

# $\beta$ -Technetium Trichloride: Formation, Structure, and First-Principles Calculations

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## Supporting Information

**ABSTRACT:** A second polymorph of technetium trichloride,  $\beta$ -TcCl<sub>3</sub>, has been identified from the reaction between Tc metal and Cl<sub>2</sub> gas. The structure of  $\beta$ -TcCl<sub>3</sub> consists of infinite layers of edge-sharing octahedra, similar to its MoCl<sub>3</sub> and RuCl<sub>3</sub> analogues. The Tc–Tc distance [2.861(3) Å] between adjacent octahedra is indicative of metal–metal bonding. Earlier theoretical work predicted that  $\beta$ -TcCl<sub>3</sub> is less stable than  $\alpha$ -TcCl<sub>3</sub>. In agreement with the prediction,  $\beta$ -TcCl<sub>3</sub> slowly transforms into  $\alpha$ -TcCl<sub>3</sub> (Tc<sub>3</sub>Cl<sub>9</sub>) over 16 days at 280 °C.

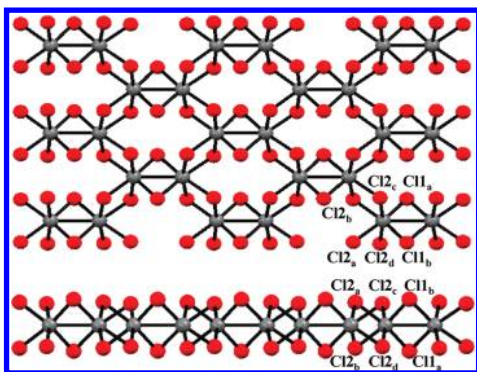
Located toward the center of the periodic table, technetium was the last transition metal and the lightest radioelement to be discovered. The <sup>99</sup>Tc isotope is a major (secondary) fission product of <sup>235</sup>U and available commercially in the form of NH<sub>4</sub>[<sup>99</sup>TcO<sub>4</sub>], while its excited isomer <sup>99m</sup>Tc, the primary decay product of <sup>99</sup>Mo, is the workhorse of diagnostic nuclear medicine.<sup>1</sup> Over the past 3 years, we have been exploring some of the fundamental chemistry of technetium, including that associated with its binary halides. Several new compounds have been synthesized and characterized, including TcBr<sub>4</sub>, TcBr<sub>3</sub>, Tc<sub>3</sub>Cl<sub>9</sub>, and TcCl<sub>2</sub>.<sup>2</sup> Technetium exhibits interesting behavior: depending on the oxidation state and coordination sphere, it can mimic its second-row neighbors, molybdenum and ruthenium, or its heavier congener, rhenium.<sup>2,3</sup> We have shown, for example, that TcBr<sub>3</sub> is isostructural to MBr<sub>3</sub> (M = Mo, Ru), while  $\alpha$ -TcCl<sub>3</sub> is isostructural to Re<sub>3</sub>Cl<sub>9</sub>.<sup>2b,d</sup> Polymorphism is common for group 6 and 8 second-row transition-metal trichlorides;<sup>4</sup> their structures comprise either layers of edge-sharing octahedra with different types of stacking ( $\alpha$ -MCl<sub>3</sub>, M = Mo, Ru, and  $\beta$ -MoCl<sub>3</sub>) or chains of face-sharing octahedra ( $\beta$ -RuCl<sub>3</sub>).<sup>5</sup> Polymorphism has not yet been observed for technetium halides, but earlier calculations from our group predicted TcCl<sub>3</sub> with the Re<sub>3</sub>Cl<sub>9</sub> structure to be slightly more stable than TcCl<sub>3</sub> with the  $\alpha$ -MoCl<sub>3</sub> or  $\beta$ -RuCl<sub>3</sub> structures.<sup>2b</sup> In the present work, we describe the stoichiometric reaction between Tc metal and Cl<sub>2</sub> and the formation of  $\beta$ -TcCl<sub>3</sub>, a second technetium trichloride polymorph. The stoichiometry of  $\beta$ -TcCl<sub>3</sub> has been confirmed by energy-dispersive X-ray spectroscopy (EDX) and its structure determined by single-crystal X-ray diffraction (XRD). The

structure and properties of  $\beta$ -TcCl<sub>3</sub> were also analyzed by first-principles calculations.

