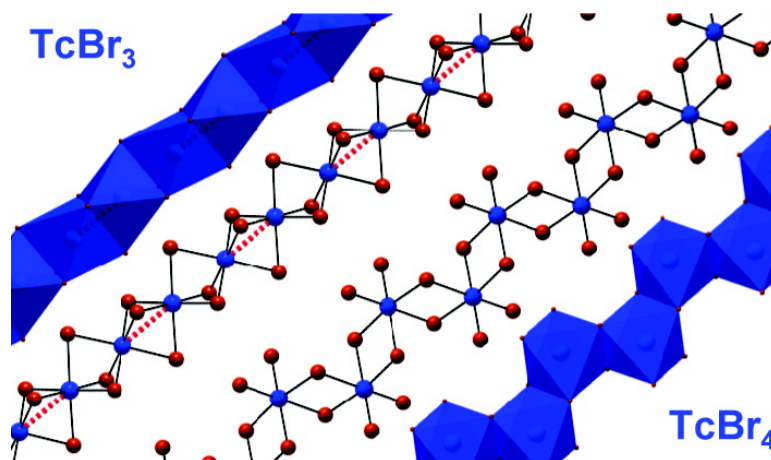


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## Preparation of the Binary Technetium Bromides: TcBr<sub>3</sub> and TcBr<sub>4</sub>

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Because technetium and rhenium are members of the same group in the periodic table, the occurrence of analogous halide, oxide, coordination, and organometallic compounds is expected.<sup>1</sup> However, the development of technetium chemistry has lagged behind that of its heavier congener, primarily because the inherent radioactivity of all Tc isotopes has limited the number of laboratories that can study the chemistry of this fascinating element. Most current studies focus on the applications of the <sup>99m</sup>Tc isotope in diagnostic nuclear medicine resulting in some curious gaps in fundamental technetium chemistry. For example, only recently has the structure of TcO<sub>2</sub> been fully determined,<sup>2</sup> and in the case of the halides, 13 binary phases have been reported for rhenium, but only 3 are known and well-characterized for technetium (TcF<sub>6</sub>, TcF<sub>5</sub>, and TcCl<sub>4</sub>).<sup>3</sup> Other halide species (e.g., Tc<sub>3</sub>Cl<sub>9</sub>) have been observed in the gas phase by mass spectrometry,<sup>4</sup> but these have neither been isolated in macroscopic amounts nor further characterized. Binary halides of transition metals are typically obtained by direct reaction of the metal and halogen at elevated temperature, and technetium hexafluoride and technetium tetrachloride were synthesized in this manner. The direct reaction between technetium metal and bromine has, to the best of our knowledge, never been reported. Herein we provide details of this reaction, which has led to the synthesis and structural characterization of TcBr<sub>3</sub> and TcBr<sub>4</sub>, the first simple halides of the element to be reported in the past 40 years. The compound TcBr<sub>3</sub> is also the first trivalent technetium halide characterized to date.

Technetium metal (<sup>99</sup>Tc, *t*<sub>1/2</sub> = 2.1 × 10<sup>5</sup> y) was prepared by hydrogen reduction of TcO<sub>2</sub> at 750 °C. A weighed quantity of the gray metallic powder (typically 20–30 mg) was placed in a Pyrex tube and then flamed under vacuum. After backfilling with prepurified argon, a stoichiometric amount of bromine (Tc:Br ≈ 1:3) was added via a calibrated syringe, and the reactants were frozen in liquid nitrogen, evacuated, and flame sealed. The tube was then placed horizontally in a tube furnace and heated to 350–400 °C for 8 h, providing a deep purple-black microcrystalline solid. Lustrous black needles, suitable for X-ray diffraction, grew by sublimation of the crude product at 400 °C to the cooler end of the tube. A detailed procedure is presented in the Supporting Information.

