

Technetium Dichloride: A New Binary Halide Containing Metal–Metal Multiple Bonds

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S Supporting Information

ABSTRACT: Technetium dichloride has been discovered. It was synthesized from the elements and characterized by several physical techniques, including single crystal X-ray diffraction. In the solid state, technetium dichloride exhibits a new structure type consisting of infinite chains of face sharing [Tc₂Cl₈] rectangular prisms that are packed in a commensurate supercell. The metal–metal separation in the prisms is 2.127(2) Å, a distance consistent with the presence of a Tc≡Tc triple bond that is also supported by electronic structure calculations.

Binary transition metal halides are key reagents in inorganic chemistry and play critical roles in synthetic inorganic, organometallic, and organic chemistry and a wide range of materials, catalytic, and medical applications.^{1–4} Approximately 200 binary transition metal halides are known, and dozens of structural types have been identified. One transition metal whose halide chemistry is relatively unexplored is the lowest atomic number radioelement, i.e., technetium ($Z = 43$), an important byproduct of nuclear fission. Roughly 6% of the primary ²³⁵U fission yield is ⁹⁹Mo (half-life or $t_{1/2} = 66$ h), which β -decays to ^{99m}Tc ($t_{1/2} = 6$ h), a low energy γ -emitter and the workhorse of diagnostic nuclear medicine,^{5,6} and then to ⁹⁹Tc ($t_{1/2} = 2.12 \times 10^5$ y). Because of its yield, long half-life, and β -radiotoxicity, ⁹⁹Tc presents handling and storage problems. It also presents an opportunity to learn more about the chemistry of the transition elements, to prepare and characterize surrogates for ^{99m}Tc radiopharmaceuticals, and to explore possibilities for ⁹⁹Tc waste forms. Until recently, only TcF₆, TcF₅, and TcCl₄ were reasonably well characterized.⁷ Over the past 2 years, we have reported three new halides, viz., TcCl₃, TcBr₃, and TcBr₄. The trichloride was obtained via the reaction between Tc₂(O₂CCH₃)₄Cl₂ and excess HCl(g) at 300 °C, while the bromides were prepared in sealed tubes by stoichiometric reaction between Tc metal and elemental bromine at 400 °C.^{8,9} The reaction of Tc metal with excess chlorine at 400 °C in a flow system provides TcCl₄, but no

sealed-tube reactions involving stoichiometric amounts of Tc metal and Cl₂ have been reported.¹⁰ Encouraged by the bromination experiments, we have begun to explore stoichiometric reactions of Tc metal with elemental chlorine, starting with the 1:1 reaction. We report here the synthesis and characterization of technetium dichloride, a new binary halide with an unprecedented extended commensurate superstructure containing metal–metal multiple bonds.

A weighted quantity of Tc metal was placed in a Pyrex tube and flamed under vacuum. After backfilling with Cl₂ gas (Tc:Cl₂ ~1:1), the reactants were frozen in liquid nitrogen, and the tube was flame-sealed and heated to 450 °C for several hours. Following the reaction, the resulting black powder, which contains TcCl₂, was removed and sealed in a second Pyrex tube under high vacuum. Black technetium dichloride needles with a metallic luster grew by sublimation at 450 °C at the center part of the tube (Figure S1).¹¹

The composition of TcCl₂ was estimated by Energy-Dispersive X-ray (EDX) spectroscopy¹² and technetium elemental analysis (Anal. Calcd for TcCl₂: Tc, 58.2; Found: Tc, 59.2). The EDX spectrum of TcCl₂ (Figure S2) shows the presence of the Tc–K ω , Tc–L ω , and the Cl–K α lines, indicating formation of a binary chloride. A [Cl:Tc] ratio of 2.1(2), determined from the integrated intensity of the Tc–K α and Cl–K α lines is consistent with the TcCl₂ stoichiometry.¹¹ The X-ray Absorption Near Edge Structure (XANES) spectrum of TcCl₂ was recorded (Figure S3), and the energy of the absorption edge was compared with those of other technetium chloro complexes (Figure 1). The shift to lower energy observed in the series TcNCl₄[–], TcOCl₄[–], TcCl₆^{2–}, Tc₂Cl₈^{2–}, Tc₂Cl₄(PMe₂Ph)₄, and TcCl₂ is correlated with a decrease in oxidation state of the Tc atoms and is consistent with the presence of divalent technetium in TcCl₂.¹³

Large needles, grown by vapor phase transport using AlCl₃, were used for the structure determination by single crystal X-ray diffraction (XRD). The apparent space group that was suggested by extinction analysis of the observed reflections was the tetragonal $I4/m$. The structure solution that was obtained in this

