J|A|C|S
COMMUNICATIONS

# Preparation of the Binary Technetium Bromides: $TcBr_3$ and $TcBr_4$

Frederic Poineau,[*,†] Efrain E. Rodriguez,[‡] Paul M. Forster,[†] Alfred P. Sattelberger,[§]
Anthony K. Cheetham,[||] and Kenneth R. Czerwinski[†]

*Department of Chemistry, University of Nevada—Las Vegas, Las Vegas, Nevada 89154, Materials Research Laboratory, University of California, Santa Barbara, California 93106, Energy Sciences and Engineering Directorate, Argonne National Laboratory, Argonne, Illinois 60439, and Department of Materials and Metallurgy, University of Cambridge, Pembroke Steet, Cambridge, CB2 3QZ, U.K.*

Received November 6, 2008; E-mail: freder29@unlv.nevada.edu

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.[1] 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 $^{99m}$Tc isotope in diagnostic nuclear medicine resulting in some curious gaps in fundamental technetium chemistry. For example, only recently has the structure of $TcO_2$ been fully determined,[2] 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 ($TcF_6$, $TcF_5$, and $TcCl_4$).[3] Other halide species (e.g., $Tc_3Cl_9$) have been observed in the gas phase by mass spectrometry,[4] 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 $TcBr_3$ and $TcBr_4$, the first simple halides of the element to be reported in the past 40 years. The compound $TcBr_3$ is also the first trivalent technetium halide characterized to date.

Technetium metal ($^{99}$Tc, $t_{1/2} = 2.1 \times 10^5$ y) was prepared by hydrogen reduction of $TcO_2$ 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 $\approx$ 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 $TcBr_3$ (**1**) (Figure 1) consists of infinite ordered chains of face-sharing $TcBr_6$ octahedra that run parallel to the *c* axis.[5] 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 $TiI_3$-type structures,[6] The disparity between paired and nonpaired metal−metal distances is comparable to observed couplings for $MoBr_3$ ($d^3$) or $RuBr_3$ ($d^5$) (Table 1). One significant structural impact of the Tc−Tc bonding is that the three Br anions between the face-sharing $TcBr_6$ 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 $MBr_3$ (M = Mo, Tc, Ru)

| | $MoBr_3$ ($d^3$)$^{6b}$ | $TcBr_3$ ($d^4$) | $RuBr_3$ ($d^5$)$^{6b}$ |
|---|---|---|---|
| M−M | 2.874(3) | 2.8283(4) | 2.732(3) |
| M···M | 3.203(3) | 3.1434(4) | 3.127(3) |
| $\Delta_{MM}$ | 0.329(4) | 0.3151(6) | 0.395(4) |

***Table 2.*** M−Br and M···Br distances (Å) in $MBr_3$ (M = Mo, Tc, Ru)

| | $MoBr_3$$^{6b}$ | $TcBr_3$ | $RuBr_3$$^{6b}$ |
|---|---|---|---|
| M−Br | 2.555(3) | 2.4893(7) | 2.470(3) |
| M···Br | 2.600(3) | 2.5231(7) | 2.520(3) |
| $\Delta_{MBr}$ | 0.045(4) | 0.034(1) | 0.050(4) |

**1** is isomorphous with $RuBr_3$ and $MoBr_3$ and is the first $d^4$ example of the "$TiI_3$" 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.[6] 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 ($\Delta_{MM}$) follow the order $\Delta_{RuRu} > \Delta_{MoMo} > \Delta_{TcTc}$ (Table 1). The difference between the M−Br short and M···Br long distance ($\Delta_{MBr}$) in the $MBr_6$ octahedra follow the order $\Delta_{RuBr} > \Delta_{MoBr} > \Delta_{TcBr}$ (Table 2); it follows that $RuBr_3$ and $MoBr_3$ exhibit more distorted octahedra than $TcBr_3$.