The structure of TcBr<sub>3</sub> (**1**) (Figure 1) consists of infinite ordered chains of face-sharing TcBr<sub>6</sub> octahedra that run parallel to the *c* axis.<sup>5</sup> A regular alternation of short (2.8283(4) Å) and long (3.1434(4) Å) Tc–Tc distances is observed. This metal–metal coupling is common for TiI<sub>3</sub>-type structures.<sup>6</sup> The disparity between paired and nonpaired metal–metal distances is comparable to

observed couplings for MoBr<sub>3</sub> (d<sup>3</sup>) or RuBr<sub>3</sub> (d<sup>5</sup>) (Table 1). One significant structural impact of the Tc–Tc bonding is that the three Br anions between the face-sharing TcBr<sub>6</sub> octahedra are pushed out from the center of the chain compared to the three along the long Tc···Tc distance (av Br···Br distance 3.454[2] Å versus 3.516[2] Å) with correspondingly shorter Tc–Br average bond distances between Tc pairs (Tc–Br distance 2.4893[7] versus 2.5231[7] Å).

**Table 1.** M–M and M···M Distances (Å) in MBr<sub>3</sub> (M = Mo, Tc, Ru)

	MoBr <sub>3</sub> (d <sup>3</sup> ) <sup>6b</sup>	TcBr <sub>3</sub> (d <sup>4</sup> )	RuBr <sub>3</sub> (d <sup>5</sup> ) <sup>6b</sup>
M–M	2.874(3)	2.8283(4)	2.732(3)
M···M	3.203(3)	3.1434(4)	3.127(3)
Δ <sub>MM</sub>	0.329(4)	0.3151(6)	0.395(4)

**Table 2.** M–Br and M···Br distances (Å) in MBr<sub>3</sub> (M = Mo, Tc, Ru)

	MoBr <sub>3</sub> <sup>6b</sup>	TcBr <sub>3</sub>	RuBr <sub>3</sub> <sup>6b</sup>
M–Br	2.555(3)	2.4893(7)	2.470(3)
M···Br	2.600(3)	2.5231(7)	2.520(3)
Δ <sub>MBr</sub>	0.045(4)	0.034(1)	0.050(4)

**1** is isomorphous with RuBr<sub>3</sub> and MoBr<sub>3</sub> and is the first d<sup>4</sup> example of the “TiI<sub>3</sub>” structure type. In this structure, the alternation of M–M distances occurs out of phase between adjacent chains, forcing a doubling of the unit cell and reduction to orthorhombic symmetry from the ideal hexagonal structure.<sup>6</sup> While difficult to detect crystallographically due to the weak reflections that violate hexagonal symmetry and common trilling, this deviation appears to be extremely common for this structure type. Technetium tribromide exhibits similar M–M and M···M distances compared with that observed in the Mo, Tc, Ru series: the difference between the M–M and M···M distances (Δ<sub>MM</sub>) follow the order Δ<sub>RuRu</sub> > Δ<sub>MoMo</sub> > Δ<sub>TcTc</sub> (Table 1). The difference between the M–Br short and M···Br long distance (Δ<sub>MBr</sub>) in the MBr<sub>3</sub> octahedra follow the order Δ<sub>RuBr</sub> > Δ<sub>MoBr</sub> > Δ<sub>TcBr</sub> (Table 2); it follows that RuBr<sub>3</sub> and MoBr<sub>3</sub> exhibit more distorted octahedra than TcBr<sub>3</sub>.

Interestingly, the reaction product between Re metal and bromine leads to a mixture of ReBr<sub>3</sub> and ReBr<sub>5</sub>. The structure of **1** differs significantly from that of rhenium(III) bromide,<sup>7</sup> which has a polymeric layered structure in which Re<sub>3</sub>Br<sub>9</sub> clusters are connected by Br bridges. In addition to the bromination of the metal, ReBr<sub>3</sub> can be obtained by several methods including the thermal decomposition of Ag<sub>2</sub>ReBr<sub>6</sub> and ReBr<sub>5</sub>, and the reaction between Re<sub>2</sub>(O<sub>2</sub>CCH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> with HBr(g).<sup>8</sup> None of these synthesis strategies has been reported for technetium. Technetium tribromide is stable in air for weeks and insoluble in common organic solvents.

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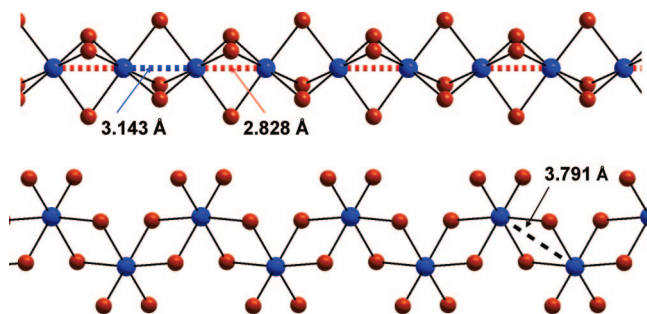
<sup>‡</sup> University of California.