Tc metal was combined with Cl<sub>2</sub> gas (Tc:Cl = 1:~2.5) in a sealed Pyrex tube at 450 °C according to the method reported previously.<sup>2c</sup> In agreement with our earlier observations, a dark powder containing Tc metal and TcCl<sub>2</sub> was obtained in the hottest part of the tube; technetium dichloride needles with a sea-urchin motif were present in the center portion, and a dark-colored hygroscopic product was present in the coldest end. The powder XRD pattern of the dark product shows three diffraction peaks at  $2\theta = 12.66^\circ$ ,  $15.11^\circ$ , and  $16.51^\circ$  (Figure S1 in the Supporting Information, SI). The first and third peaks are consistent with the presence of (hygroscopic) TcCl<sub>4</sub>, while the peak at  $15.11^\circ$  could not be assigned to any of the known technetium chlorides.<sup>2b,c,6</sup> In order to separate TcCl<sub>4</sub> from the other crystalline products, the dark product was sealed in a clean tube under vacuum and heated for 6 days at 280 °C. After this time, a small amount of dark crystalline product was obtained at the warm end of the tube and a red film of TcCl<sub>4</sub> at the cold end. Analysis of the crystalline product by scanning electron microscopy revealed layered crystals with a hexagonal shape (Figure S2 in the SI). The elemental composition of these crystals was determined by EDX (Figure S3 in the SI), which gave a Cl:Tc ratio of 2.99(9); yield ~2%.

The compound crystallizes with a distorted AlCl<sub>3</sub> structure type similar to that of  $\alpha$ -MoCl<sub>3</sub>.<sup>5,7</sup> This phase will be denoted as  $\beta$ -TcCl<sub>3</sub> to distinguish it from TcCl<sub>3</sub> with the Re<sub>3</sub>Cl<sub>9</sub> structure type (i.e.,  $\alpha$ -TcCl<sub>3</sub>). The structure of  $\beta$ -TcCl<sub>3</sub> consists of infinite-ordered layers of edge-sharing TcCl<sub>6</sub> octahedra that are oriented parallel to the *ab* plane (Figure 1). Within a layer, the Tc atoms form an infinite sheet with a distorted honeycomb pattern, which is sandwiched by two layers of Cl atoms. The stacking of the TcCl<sub>3</sub> layers is similar to that of  $\alpha$ -MoCl<sub>3</sub>, and a separation of 5.87 Å between Tc sheets is observed. The shortest interatomic distance between TcCl<sub>3</sub> layers (Cl...Cl = 3.561 Å) is close to the sum of the van der Waals radii (3.60 Å) and suggests a weak interaction between layers. Within a layer, coupling of Tc atoms into Tc<sub>2</sub><sup>6+</sup> pairs oriented along the *b* axis occurs and two sets of Tc–Tc distances are observed [i.e., Tc–Tc = 2.861(3) Å and Tc...Tc' = 3.601(2) Å]. The Tc–Tc

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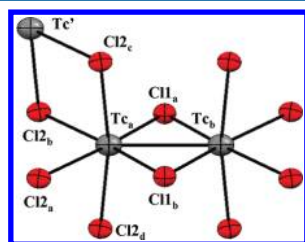
**Figure 1.** Ball-and-stick representation of a  $\beta$ - $\text{TcCl}_3$  layer. View perpendicular to the  $ab$  plane (top) and in the  $a$  direction (bottom). The Cl and Tc atoms are red and gray, respectively.

distance in the  $\text{Tc}_2^{6+}$  pair is indicative of a significant metal–metal-bonding interaction (vide infra), while the  $\text{Tc}\cdots\text{Tc}'$  distance is similar to the nonbonded one observed in  $\text{TcCl}_4$  [i.e., 3.605(1) Å].<sup>6</sup> In the other layered trichlorides, strong coupling between metal atoms occurs in  $\alpha$ - $\text{MoCl}_3$  [ $\text{Mo}\text{--}\text{Mo}$  = 2.757(3) Å] but not in  $\alpha$ - $\text{RuCl}_3$ . Weak coupling of the Ru atoms in  $\alpha$ - $\text{RuCl}_3$  has been proposed based on scanning tunneling microscopy.<sup>8</sup> The disparity ( $\Delta\text{MM}$ ) between paired and nonpaired metal–metal distances in layered  $\text{MCl}_3$  ( $\text{M} = \text{Mo}, \text{Tc}, \text{Ru}$ ; Table 1) follows the order  $\Delta\text{MoMo} > \Delta\text{TcTc} >$