Interestingly, the reaction product between Re metal and bromine leads to a mixture of $ReBr_3$ and $ReBr_5$. The structure of **1** differs significantly from that of rhenium(III) bromide,[7] which has a polymeric layered structure in which $Re_3Br_9$ clusters are connected by Br bridges. In addition to the bromination of the metal, $ReBr_3$ can be obtained by several methods including the thermal decomposition of $Ag_2ReBr_6$ and $ReBr_5$, and the reaction between $Re_2(O_2CCH_3)_4Cl_2$ with HBr(g).[8] None of these synthesis strategies has been reported for technetium. Technetium tribromide is stable in air for weeks and insoluble in common organic solvents.

---

[†] University of Nevada—Las Vegas.
[‡] University of California.
[§] Argonne National Laboratory.
[||] University of Cambridge.

10.1021/ja808597r CCC: $40.75

In a second reaction, technetium metal was sealed in a glass tube with a stoichiometric amount of bromine (Tc:Br ≈ 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 $TcBr_3$, $TcBr_4$, and unreacted Tc metal. XRD single crystal analysis on a needle revealed the structure of technetium tetrabromide.[9] The $TcBr_4$ (**2**) (Figure 1) consists of infinite ordered chains of edge-sharing $TcBr_6$ octahedra. The interpolymer Br···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).[10] 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 ($d_{av}$ = 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 $TcCl_4$ where the origins have already been discussed.[11]

In **2**, Tc has the $d^3$ electronic configuration. It is isomorphous with $TcCl_4$, $PtBr_4$, and $OsBr_4$ and is the only tetravalent binary bromide of group VII that has been characterized by single crystal diffraction.[12] We note that neither $RuBr_4$ nor $MoBr_4$ has been structurally characterized as a solid.

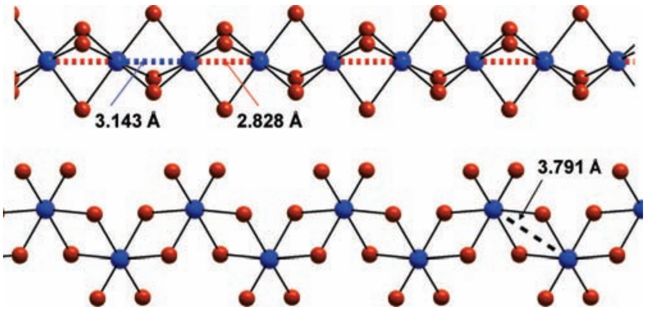

***Figure 1.*** Ball and stick representation of (a) $TcBr_3$ (top) and $TcBr_4$ (bottom) infinite chains showing the metal−metal distances.

The congruent formation of $TcBr_3$ and $TcBr_4$ could be due to inhomogeneous reaction conditions or kinetic considerations (i.e., formation of $TcBr_4$ from $TcBr_3$ is faster than formation of $TcBr_3$ from Tc metal). The congruent formation of tribromide and tetrabromide has already been observed during the reaction between platinum metal and bromine.[13] 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 $H_2PtBr_6 \cdot xH_2O$ in a bromine stream was developed. In contrast to a previous report, **2** does not decompose by spontaneous bromine loss;[14] 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, $TcBr_3$ and $TcBr_4$ have been synthesized by reaction between Tc metal and elemental bromine and characterized by single crystal XRD. The $TcBr_3$ exhibits the $TiI_3$ structure type and $TcBr_4$ is isomorphous with $TcCl_4$. 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. $TcBr_3$ is the first example of the $TiI_3$ structure prepared with a $d^4$ 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.

**Acknowledgment.** The authors thank Dr. Charles Campana (Bruker AXS) for useful discussions and Mr. Tom O'Dou for outstanding health physics support. We also acknowledge Dr. Carol J. Burns (Los Alamos) for a generous loan of ammonium pertechnetate. Funding for this research was provided by the US Department of Energy, agreement no. DE-FG52-06NA26399.