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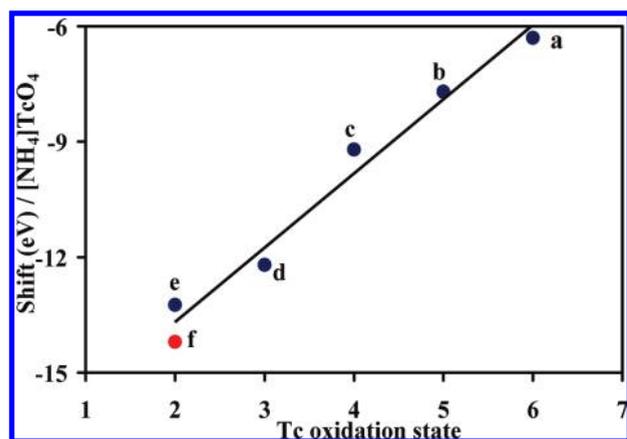


Figure 1. Chemical shift ΔE (eV) of the Tc–K edge relative to NH_4TcO_4 versus formal oxidation state for (a) $(n\text{-Bu}_4\text{N})\text{TcNCl}_4$, (b) $(n\text{-Bu}_4\text{N})\text{TcOCl}_4$, (c) $(\text{Me}_4\text{N})_2\text{TcCl}_6$, (d) $(n\text{-Bu}_4\text{N})_2[\text{Tc}_2\text{Cl}_8]$, (e) $\text{Tc}_2\text{Cl}_4(\text{PMe}_2\text{Ph})_4$, and (f) TcCl_2 (red dot).

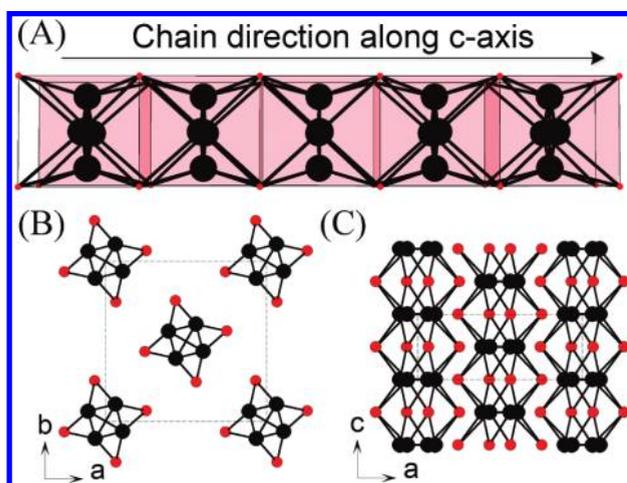


Figure 2. (A) View of the “disordered” TcCl_2 infinite chain along the c -axis. Packing of the TcCl_2 chains viewed (B) down the c -axis where the presence of Tc squares is apparent due to the symmetry related disorder and (C) down the b -axis where each adjacent chain is translated by half the length of the c -axis.

symmetry gave a disordered model (Figure 2). The model exhibits a new structure type that consists of infinite chains of eclipsed $[\text{Tc}_2\text{Cl}_8]$ units running along the c -axis (Figure 2A).¹¹ The eight Cl atoms form a rectangular prism comprised of two square and four rectangular faces with the Tc–Tc vector parallel to the square faces. In the chain, the prisms share the square face, and the rectangular face is parallel to the c -axis (Figure 2A). The presence of a crystallographic 4-fold rotation axis at the center of the chain axis necessitates a disordered Tc–Tc bond, with each orthogonal Tc–Tc position at one-half occupancy (Figure 2B). The packing of the TcCl_2 chains (Figure 2C) indicates that the square planes of Tc atoms in adjacent chains are translated by half the length of the c -axis. The shorter interchain Cl···Cl distance (3.522(1) Å) is slightly less than the sum of van der Waals radii (3.60 Å). Two types of disorder are possible in the crystal: intra- and interchain. For the first type, the Tc–Tc axes are randomly orientated within a chain where the Tc–Tc pairs of two adjacent $[\text{Tc}_2\text{Cl}_8]$ units can be either parallel or perpendicular to each

