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β-Technetium Trichloride: Formation, Structure, and First-Principles Calculations

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Ⓢ *Supporting Information*

ABSTRACT: A second polymorph of technetium trichloride, β-$TcCl_3$, has been identified from the reaction between Tc metal and Cl_2 gas. The structure of β-$TcCl_3$ consists of infinite layers of edge-sharing octahedra, similar to its $MoCl_3$ and $RuCl_3$ analogues. The Tc−Tc distance [2.861(3) Å] between adjacent octahedra is indicative of metal−metal bonding. Earlier theoretical work predicted that β-$TcCl_3$ is less stable than α-$TcCl_3$. In agreement with the prediction, β-$TcCl_3$ slowly transforms into α-$TcCl_3$ (Tc_3Cl_9) 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 ^{99}Tc isotope is a major (secondary) fission product of ^{235}U and available commercially in the form of $NH_4[^{99}TcO_4]$, while its excited isomer ^{99m}Tc, the primary decay product of ^{99}Mo, is the workhorse of diagnostic nuclear medicine.[1] 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 $TcBr_4$, $TcBr_3$, Tc_3Cl_9, and $TcCl_2$.[2] 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.[2,3] We have shown, for example, that $TcBr_3$ is isostructural to MBr_3 (M = Mo, Ru), while α-$TcCl_3$ is isostructural to Re_3Cl_9.[2b,d] Polymorphism is common for group 6 and 8 second-row transition-metal trichlorides;[4] their structures comprise either layers of edge-sharing octahedra with different types of stacking (α-MCl_3, M = Mo, Ru, and β-$MoCl_3$) or chains of face-sharing octahedra (β-$RuCl_3$).[5] Polymorphism has not yet been observed for technetium halides, but earlier calculations from our group predicted $TcCl_3$ with the Re_3Cl_9 structure to be slightly more stable than $TcCl_3$ with the α-$MoCl_3$ or β-$RuCl_3$ structures.[2b] In the present work, we describe the stoichiometric reaction between Tc metal and Cl_2 and the formation of β-$TcCl_3$, a second technetium trichloride polymorph. The stoichiometry of β-$TcCl_3$ 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 β-$TcCl_3$ were also analyzed by first-principles calculations.

Tc metal was combined with Cl_2 gas (Tc:Cl = 1:∼2.5) in a sealed Pyrex tube at 450 °C according to the method reported previously.[2c] In agreement with our earlier observations, a dark powder containing Tc metal and $TcCl_2$ 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 $2\theta = 12.66°$, 15.11°, and 16.51° (Figure SI in the Supporting Information, SI). The first and third peaks are consistent with the presence of (hygroscopic) $TcCl_4$, while the peak at 15.11° could not be assigned to any of the known technetium chlorides.[2b,c,6] In order to separate $TcCl_4$ 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 $TcCl_4$ at the cold end. Analysis of the crystalline product by scanning electron microscopy revealed layered crystals with an 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 $AlCl_3$ structure type similar to that of α-$MoCl_3$.[5,7] This phase will be denoted as β-$TcCl_3$ to distinguish it from $TcCl_3$ with the Re_3Cl_9 structure type (i.e., α-$TcCl_3$). The structure of β-$TcCl_3$ consists of infinite-ordered layers of edge-sharing $TcCl_6$ 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 $TcCl_3$ layers is similar to that of α-$MoCl_3$, and a separation of 5.87 Å between Tc sheets is observed. The shortest interatomic distance between $TcCl_3$ 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_2^{6+} 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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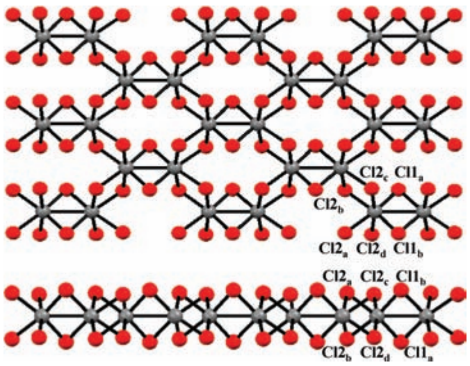

Figure 1. Ball-and-stick representation of a β-$TcCl_3$ layer. View perpendicular to the *ab* plane (top) and in the *a* direction (bottom). The Cl and Tc atoms are red and gray, respectively.