**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.

## References

(1) (a) Alberto, R. *Comp. Coord. Chem II* **2004**, *5*, 127–270. (b) Sattelberger, A. P.; Poineau, F.; Scott, B. L. *Comp. Coord. Chem III* **2007**, *5*, 833–854.
(2) Rodriguez, E. E.; Poineau, F.; Llobet, A.; Sattelberger, A. P.; Bhattacharjee, J.; Waghmare, U. V.; Hartmann, T.; Cheetham, A. K. *J. Am. Chem. Soc.* **2007**, *129*, 10244–10248.
(3) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6 th ed.; John Wiley and Sons: New York, 1999, Chapter 18-D. (b) Schwochau, K. *Technetium: Chemistry and Radiopharmaceutical. Applications*; Wiley-VCH: Weinheim, Germany, 2000.
(4) Rinke, K.; Klein, M.; Schaefer, H. *J. Less-Common Met.* **1967**, *12*, 497–503.
(5) Crystal data for TcBr3: *Pmmn* ($a$ = 11.0656(2) Å, $b$ = 5.9717(1) Å, $c$ = 6.3870(1) Å), $R_1$ = 4.70%, GOF 1.06, 3458 reflections, 29 refined parameters. Full refinement details are included in Supporting Information.
(6) (a) Lin, J.; Miller, G. J. *Inorg. Chem.* **1993**, *32*, 1476–1487. (b) Merlino, S.; Labella, L.; Marchetti, F.; Toscani, S. *Chem. Mater.* **2004**, *16*, 3895–3903. (c) Hillebrecht, H.; Ludwig, Th.; Thiele, G. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2199–2204. (d) Lachgar, A.; Dudis, D. S.; Corbett, J. D. *Inorg. Chem.* **1990**, *29*, 2242–2246.
(7) (a) Aslanov, L. A.; Volkov, S. V.; Kolesnichenko, V. L.; Rybakov, V. B.; Timoshchenko, N. I. *Ukr. Khim. Zh.* **1992**, *58*, 279–281. (b) Kolbin, N. I.; Ovchinnikov, K. V. *Zh. Neorg. Khim.* **1968**, *13*, 2306–2307.
(8) (a) Thompson, R. J.; Foster, R. E.; Booker, J. L. *Inorg. Synth.* **1967**, *10*, 58–61. (b) Glicksman, H. D.; Hamer, A. D.; Smith, T. J.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 2205–2209. (c) Cotton, F. A.; Lippard, S. J.; Mague, J. Y. *Inorg. Chem.* **1965**, *4*, 508–514. (d) Colton, R. *J. Chem. Soc.* **1962**, 2078–2080.
(9) Crystal data for $TcBr_4$: *Pbca* ($a$ = 6.3237(5) Å, $b$ = 12.1777(9) Å, $c$ = 14.7397(11) Å), $R1$ = 2.16%, GOF 1.071, 1969 peaks > 2$\sigma$, 46 refined parameters. Full refinement details are included in Supporting Information.
(10) Batsanov, S. S. *Inorg. Mater.* **2001**, *37*, 871–885.
(11) Elder, M.; Penfold, B. R. *Inorg. Chem.* **1966**, *5*, 1197–1200.
(12) (a) Thiele, G.; Wochner, H.; Wagner, H. *Z. Anorg. Allg. Chem.* **1985**, *530*, 178–186. (b) Pilbrow, M. F. *J. Chem. Soc., Chem. Comm.* **1972**, *5*, 270–271.
(13) Degner, M.; Holle, Bernd; Kamm, J.; Pilbrow, M. F.; Thiele, G.; Wagner, D.; Weigl, W.; Woditsch, P. *Transition Met. Chem.* **1976**, *1*, 41–47.
(14) Fergusson, J. E.; Hickford, J. H. *Aust. J. Chem.* **1970**, *23*, 453–61.

JA808597R