

## 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.  $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$  [ $P\bar{1}$ ;  $a = 6.0303(12)$  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  $\text{Tc}_3\text{Cl}_9$  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  $\text{TcX}_3$  ( $X = \text{Cl}, \text{Br}$ ) have confirmed the stability of  $\text{TcCl}_3$  and suggest the existence of a polymorph of  $\text{TcBr}_3$  with the  $\text{ReBr}_3$  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.<sup>1</sup> The higher-valence chlorides are accessible for the early second- and third-row metals and adopt molecular octahedral ( $\text{MCl}_6$ ;  $M = \text{W}, \text{Re}$ ) and edge-sharing bioctahedral ( $\text{M}_2\text{Cl}_{10}$ ;  $M = \text{Nb}, \text{Ta}, \text{Mo}, \text{W}, \text{Re}$ ) structures.<sup>1</sup> Extended structures and/or cluster compounds are encountered for the lower valences (I–IV). The structures consist of infinite chains of edge-sharing  $\text{MCl}_6$  octahedra for the heavier tetrachlorides of groups 4 to 7;<sup>2</sup> octahedral  $\text{M}_6\text{Cl}_{12}$  clusters ( $M = \text{Zr}, \text{Mo}, \text{W}, \text{Pt}, \text{Pd}$ )<sup>3a,b</sup> for the dichlorides; and stacked, hexagonally packed layers of either all metal ( $\text{Hf}, \text{Zr}$ ) or all chlorine atoms for the monochlorides.<sup>3a</sup> 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.<sup>4</sup> All of the second- and third-row metal trichlorides of groups 4 to 9 have been characterized except for technetium trichloride.

The radioelement  $^{99}\text{Tc}$  ( $t_{1/2} = 2.12 \times 10^5$  years) has a high fission yield (near 6%) in spent nuclear fuel. Its excited nuclear state,  $^{99m}\text{Tc}$ , is the workhorse of diagnostic nuclear medicine.<sup>5</sup> The halide chemistry of technetium has lain dormant for decades, and until recently, only  $\text{TcF}_6$ ,  $\text{TcF}_5$ , and  $\text{TcCl}_4$  had been reasonably well characterized.<sup>6</sup> Recent advances in  $^{99}\text{Tc}$  chemistry include the synthesis and characterization of  $\text{TcBr}_3$  and  $\text{TcBr}_4$ . Technetium tribromide differs from rhenium tribromide and is isostructural with

$\text{MoBr}_3$  and  $\text{RuBr}_3$ .<sup>7</sup> A trichloride, as  $\text{Tc}_3\text{Cl}_9$ , has been observed in the gas phase but has never been isolated and characterized as a solid.<sup>8</sup>

Encouraged by our recent discovery of  $\text{TcBr}_3$ , we decided to pursue the synthesis of  $\text{TcCl}_3$  and transpose to technetium the methods used for the  $\text{ReCl}_3$  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.<sup>9</sup> 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  $\text{TcCl}_3$ .

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.<sup>10a,b</sup> 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 ( $\sim 100$  °C) and then to black ( $\sim 250$  °C) was noted.<sup>11</sup>

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  $\text{ReCl}_3$ , consisting of triangular  $\text{Tc}_3\text{Cl}_9$  units with  $C_{3v}$  symmetry.<sup>12,13</sup> In  $\text{TcCl}_3$ , 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  $\text{ReCl}_3$  and is indicative of a  $\text{Tc}=\text{Tc}$  double bond.

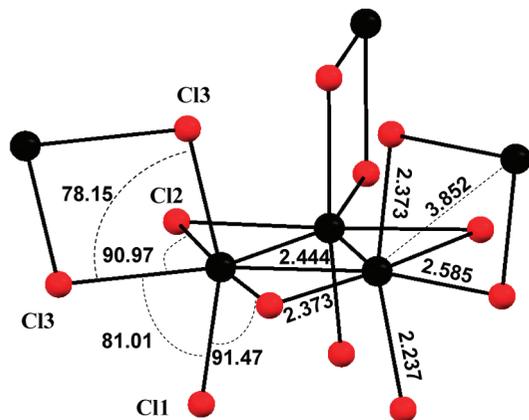
Each  $\text{Tc}_3\text{Cl}_9$  unit possesses three terminal Cl atoms (Cl1), three bridging Cl atoms (Cl2), and six intermolecular bridging Cl atoms (Cl3) shared with three adjacent  $\text{Tc}_3\text{Cl}_9$  units. The three terminal chlorine atoms are chemically equivalent, and the  $\text{Tc}-\text{Cl1}$  distance [2.237(2) Å] is significantly shorter than those found in several dinuclear  $\text{Tc}(\text{III})$  complexes.<sup>14</sup> 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  $\text{Tc}_3^{9+}$  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  $[\text{Me}_4\text{N}]_2[\text{Tc}_6\text{Cl}_6(\mu\text{-Cl})_6]$ .<sup>15</sup> 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.<sup>12</sup> The  $\text{Tc}_3\text{Cl}_9$

