valences (I–IV). The structures consist of infinite chains of edge-sharing MCl_6 octahedra for the heavier tetrachlorides of groups 4 to 7;² octahedral M_6Cl_{12} clusters ($M = \text{Zr}, \text{Mo}, \text{W}, \text{Pt}, \text{Pd}$)^{3a,b} for the dichlorides; and stacked, hexagonally packed layers of either all metal (Hf, Zr) or all chlorine atoms for the monochlorides.^{3a} The trichlorides exhibit a very rich chemistry, and more than 20 binary trihalide structure types are now known, including chains, layers, and three-dimensional networks containing metal–halide clusters.⁴ All of the second- and third-row metal trichlorides of groups 4 to 9 have been characterized except for technetium trichloride.

The radioelement ^{99}Tc ($t_{1/2} = 2.12 \times 10^5$ years) has a high fission yield (near 6%) in spent nuclear fuel. Its excited nuclear state, ^{99m}Tc , is the workhorse of diagnostic nuclear medicine.⁵ The halide chemistry of technetium has lain dormant for decades, and until recently, only TcF_6 , TcF_5 , and TcCl_4 had been reasonably well characterized.⁶ Recent advances in ^{99}Tc chemistry include the synthesis and characterization of TcBr_3 and TcBr_4 . Technetium tribromide differs from rhenium tribromide and is isostructural with

MoBr_3 and RuBr_3 .⁷ A trichloride, as Tc_3Cl_9 , has been observed in the gas phase but has never been isolated and characterized as a solid.⁸

Encouraged by our recent discovery of TcBr_3 , we decided to pursue the synthesis of TcCl_3 and transpose to technetium the methods used for the ReCl_3 synthesis. Among the various options, the reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $\text{HX}(\text{g})$ ($X = \text{Cl}, \text{Br}, \text{I}$) at elevated temperature is the only general method that provides the three Re trihalides in high yield.⁹ Here we provide details on the reaction between $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with $\text{HCl}(\text{g})$ at 300 °C and report the isolation and characterization of TcCl_3 .

Ditechnetium(III) tetraacetate dichloride, $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, was prepared by refluxing $(n\text{-Bu}_4\text{N})_2\text{Tc}_2\text{Cl}_8$ in acetic acid/acetic anhydride as described previously.^{10a,b} A weighed quantity of pink $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ was evenly dispersed on the bottom of a quartz boat, which was placed in a 50 cm long quartz tube; the tube was then positioned in a clamshell furnace with the quartz boat located at the center of the furnace. The apparatus was continuously purged with $\text{HCl}(\text{g})$, and the temperature was slowly raised to 300 °C and held there for 3 h. During the heating, a color change from pink to green (~ 100 °C) and then to black (~ 250 °C) was noted.¹¹

After the reaction, the black powder was placed in a clean Pyrex tube, which was evacuated and flame-sealed. The tube was placed in the tube furnace at 450 °C for 12 h. After the reaction, a black film and small hexagonal crystals were observed at the cold end (280 °C) of the tube. Analysis of a hexagonal crystal by single-crystal X-ray diffraction (SCXRD) showed the compound to be isostructural with ReCl_3 , consisting of triangular Tc_3Cl_9 units with C_{3v} symmetry.^{12,13} In TcCl_3 , each of the Tc atoms is coordinated to two Tc neighbors and five chloride ligands (Figure 1). The Tc atoms form an equilateral triangle with $\text{Tc}-\text{Tc}$ distances of 2.444(1) Å. This distance is 0.045 Å shorter than the $\text{Re}-\text{Re}$ distance found in ReCl_3 and is indicative of a $\text{Tc}=\text{Tc}$ double bond.

Each Tc_3Cl_9 unit possesses three terminal Cl atoms (Cl1), three bridging Cl atoms (Cl2), and six intermolecular bridging Cl atoms (Cl3) shared with three adjacent Tc_3Cl_9 units. The three terminal chlorine atoms are chemically equivalent, and the $\text{Tc}-\text{Cl1}$ distance [2.237(2) Å] is significantly shorter than those found in several dinuclear $\text{Tc}(\text{III})$ complexes.¹⁴ The three bridging Cl2 atoms are also equivalent and form an equilateral triangle [edge = 4.744(2) Å] that is shifted by 0.068(1) Å from the Tc_3^{9+} plane. The $\text{Tc}-\text{Cl2}$ distance [2.373(1) Å] is similar to the $\text{Tc}-(\mu\text{-Cl})$ distance in the hexanuclear cluster $[\text{Me}_4\text{N}]_2[\text{Tc}_6\text{Cl}_6(\mu\text{-Cl})_6]$.¹⁵ The Cl3 bridging chlorine atoms are not chemically equivalent, as two distinct distances [2.373(1) and 2.585(2) Å] are present. The larger $\text{Tc}-\text{Cl}$ distance is associated with the chlorine atoms trans to Tc atoms; a similar distribution of metal–chlorine bond distances has already been catalogued and discussed for the Re homologue.¹² The Tc_3Cl_9