distance in the Tc_2^{6+} pair is indicative of a significant metal–metal-bonding interaction (vide infra), while the Tc···Tc′ distance is similar to the nonbonded one observed in $TcCl_4$ [i.e., 3.605(1) Å].[6] In the other layered trichlorides, strong coupling between metal atoms occurs in α-$MoCl_3$ [Mo–Mo = 2.757(3) Å] but not in α-$RuCl_3$. Weak coupling of the Ru atoms in α-$RuCl_3$ has been proposed based on scanning tunneling microscopy.[8] The disparity (ΔMM) between paired and nonpaired metal–metal distances in layered MCl_3 (M = Mo, Tc, Ru; Table 1) follows the order ΔMoMo > ΔTcTc > ΔRuRu. The reason for the disparity between the MM paired and nonpaired distances has already been discussed for trichlorides having the $AlCl_3$ structure type,[4a] and a Peierls distortion is likely the origin of dimerization (i.e., formation of M_2^{6+} unit). Two significant structural consequences of the Tc–Tc coupling are deformation of the $TcCl_6$ 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 Tc–Cl bond distances (Figure 2). The shortest bond involves the bridging chlorine within the Tc_2^{6+} pair [Tc–Cl1 = 2.316(3) Å], while the longest bonds are the $Cl2_{(a,b)}$ atoms in trans positions to the Cl1 atoms [Tc–$Cl2_{(a,b)}$ = 2.434(3) Å]. Finally, a Tc–Cl distance of 2.403(2) Å is observed for the $Cl2_{(c,d)}$ 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.

Table 1. M–M and M···M Distances in *α*-MCl_3 (M = Mo, Ru) and *β*-$TcCl_3$

distance (Å)	$MoCl_3$[5d]	$TcCl_3$	$RuCl_3$[5b]
M–M	2.757(3)	2.861(3)	3.44(1)
M···M	3.714(3)	3.601(2)	3.45(1)
ΔMM	0.957(4)	0.740(3)	0.01(1)

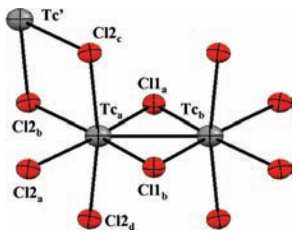

Figure 2. Thermal ellipsoid (60%) representation of the edge-sharing octahedra in β-$TcCl_3$. The Cl and Tc atoms are red and gray, respectively. Selected distances (Å) and angles (deg): Tc_a–Tc_b 2.861(3), Tc_a–Tc′ 3.601(2), Tc_a–$Cl1_{(a,b)}$ 2.316(3), Tc_a–$Cl2_{(a,b)}$ 2.434(3), Tc_a–$Cl2_{(c,d)}$ 2.403(2), $Cl1_a$–$Cl1_b$ 3.642(4). Tc_b–Tc_a–$Cl2_{(c,d)}$ 95.13(6), $Cl1_a$–Tc_a–$Cl1_b$ 103.71(12), $Cl2_a$–Tc_a–$Cl2_b$ 85.50(8), $Cl2_c$–Tc_a–$Cl1_a$ 94.07(10), $Cl2_c$–Tc_a–$Cl1_b$ 92.25(10), $Cl2_c$–Tc_a–$Cl2_a$ 88.69(8), $Cl2_c$–Tc_a–$Cl2_b$ 83.78(9).

The structure of β-$TcCl_3$ 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.[2,9] The relaxed β-$TcCl_3$ structure crystallizing in the space group *C*2/*m* is energetically less favorable than the α-$TcCl_3$ structure with *R*3*m* symmetry by ca. 0.34 eV per formula unit.