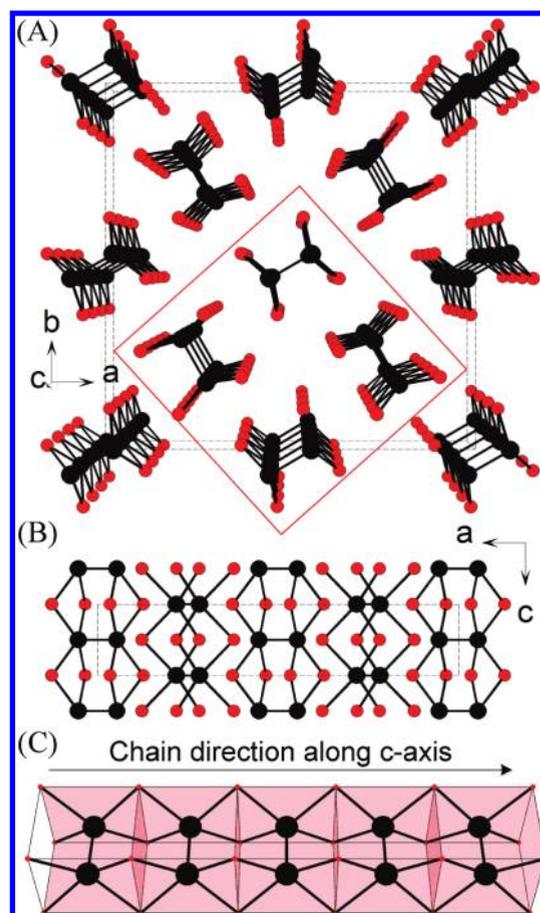


Figure 3. View of the TcCl_2 superstructure: (A) down the c -axis and (B) down the b -axis showing the packing of the TcCl_2 chains. (C) Single undistorted TcCl_2 chain. The $2 \times 2 \times 1$ supercell is represented in dashed line, and the reduced supercell in red solid line.

other. For the second type, each chain has coincident Tc–Tc axes, but one-half of the chains in the crystal are rotated 90° about their chain axis with respect to the other half. Careful examination of the single crystal synthetic precession photographs revealed the presence of additional diffuse supercell reflections centered at $1/2a^* + 1/2b^*$ with respect to the $I4/m$ cell (Figure S4A). Taking into account the absence of additional reflections or diffuse intensity along the c -axis, it is safe to conclude that no intrachain disorder is present.

A $(3+1)$ -dimensional crystallographic approach was used in order to decouple the effect of disorder that is exclusively observed on the supercell reflections from the subcell (Figure S4A). A tetragonal subcell with $a = b = 8.573(5)$ Å, $c = 3.424(2)$ Å and a diagonal commensurate q -vector at $1/2a^* + 1/2b^*$ were used for the structure refinement. Although the subcell has a tetragonal symmetry, none of the tetragonal superspace groups gave a satisfactory solution with agreement factors for the supercell reflections greater than 30%. The best solution was obtained with the monoclinic superspace group $P2/m(\alpha\beta 0)00$ and a pseudomerohedral twin law of 90° rotation along the c -axis.¹¹ The overall agreement factor, taking into account both subcell and supercell reflections, was 4.24% for the observed reflections ($I > 2\sigma(I)$) and 6.08% for all collected reflections.

The $2 \times 2 \times 1$ supercell and the reduced supercell are shown in Figure 3A. There are four TcCl_2 chains in the reduced

supercell. The infinite TcCl_2 chains that run down the c -axis are primarily oriented ($\sim 85\%$) according to the structure shown in Figure 3A which also supports the interchain disordered scenario. The degree of disorder was calculated from the refined occupancy of the additional Tc sites in the superstructure that are similar in position with the ones found in the average cell (Figure 2B). The $\sim 15\%$ short-range disorder that is suggested from the observed diffuse supercell reflections may come from a random intergrowth of TcCl_2 chains with different orientations. A side view along the a -axis showing the packing of the TcCl_2 chains is illustrated in Figure 3B where the arrangement of the Tc vectors is again translated half the length of the c -axis along adjacent chains. This specific stacking also prevents rotational disorder among adjacent chains since no additional electron density was observed on the Cl planes. The undistorted structure of a single TcCl_2 chain (Figure 3C) consists of $[\text{Tc}_2\text{Cl}_8]$ units ($\text{Tc}-\text{Tc} = 2.127(2)$ Å) and $\text{Tc}-\text{Cl} = 2.372(9)$ Å) running along the c -axis. The $\text{Tc}-\text{Tc}$ vectors of adjacent units are parallel, and the distances between Tc atoms of the adjacent units ($3.417(2)$ Å) preclude any metal–metal bonding between these units.¹⁴