<sup>§</sup> Argonne National Laboratory.

<sup>||</sup> University of Cambridge.

In a second reaction, technetium metal was sealed in a glass tube with a stoichiometric amount of bromine (Tc:Br  $\approx$  1:4) and heated to 400 °C for 6 h. After the reaction, black crystals were obtained at the cooler end of the tube. Analysis by powder XRD showed the presence of TcBr<sub>3</sub>, TcBr<sub>4</sub>, and unreacted Tc metal. XRD single crystal analysis on a needle revealed the structure of technetium tetrabromide.<sup>9</sup> The TcBr<sub>4</sub> (**2**) (Figure 1) consists of infinite ordered chains of edge-sharing TcBr<sub>6</sub> octahedra. The interpolymer Br $\cdots$ Br contact distances range from 3.6913(4) to 3.7767(4) Å, slightly less than the sum of Van der Waals radii (3.8 Å).<sup>10</sup> In a chain, the Tc atoms are equidistant and the metal–metal separation (i.e., 3.7914(4) Å) precludes metal–metal bonding. There are three classes of Tc–Br bond distances within this structure. The shortest bond involves the terminal bromine, (av Tc–Br = 2.3953(4) Å). Significant differences ( $d_{\text{av}} = 2.5256[4]$  versus 2.6234[4] Å) are seen between the two types of Tc–Br distances involving the bridging bromine atoms. Similar overall distributions of bond distances are observed in TcCl<sub>4</sub> where the origins have already been discussed.<sup>11</sup>

In **2**, Tc has the d<sup>3</sup> electronic configuration. It is isomorphous with TcCl<sub>4</sub>, PtBr<sub>4</sub>, and OsBr<sub>4</sub> and is the only tetravalent binary bromide of group VII that has been characterized by single crystal diffraction.<sup>12</sup> We note that neither RuBr<sub>4</sub> nor MoBr<sub>4</sub> has been structurally characterized as a solid.



**Figure 1.** Ball and stick representation of (a) TcBr<sub>3</sub> (top) and TcBr<sub>4</sub> (bottom) infinite chains showing the metal–metal distances.

The congruent formation of TcBr<sub>3</sub> and TcBr<sub>4</sub> could be due to inhomogeneous reaction conditions or kinetic considerations (i.e., formation of TcBr<sub>4</sub> from TcBr<sub>3</sub> is faster than formation of TcBr<sub>3</sub> from Tc metal). The congruent formation of tribromide and tetrabromide has already been observed during the reaction between platinum metal and bromine.<sup>13</sup> It was concluded that the direct bromination of the metal was not the optimal route to produce pure platinum tetrabromide and a method involving decomposition of H<sub>2</sub>PtBr<sub>6</sub>·xH<sub>2</sub>O in a bromine stream was developed. In contrast to a previous report, **2** does not decompose by spontaneous bromine loss;<sup>14</sup> it is air stable and can be kept in normal atmosphere for weeks without degrading. The compound **2** is slightly soluble in tetrahydrofuran and dimethoxyethane.

In the present work, TcBr<sub>3</sub> and TcBr<sub>4</sub> have been synthesized by reaction between Tc metal and elemental bromine and characterized

by single crystal XRD. The TcBr<sub>3</sub> exhibits the TiI<sub>3</sub> structure type and TcBr<sub>4</sub> is isomorphous with TcCl<sub>4</sub>. In contrast to expectations, the bromides of technetium are unique and do not match the behavior of Re, implying that much remains to be learned about fundamental Tc chemistry. TcBr<sub>3</sub> is the first example of the TiI<sub>3</sub> structure prepared with a d<sup>4</sup> metal, and will undoubtedly contribute toward understanding metal–metal bonding interactions for this structure type. We are currently investigating reactions aimed at obtaining phase pure samples of these bromides and scaling up the syntheses, and will publish a full article detailing the physical properties of these compounds in due course. It is our expectation that the new bromides will serve as precursors for the synthesis of other interesting technetium compounds.

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**Supporting Information Available:** Additional synthetic procedures, crystallographic tables, and X-ray crystallographic data in CIF format for **1** and **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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