**Table 1.**  $\text{M}\text{--}\text{M}$  and  $\text{M}\cdots\text{M}$  Distances in  $\alpha$ - $\text{MCl}_3$  ( $\text{M} = \text{Mo}, \text{Ru}$ ) and  $\beta$ - $\text{TcCl}_3$

distance (Å)	$\text{MoCl}_3^{5d}$	$\text{TcCl}_3$	$\text{RuCl}_3^{5b}$
$\text{M}\text{--}\text{M}$	2.757(3)	2.861(3)	3.44(1)
$\text{M}\cdots\text{M}$	3.714(3)	3.601(2)	3.45(1)
$\Delta\text{MM}$	0.957(4)	0.740(3)	0.01(1)

$\Delta\text{RuRu}$ . The reason for the disparity between the MM paired and nonpaired distances has already been discussed for trichlorides having the  $\text{AlCl}_3$  structure type,<sup>4a</sup> and a Peierls distortion is likely the origin of dimerization (i.e., formation of  $\text{M}_2^{6+}$  unit). Two significant structural consequences of the  $\text{Tc}\text{--}\text{Tc}$  coupling are deformation of the  $\text{TcCl}_6$  octahedra as well as of the Tc honeycomb ( $b/a = 1.624$ ) from the hexagonal geometry ( $b/a = \sqrt{3} \cong 1.732$ ). There are two types of Cl atoms and three distinct  $\text{Tc}\text{--}\text{Cl}$  bond distances (Figure 2). The shortest bond involves the bridging chlorine within the  $\text{Tc}_2^{6+}$



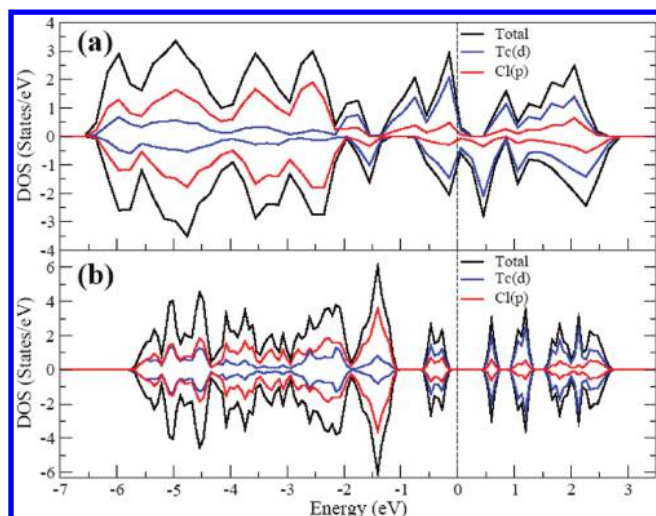
**Figure 2.** Thermal ellipsoid (60%) representation of the edge-sharing octahedra in  $\beta$ - $\text{TcCl}_3$ . The Cl and Tc atoms are red and gray, respectively. Selected distances (Å) and angles (deg):  $\text{Tc}_a\text{--}\text{Tc}_b$  2.861(3),  $\text{Tc}_a\text{--}\text{Tc}'$  3.601(2),  $\text{Tc}_a\text{--}\text{Cl1}_{(a,b)}$  2.316(3),  $\text{Tc}_a\text{--}\text{Cl2}_{(a,b)}$  2.434(3),  $\text{Tc}_a\text{--}\text{Cl2}_{(c,d)}$  2.403(2),  $\text{Cl1}_a\text{--}\text{Cl1}_b$  3.642(4).  $\text{Tc}_b\text{--}\text{Tc}_a\text{--}\text{Cl2}_{(c,d)}$  95.13(6),  $\text{Cl1}_a\text{--}\text{Tc}_a\text{--}\text{Cl1}_b$  103.71(12),  $\text{Cl2}_a\text{--}\text{Tc}_a\text{--}\text{Cl2}_b$  85.50(8),  $\text{Cl2}_c\text{--}\text{Tc}_a\text{--}\text{Cl1}_a$  94.07(10),  $\text{Cl2}_c\text{--}\text{Tc}_a\text{--}\text{Cl1}_b$  92.25(10),  $\text{Cl2}_c\text{--}\text{Tc}_a\text{--}\text{Cl2}_a$  88.69(8),  $\text{Cl2}_c\text{--}\text{Tc}_a\text{--}\text{Cl2}_b$  83.78(9).