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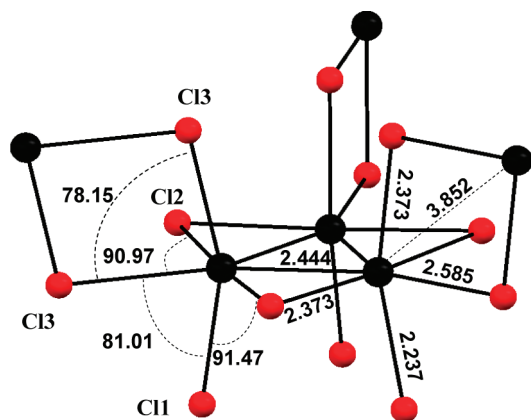


Figure 1. Ball-and-stick representation of the Tc_3Cl_9 cluster in TcCl_3 . Portions of the three neighboring clusters are also presented. Angles (deg) and distances (Å) are shown.

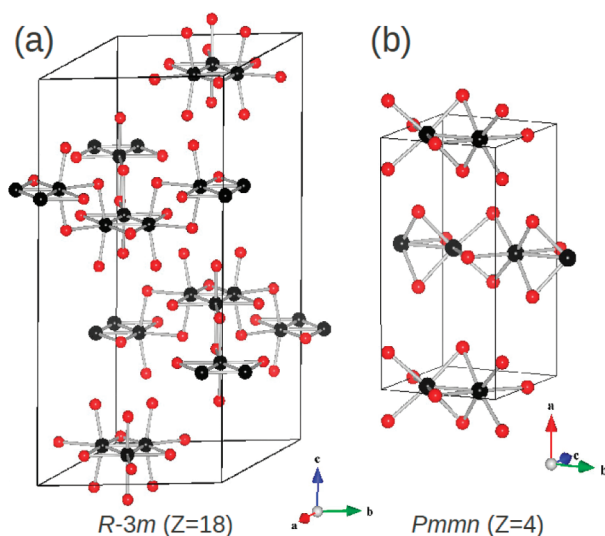


Figure 2. Ball-and-stick representations of the DFT-calculated structures of technetium trichloride: (a) the ReCl_3 structure ($R\bar{3}m$); (b) the RuCl_3 structure ($Pmnn$). Energy (eV/formula unit) and calculated cell parameters (Å) for TcCl_3 : (a) ReCl_3 structure: $E = -18.743$; $a = b = 10.31$, $c = 22.41$. (b) RuCl_3 structure: $E = -18.354$; $a = 11.49$, $b = 5.85$, $c = 6.65$.

units are linked by the Cl atoms, forming infinite layers that are four atoms thick (6.80 Å) and perpendicular to the c axis. The shortest interlayer distance $[\text{Cl1} \cdots \text{Cl2} = 3.451(2) \text{ Å}]$ is less than the sum of the van der Waals radii (3.60 Å).¹⁶ The intermolecular metallic distance $[\text{Tc} \cdots \text{Tc}' = 3.852(1) \text{ Å}]$ precludes any metal–metal bonding between the units.

Interestingly, TcCl_3 is isostructural with ReCl_3 ($R\bar{3}m$), while TcBr_3 is isostructural with MBr_3 ($Pmnn$) ($M = \text{Mo}, \text{Ru}$).⁷ Prior to its isolation, we assumed that TcCl_3 would crystallize with the MoCl_3 structure ($C2/m$) or the RuCl_3 structure ($Pmnn$).¹⁷ In order to provide a theoretical framework, first-principles density functional theory (DFT) calculations on technetium trichloride with the ReCl_3 , RuCl_3 , and MoCl_3 structures were carried out (see the Supporting Information). This approach was previously found to accurately reproduce structural parameters observed experimentally for the Tc halide systems.¹⁸ The calculations predicted the ReCl_3 -type structure to be the most stable TcCl_3 structure (Figure 2). Technetium trichloride with the RuCl_3 structure ($Pmnn$) was also found to be stable, while no stable MoCl_3 structure ($C2/m$) for TcCl_3 was found.

The calculated structural parameters for TcCl_3 are in very good agreement with the experimental ones. Similar calculations on the bromine system predict that TcBr_3 with the ReX_3 structure is slightly more stable than the MoBr_3 -type structure, suggesting that dimorphism is likely to occur for TcBr_3 . Further details of the TcCl_3 electronic structure will be presented elsewhere.¹⁹

In summary, technetium trichloride has been synthesized by the reaction between $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and $\text{HCl}(\text{g})$ at 300 °C and structurally characterized. Its discovery brings to six the number of known Tc binary halides: TcF_6 , TcF_5 , TcCl_4 , TcCl_3 , TcBr_3 , and TcBr_4 .²⁰ We anticipate that the reactions of $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with HBr and HI will provide routes to the remaining Tc_3X_9 clusters ($X = \text{Br}, \text{I}$).

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Supporting Information Available: Additional synthetic and characterization details, computational chemistry, crystallographic tables, and X-ray crystallographic data in CIF format for $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ and TcCl_3 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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