The space group of the relaxed structure of β-$TcCl_3$ was determined with ~0.01 Å accuracy. The computed lattice parameters of β-$TcCl_3$ are a = 6.15 Å, b = 9.68 Å, c = 6.65 Å, and β = 107.7°. The calculations confirm the structural impact of the Tc–Tc bonding (i.e., deformation of the Tc honeycomb and $TcCl_6$ octahedra). The calculated bond distances (Tc–Tc = 2.74, Tc···Tc′ = 3.72 Å, and Tc–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 MCl_3 systems can be approached by the study of molecules containing the [M(μ-Cl)$_2$M] fragment (M = Mo, Tc). Previous studies of the hypothetical $Mo_2Cl_6(PH_3)_4$ complex have shown that the metal–metal bond can be described as a double bond with σ and π character;[10] this result further supported the presence of a weak double bond in α-$MoCl_3$ that was reported.[5] For technetium, we studied the hypothetical $[Cl_4Tc(\mu\text{-}Cl)_2TcCl_4]^{4-}$ 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–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.[11] The computed Tc═Tc bond distance was found to be 2.71 Å for S = 0 and 3.87 Å for S = 2. We note that the Tc═Tc bond distance for S = 0 is close to the value of 2.74 Å found in the β-$TcCl_3$ 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 α-$MoCl_3$, a weak Tc═Tc double bond with σ and π character is suggested between the Tc atoms. Chemical bonding in the Tc_3Cl_9 cluster has been analyzed recently by theoretical methods.[12] The results indicate the presence of a Tc═Tc double bond between the Tc atoms within the Tc_3^{9+} core. Occupation number calculations show the presence of 1.99 electrons on both the σ and π orbitals, which lead to an effective bond order of 1.99. In summary, calculations show that both α-$TcCl_3$ and β-$TcCl_3$ exhibit a Tc═Tc double bond with σ and π character; bond-order calculations show the Tc═Tc bond to be stronger for α-$TcCl_3$ than for β-$TcCl_3$. DFT calculations also predict β-$TcCl_3$ to be slightly paramagnetic, with a magnetization of 0.9 μ_B/Tc. This value is within the range of the experimentally observed magnetic moments for α-$MoCl_3$ (0.49 μ_B) and α-$RuCl_3$ (2.25 μ_B).[5,13] Density-of-state (DOS) calculations are consistent with metallic character; this contrasts with α-$TcCl_3$, a semiconductor featuring a band gap of ~0.6 eV (Figure 3), and with α-$RuCl_3$, which is a Mott insulator.[14] In β-$TcCl_3$, the metallic character stems predominantly from Tc 4d orbitals, which are dominant in the vicinity of the Fermi level, with significant orbital

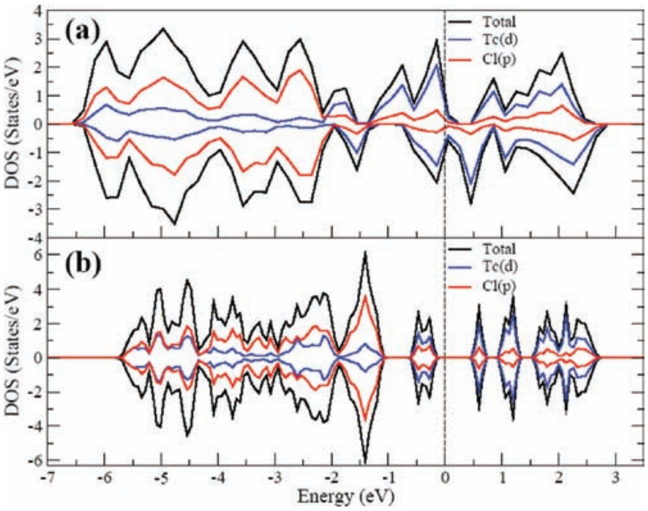

Figure 3. Total and partial DOSs per formula unit of (a) β-$TcCl_3$ and (b) α-$TcCl_3$. Orbital-projected DOSs are represented for Tc 4d and Cl 2p orbitals. Positive and negative values of the DOS correspond to spin-up and spin-down contributions.

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 ~2 eV.

In summary, a new form of technetium trichloride, β-$TcCl_3$, has been identified from the reaction between Tc metal and elemental Cl. β-$TcCl_3$ crystallizes with the layered $AlCl_3$ 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 Tc_2^{6+} pairs occurs, and the presence of metal−metal bonds was confirmed by DFT. The calculations indicate that β-$TcCl_3$ is energetically less stable than α-$TcCl_3$. Consistent with the latter, we find that when samples of β-$TcCl_3$ are heated to 280 °C for 16 days, only the characteristic powder pattern of α-$TcCl_3$ remains. Because of its layered structure, β-$TcCl_3$ may exhibit interesting intercalative properties that mimic those of α-$RuCl_3$.[15] Similar to its molybdenum neighbor, β-$TcCl_3$ 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.[16] Current work in our laboratory is focused on the development of higher yield routes to β-$TcCl_3$ and measurements of its physical properties.

■ ASSOCIATED CONTENT

S Supporting Information

Additional synthetic and characterization details, computational chemistry, crystallographic tables, and X-ray crystallographic data in CIF format for β-$TcCl_3$. 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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■ REFERENCES

(1) (a) Schwochau, K. *Technetium: Chemistry and Radiopharmaceutical. Applications*; Wiley-VCH: Weinheim, Germany, 2000. (b) Alberto, R.; Braband, H.; N'Dongo, H. W. P. *Curr. Radiopharm.* **2009**, *2*, 254−267.