pair [ $\text{Tc}\text{--}\text{Cl1} = 2.316(3)$  Å], while the longest bonds are the  $\text{Cl2}_{(a,b)}$  atoms in trans positions to the Cl1 atoms [ $\text{Tc}\text{--}\text{Cl2}_{(a,b)} = 2.434(3)$  Å]. Finally, a  $\text{Tc}\text{--}\text{Cl}$  distance of 2.403(2) Å is observed for the  $\text{Cl2}_{(c,d)}$  atoms located in cis positions to the Cl1 atom. As a result of metal–metal bond formation, the Cl1 atoms are pushed away from the center of the layer and are located in a plane 0.38 Å above the plane formed by the Cl2 atoms.

The structure of  $\beta$ - $\text{TcCl}_3$  was further analyzed utilizing density functional theory (DFT). This approach was found in previous studies to accurately reproduce structural parameters observed experimentally for several technetium halide systems.<sup>2,9</sup> The relaxed  $\beta$ - $\text{TcCl}_3$  structure crystallizing in the space group  $\text{C2}/m$  is energetically less favorable than the  $\alpha$ - $\text{TcCl}_3$  structure with  $\text{R3}m$  symmetry by ca. 0.34 eV per formula unit.

The space group of the relaxed structure of  $\beta$ - $\text{TcCl}_3$  was determined with  $\sim 0.01$  Å accuracy. The computed lattice parameters of  $\beta$ - $\text{TcCl}_3$  are  $a = 6.15$  Å,  $b = 9.68$  Å,  $c = 6.65$  Å, and  $\beta = 107.7^\circ$ . The calculations confirm the structural impact of the  $\text{Tc}\text{--}\text{Tc}$  bonding (i.e., deformation of the Tc honeycomb and  $\text{TcCl}_6$  octahedra). The calculated bond distances ( $\text{Tc}\text{--}\text{Tc} = 2.74$ ,  $\text{Tc}\cdots\text{Tc}' = 3.72$  Å, and  $\text{Tc}\text{--}\text{Cl} = 2.33, 2.43,$  and  $2.46$  Å) are in overall fair agreement with the experimental data.