Technetium dichloride is the first transition metal binary halide reported to date with a prismatic, $M-M$ bonded M_2X_8 unit. The $[\text{Tc}_2\text{Cl}_8]$ unit exhibits an eclipsed conformation similar to the one found in the $[\text{Tc}_2\text{Cl}_8]^{n-}$ ($n = 2, 3$) ions.¹⁵ The conformation of the $[\text{Tc}_2\text{Cl}_8]$ unit in TcCl_2 differs from the one found in the salt $\text{K}_2\text{Tc}_2\text{Cl}_6$.¹⁶ The structure of the latter consists of infinite chains of edge-sharing $[\text{Tc}_2\text{Cl}_8]$ units with staggered conformations. The change of conformation from eclipsed to staggered is accompanied by a 0.08 Å decrease in the $\text{Tc}-\text{Tc}$ separation. This observation is likely due to steric effects, which will be more pronounced in the eclipsed conformation. The metal–metal separation in TcCl_2 is similar to that observed in a number of Tc(II) dimers and consistent with the presence of a metal–metal triple bond, which would make it the highest bond multiplicity reported so far in a binary halide.¹⁵ Further evidence for triple bonds in TcCl_2 is provided by first-principles calculations of the natural bond orbital (NBO) occupancy of the $\text{Tc}-\text{Tc}$ bond, $\text{NBO} = 5.30$, i.e., close to a perfect triple covalent bond ($\text{NBO} = 6.00$).¹⁷ In the known technetium chlorides, the change of the electronic configuration of the metal atom from d^3 (TcCl_4) to d^4 (TcCl_3) to d^5 (TcCl_2) is accompanied by formation of metal–metal bonds in the coordination polyhedra. In TcCl_4 , there is no appreciable metal–metal interaction and the $\text{Tc}-\text{Tc}$ separation is $3.62(1)$ Å. For TcCl_3 , which contains the triangular Tc_3Cl_9 cluster, a $\text{Tc}=\text{Tc}$ double bond ($2.444(1)$ Å) is proposed.⁸

In order to further characterize the undistorted TcCl_2 chain, total-energy calculations based on density functional theory (DFT) were performed. The calculated bond distances, $\text{Tc}-\text{Tc} = 2.05$ Å and $\text{Tc}-\text{Cl} = 2.42$ Å, are in good agreement with experimental data. Density of states calculations (Figure 4) predict the chain to be semiconducting with a band gap of ~ 0.8 eV. The Tc 4d character is dominant in the vicinity of the Fermi level, with significant Cl 2p and Tc 4d hybridization occurring below -2 eV. Calculations also predict the TcCl_2 chains to be diamagnetic.¹⁴

In summary, technetium dichloride has been synthesized directly from the elements. It exhibits a new solid-state structure type with metal–metal multiple bonds. We believe the “ TcCl_2 structure type” is likely to be encountered for other metals which are known to form molecular complexes containing metal–metal bonded M_2X_8 units (e.g., $M = \text{Mo}, \text{W}, \text{Re}, \text{Os}$; $X = \text{Cl}, \text{Br}, \text{I}$). In this context, we note that $\beta\text{-MoCl}_2$, ReI_2 , and OsI_2 have

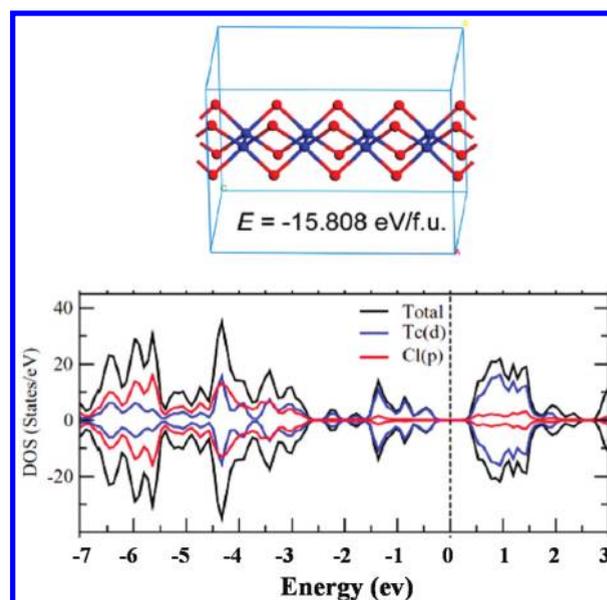


Figure 4. Relaxed structure of the undistorted TcCl_2 chain with $Z = 8$ (top) and associated density of states (bottom) calculated using spin-polarized DFT. Positive and negative values of the density of states correspond to spin-up and spin-down contributions. The total energy (eV) per TcCl_2 formula unit (f.u.) is -15.808 eV.

been reported, but their solid state structures are currently unknown.^{18,19} For technetium, two $[\text{Tc}_2\text{Br}_8]^{n-}$ ($n = 2, 3$) ions have been reported¹⁵ and TcBr_2 may be accessible using a bromine variant of the reaction reported here for TcCl_2 . Although further experimentation is needed, TcCl_2 , because of its insolubility in aqueous media, holds promise as a waste storage form. In this context, the relationship of metal–metal bonding to the solubility properties of solid-state technetium compounds merits further investigation. We also envision technetium(II) halides as starting materials for other low-valent technetium compounds.

■ ASSOCIATED CONTENT

S Supporting Information. Additional synthetic and characterization details, computational chemistry, crystallographic tables, and X-ray crystallographic data in CIF format for TcCl_2 . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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