(2) (a) Poineau, F.; Rodriguez, E. E.; Forster, P. M.; Sattelberger, A. P.; Cheetham, A. K.; Czerwinski, K. R. *J. Am. Chem. Soc.* **2009**, *131*, 910−911. (b) Poineau, F.; Johnstone, E. V.; Weck, P. F.; Kim, E.; Forster, P. M.; Scott, B. L.; Sattelberger, A. P.; Czerwinski, K. R. *J. Am. Chem. Soc.* **2010**, *132*, 15864−15685. (c) Poineau, F.; Malliakas, C. D.; Weck, P. F.; Scott, B. L.; Johnstone, E. V.; Forster, P. M.; Kim, E; Kanatzidis, M. G.; Czerwinski, K. R.; Sattelberger, A. P. *J. Am. Chem. Soc.* **2011**, *133*, 8814−8817. (d) Canterford, J. H.; Colton, R. *Halides of the Second and Third Row Transition Metals*; John Wiley and Sons: New York, 1968.

(3) (a) Muller, O.; White, W. B.; Roy, R. *Inorg. Nucl. Chem.* **1964**, *26*, 2075−2086. (b) Rodriguez, E. E.; Poineau, F.; Llobet, A.; Czerwinski, K.; Seshadri, R.; Cheetham, A. K. *Inorg. Chem.* **2008**, *47*, 6281−6288. (c) Poineau, F.; Weck, P. F.; Forster, P. M.; Sattelberger, A. P.; Czerwinski, K. R. *Dalton Trans.* **2009**, *46*, 10338−10342.

(4) (a) Lin, J.; Miller, G. J. *Inorg. Chem.* **1993**, *32*, 1476−1487. (b) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed.; John Wiley and Sons: New York, 1999.

(5) (a) Fletcher, J. M.; Gardner, W. E.; Fox, A. C.; Topping, G. *J. Chem. Soc. A* **1967**, *7*, 1038−1045. (b) Stroganov, E. V.; Ovchinnikov, K. V. *Vestn. Leningr. Univ.* **1957**, *12*, 152. (c) Hillebrecht, H.; Ludwig, Th.; Thiele, G. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2199−2204. (d) Hillebrecht, H.; Schmidt, P. J.; Rotter, H. W.; Thiele, G.; Zoennchen, P.; Bengel, H.; Cantow, H. J.; Magonov, S. N.; Whangbo, M. H. *J. Alloys Compd.* **1997**, *246*, 70−79. (e) Schaefer, H.; Schnering, H. G.; Tillack, J.; Kuhnen, F.; Woehrle, H. T.; Baumann, H. *Z. Anorg. Allg. Chem.* **1967**, *353*, 281−310. (f) Baernighausen, H.; Handa, B. K. *J. Less-Common Met.* **1964**, *6*, 226−231.

(6) Elder, M.; Penfold, B. R. *Inorg. Chem.* **1966**, *5*, 1197−1200.

(7) Crystal data for β-$TcCl_3$: $C2/m$, a = 5.986(3) Å, b = 9.725(5) Å, c = 6.194(3) Å, β = 108.687(6)°; R1 = 7.03%, GOF = 1.18; 447 reflections, 22 refined parameters.

(8) Cantow, H. J.; Hillebrecht, H.; Maganov, S. N.; Rotter, H.; Drechsler, M.; Thiele, G. *Angew. Chem., Int. Ed.* **1990**, *29*, 537−541.

(9) Weck, P. F.; Kim, E.; Poineau, F.; Rodriguez, E. E.; Sattelberger, A. P.; Czerwinski, K. R. *Inorg. Chem.* **2009**, *48*, 6555−6558.

(10) Cotton, F. A.; Feng, X. *Int. J. Quantum Chem.* **1996**, *58*, 671−680.

(11) Cavigliasso, G.; Yu, C. Y.; Stranger, R. *Polyhedron* **2007**, *26*, 2942−2948.

(12) Weck, P. F.; Sergeeva, A. P.; Kim, E.; Boldyrev, A. I.; Czerwinski, K. R. *Inorg. Chem.* **2011**, *50*, 1039−1046.

(13) Kobayashi, Y.; Okada, T.; Asai, K.; Katada, M.; Sano, H.; Ambe, F. *Inorg. Chem.* **1992**, *31*, 4570−457.

(14) Pollini, I. *Phys. Rev. B* **1994**, *50*, 2095−2103.

(15) Wang, L.; Brazis, P.; Rocci, M.; Kannewurf, C. R.; Kanatzidis, M. G. *Chem. Mater.* **1998**, *10*, 3298−3300.

(16) (a) Nartowski, A. M.; Parkin, I. P.; MacKenzie, M.; Craven, A. J.; MacLeod, I. *J. Mater. Chem.* **1999**, *9*, 1275−1281. (b) Hector, A. L.; Parkin, I. P. *J. Mater. Chem.* **1994**, *4*, 279−283.