An understanding of the metal–metal bonding in layered  $\text{MCl}_3$  systems can be approached by the study of molecules containing the  $[\text{M}(\mu\text{--}\text{Cl})_2\text{M}]$  fragment ( $\text{M} = \text{Mo}, \text{Tc}$ ). Previous studies of the hypothetical  $\text{Mo}_2\text{Cl}_6(\text{PH}_3)_4$  complex have shown that the metal–metal bond can be described as a double bond with  $\sigma$  and  $\pi$  character;<sup>10</sup> this result further supported the presence of a weak double bond in  $\alpha$ - $\text{MoCl}_3$  that was reported.<sup>5</sup> For technetium, we studied the hypothetical  $[\text{Cl}_4\text{Tc}(\mu\text{--}\text{Cl})_2\text{TcCl}_4]^{4-}$  fragment. The occupancy of the metal-based orbitals in the metal–metal-bonded singlet state ( $S = 0$ ) and the highest-multiplicity state ( $S = 2$ ) for the  $d^4\text{--}d^4$  configuration can be idealized as  $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*0}\sigma^{*0}$  and  $\sigma^1\pi^1\delta^2\delta^{*2}\pi^{*1}\sigma^{*1}$ , respectively.<sup>11</sup> The computed  $\text{Tc}=\text{Tc}$  bond distance was found to be 2.71 Å for  $S = 0$  and 3.87 Å for  $S = 2$ . We note that the  $\text{Tc}=\text{Tc}$  bond distance for  $S = 0$  is close to the value of 2.74 Å found in the  $\beta$ - $\text{TcCl}_3$  crystal structure relaxed with DFT. The effective bond order calculated for the  $S = 0$  configuration (i.e., 1.38) indicates the presence of a weak double bond. Therefore, similar to the case of  $\alpha$ - $\text{MoCl}_3$ , a weak  $\text{Tc}=\text{Tc}$  double bond with  $\sigma$  and  $\pi$  character is suggested between the Tc atoms. Chemical bonding in the  $\text{Tc}_3\text{Cl}_9$  cluster has been analyzed recently by theoretical methods.<sup>12</sup> The results indicate the presence of a  $\text{Tc}=\text{Tc}$  double bond between the Tc atoms within the  $\text{Tc}_3^{9+}$  core. Occupation number calculations show the presence of 1.99 electrons on both the  $\sigma$  and  $\pi$  orbitals, which lead to an effective bond order of 1.99. In summary, calculations show that both  $\alpha$ - $\text{TcCl}_3$  and  $\beta$ - $\text{TcCl}_3$  exhibit a  $\text{Tc}=\text{Tc}$  double bond with  $\sigma$  and  $\pi$  character; bond-order calculations show the  $\text{Tc}=\text{Tc}$  bond to be stronger for  $\alpha$ - $\text{TcCl}_3$  than for  $\beta$ - $\text{TcCl}_3$ . DFT calculations also predict  $\beta$ - $\text{TcCl}_3$  to be slightly paramagnetic, with a magnetization of  $0.9 \mu_B/\text{Tc}$ . This value is within the range of the experimentally observed magnetic moments for  $\alpha$ - $\text{MoCl}_3$  ( $0.49 \mu_B$ ) and  $\alpha$ - $\text{RuCl}_3$  ( $2.25 \mu_B$ ).<sup>5,13</sup> Density-of-state (DOS) calculations are consistent with metallic character; this contrasts with  $\alpha$ - $\text{TcCl}_3$ , a semiconductor featuring a band gap of  $\sim 0.6$  eV (Figure 3), and with  $\alpha$ - $\text{RuCl}_3$ , which is a Mott insulator.<sup>14</sup> In  $\beta$ - $\text{TcCl}_3$ , the metallic character stems predominantly from Tc 4d orbitals, which are dominant in the vicinity of the Fermi level, with significant orbital



**Figure 3.** Total and partial DOSs per formula unit of (a)  $\beta$ - $\text{TcCl}_3$  and (b)  $\alpha$ - $\text{TcCl}_3$ . Orbital-projected DOSs are represented for Tc 4d and Cl 2p orbitals. Positive and negative values of the DOS correspond to spin-up and spin-down contributions.

hybridization with Cl 2p. Plotting individual  $d_{x^2-y^2}$ ,  $d\pi$ , and  $d\delta$  contributions to the DOS is not possible with the software package used for the calculations (VASP). The Cl 2p valence states become the major contribution to the DOS below  $\sim 2$  eV.

In summary, a new form of technetium trichloride,  $\beta$ - $\text{TcCl}_3$ , has been identified from the reaction between Tc metal and elemental Cl.  $\beta$ - $\text{TcCl}_3$  crystallizes with the layered  $\text{AlCl}_3$  structure type and consists of infinite layers of edge-sharing octahedra. It is the first example of a  $d^4$  metal with this structure. Coupling of Tc atoms into  $\text{Tc}_2^{6+}$  pairs occurs, and the presence of metal–metal bonds was confirmed by DFT. The calculations indicate that  $\beta$ - $\text{TcCl}_3$  is energetically less stable than  $\alpha$ - $\text{TcCl}_3$ . Consistent with the latter, we find that when samples of  $\beta$ - $\text{TcCl}_3$  are heated to 280 °C for 16 days, only the characteristic powder pattern of  $\alpha$ - $\text{TcCl}_3$  remains. Because of its layered structure,  $\beta$ - $\text{TcCl}_3$  may exhibit interesting intercalative properties that mimic those of  $\alpha$ - $\text{RuCl}_3$ .<sup>15</sup> Similar to its molybdenum neighbor,  $\beta$ - $\text{TcCl}_3$  could be used as a precursor for the synthesis of binary carbides or phosphides, which have found applications in the development of Tc waste forms.<sup>16</sup> Current work in our laboratory is focused on the development of higher yield routes to  $\beta$ - $\text{TcCl}_3$  and measurements of its physical properties.

## ■ ASSOCIATED CONTENT

### Supporting Information

Additional synthetic and characterization details, computational chemistry, crystallographic tables, and X-ray crystallographic data in CIF format for  $\beta$ - $\text{TcCl}_3$ . 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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