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Synthesis and Structure of Technetium Trichloride

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Abstract: Technetium trichloride has been synthesized by reaction of $Tc_2(O_2CCH_3)_4Cl_2$ with HCl(g) at 300 °C. The mechanism of formation mimics the one described earlier in the literature for rhenium. $Tc_2(O_2CCH_3)_2Cl_4$ [$P\bar{1}$; $a = 6.0303(12)$ Å, $b = 6.5098(13)$ Å, $c = 8.3072(16)$ Å, $\alpha = 112.082(2)°$, $\beta = 96.667(3)°$, $\gamma = 108.792(3)°$; Tc−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 Tc−Tc separation is 2.444(1) Å. Calculations on TcX_3 (X = Cl, 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 = W, Re) and edge-sharing bioctahedral (M_2Cl_{10}; M = Nb, Ta, Mo, W, 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 = Zr, Mo, W, Pt, 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 $Re_2(O_2CCH_3)_4Cl_2$ with HX(g) (X = Cl, Br, 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 $Tc_2(O_2CCH_3)_4Cl_2$ with HCl(g) at 300 °C and report the isolation and characterization of $TcCl_3$.

Ditechnetium(III) tetraacetate dichloride, $Tc_2(O_2CCH_3)_4Cl_2$, was prepared by refluxing $(n\text{-}Bu_4N)_2Tc_2Cl_8$ in acetic acid/acetic anhydride as described previously.[10a,b] A weighed quantity of pink $Tc_2(O_2CCH_3)_4Cl_2$ 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 HCl(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 Tc−Tc distances of 2.444(1) Å. This distance is 0.045 Å shorter than the Re−Re distance found in $ReCl_3$ and is indicative of a Tc═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 Tc−Cl1 distance [2.237(2) Å] is significantly shorter than those found in several dinuclear Tc(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 Tc−Cl2 distance [2.373(1) Å] is similar to the Tc−(μ-Cl) distance in the hexanuclear cluster $[Me_4N]_2[Tc_6Cl_6(\mu\text{-}Cl)_6]$.[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 Tc−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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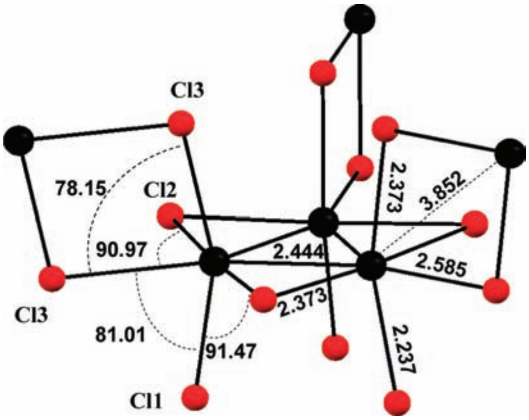

Figure 1. Ball-and-stick representation of the Tc_3Cl_9 cluster in $TcCl_3$. Portions of the three neighboring clusters are also presented. Angles (deg) and distances (Å) are shown.

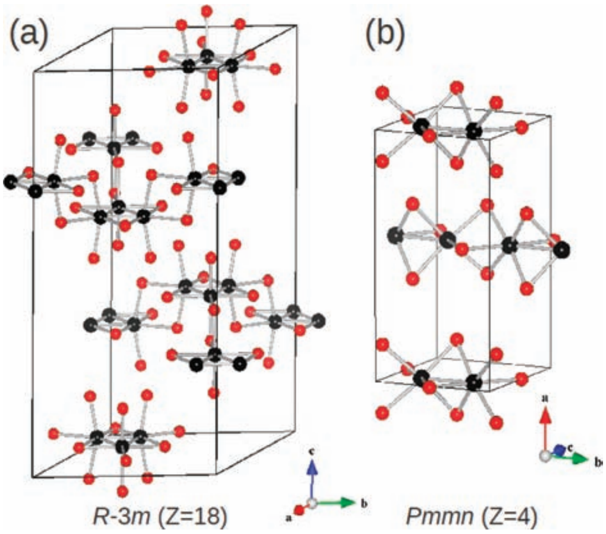

Figure 2. Ball-and-stick representations of the DFT-calculated structures of technetium trichloride: (a) the $ReCl_3$ structure ($R\bar{3}m$); (b) the $RuCl_3$ structure (*Pmmm*). Energy (eV/formula unit) and calculated cell parameters (Å) for $TcCl_3$: (a) $ReCl_3$ structure: $E = -18.743$; $a = b = 10.31$, $c = 22.41$. (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 [Cl1···Cl2 = 3.451(2) Å] is less than the sum of the van der Waals radii (3.60 Å).[16] The intermolecular metallic distance [Tc···Tc′ = 3.852(1) 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 (*Pmmn*) (M = Mo, Ru).[7] Prior to its isolation, we assumed that $TcCl_3$ would crystallize with the $MoCl_3$ structure (*C*2/*m*) or the $RuCl_3$ structure (*Pmmm*).[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 (*Pmmm*) was also found to be stable, while no stable $MoCl_3$ structure (*C*2/*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 $Tc_2(O_2CCH_3)_4Cl_2$ and HCl(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 $Tc_2(O_2CCH_3)_4Cl_2$ with HBr and HI will provide routes to the remaining Tc_3X_9 clusters (X = Br, 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 $Tc_2(O_2CCH_3)_2Cl_4$ and $TcCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) ***Caution!*** Techetium-99 is a weak β emitter (E_{max} = 292 keV). All manipulations were performed in a radiochemistry laboratory designed for chemical synthesis using efficient HEPA-filtered fume hoods and Schlenk and glovebox techniques, and locally approved radioisotope handling and monitoring procedures were followed. (b) Poineau, F.; Sattelberger, A. P.; Czerwinski, K. *J. Coord. Chem.* **2008**, *61*, 2356–2370.
(11) Single crystals of the green intermediate were grown at 150 °C. SCXRD measurements showed the compound to be $Tc_2(O_2CCH_3)_2Cl_4$. The structure consists of two bridging *trans*-acetate ligands and four terminal chlorides. The Tc−Tc separation is 2.150(1) Å. Additional synthetic and characterization details are included in the Supporting Information.
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