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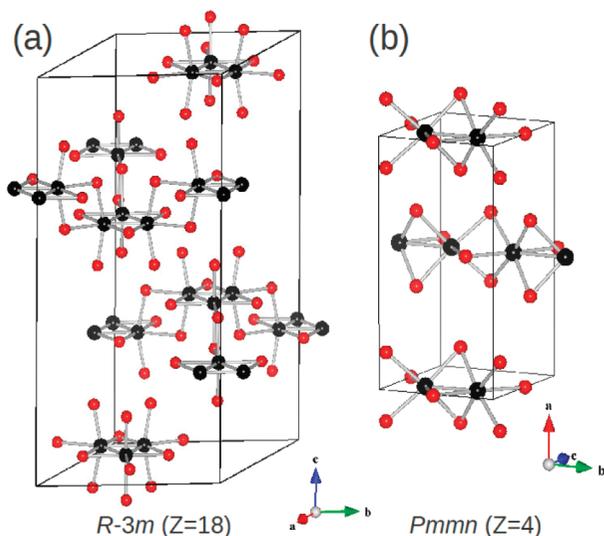
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**Figure 1.** Ball-and-stick representation of the  $\text{Tc}_3\text{Cl}_9$  cluster in  $\text{TcCl}_3$ . Portions of the three neighboring clusters are also presented. Angles (deg) and distances (Å) are shown.



**Figure 2.** Ball-and-stick representations of the DFT-calculated structures of technetium trichloride: (a) the  $\text{ReCl}_3$  structure ( $R\bar{3}m$ ); (b) the  $\text{RuCl}_3$  structure ( $Pm\bar{3}m$ ). Energy (eV/formula unit) and calculated cell parameters (Å) for  $\text{TcCl}_3$ : (a)  $\text{ReCl}_3$  structure:  $E = -18.743$ ;  $a = b = 10.31$ ,  $c = 22.41$ . (b)  $\text{RuCl}_3$  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 [ $\text{Cl1} \cdots \text{Cl2} = 3.451(2)$  Å] is less than the sum of the van der Waals radii (3.60 Å).<sup>16</sup> The intermolecular metallic distance [ $\text{Tc} \cdots \text{Tc}' = 3.852(1)$  Å] precludes any metal–metal bonding between the units.

Interestingly,  $\text{TcCl}_3$  is isostructural with  $\text{ReCl}_3$  ( $R\bar{3}m$ ), while  $\text{TcBr}_3$  is isostructural with  $\text{MBr}_3$  ( $Pm\bar{3}m$ ) ( $M = \text{Mo}, \text{Ru}$ ).<sup>7</sup> Prior to its isolation, we assumed that  $\text{TcCl}_3$  would crystallize with the  $\text{MoCl}_3$  structure ( $C2/m$ ) or the  $\text{RuCl}_3$  structure ( $Pm\bar{3}m$ ).<sup>17</sup> In order to provide a theoretical framework, first-principles density functional theory (DFT) calculations on technetium trichloride with the  $\text{ReCl}_3$ ,  $\text{RuCl}_3$ , and  $\text{MoCl}_3$  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.<sup>18</sup> The calculations predicted the  $\text{ReCl}_3$ -type structure to be the most stable  $\text{TcCl}_3$  structure (Figure 2). Technetium trichloride with the  $\text{RuCl}_3$  structure ( $Pm\bar{3}m$ ) was also found to be stable, while no stable  $\text{MoCl}_3$  structure ( $C2/m$ ) for  $\text{TcCl}_3$  was found.

The calculated structural parameters for  $\text{TcCl}_3$  are in very good agreement with the experimental ones. Similar calculations on the bromine system predict that  $\text{TcBr}_3$  with the  $\text{ReX}_3$  structure is slightly more stable than the  $\text{MoBr}_3$ -type structure, suggesting that dimorphism is likely to occur for  $\text{TcBr}_3$ . Further details of the  $\text{TcCl}_3$  electronic structure will be presented elsewhere.<sup>19</sup>

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:  $\text{TcF}_6$ ,  $\text{TcF}_5$ ,  $\text{TcCl}_4$ ,  $\text{TcCl}_3$ ,  $\text{TcBr}_3$ , and  $\text{TcBr}_4$ .<sup>20</sup> We anticipate that the reactions of  $\text{Tc}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$  with  $\text{HBr}$  and  $\text{HI}$  will provide routes to the remaining  $\text{Tc}_3\text{X}_9$  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  $\text{Tc}_2(\text{O}_2\text{CCH}_3)_2\text{Cl}_4$  and  $\text{TcCl}_3$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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