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Recent Advances in Technetium Halide Chemistry

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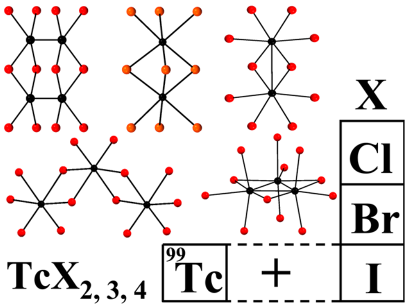

Transition metal binary halides are fundamental compounds, and the study of their structure, bonding, and other properties gives chemists a better understanding of physicochemical trends across the periodic table. One transition metal whose halide chemistry is underdeveloped is technetium, the lightest radioelement. For half a century, the halide chemistry of technetium has been defined by three compounds: TcF_6, TcF_5, and $TcCl_4$. The absence of Tc binary bromides and iodides in the literature was surprising considering the existence of such compounds for all of the elements surrounding technetium. The common synthetic routes that scientists use to obtain binary halides of the neighboring elements, such as sealed tube reactions between elements and flowing gas reactions between a molecular complex and HX gas (X = Cl, Br, or I), had not been reported for technetium. In this Account, we discuss how we used these routes to revisit the halide chemistry of technetium. We report seven new phases: $TcBr_4$, $TcBr_3$, α/β-$TcCl_3$, α/β-$TcCl_2$, and TcI_3.

Technetium tetrachloride and tetrabromide are isostructural to PtX_4 (X = Cl or Br) and consist of infinite chains of edge-sharing TcX_6 octahedra. Trivalent technetium halides are isostructural to ruthenium and molybdenum (β-$TcCl_3$, $TcBr_3$, and TcI_3) and to rhenium (α-$TcCl_3$). Technetium tribromide and triiodide exhibit the TiI_3 structure-type and consist of infinite chains of face-sharing TcX_6 (X = Br or I) octahedra. Concerning the trichlorides, β-$TcCl_3$ crystallizes with the $AlCl_3$ structure-type and consists of infinite layers of edge-sharing $TcCl_6$ octahedra, while α-$TcCl_3$ consists of infinite layers of Tc_3Cl_9 units. Both phases of technetium dichloride exhibit new structure-types that consist of infinite chains of $[Tc_2Cl_8]$ units.

For the technetium binary halides, we studied the metal–metal interaction by theoretical methods and magnetic measurements. The change of the electronic configuration of the metal atom from d^3 (Tc(IV)) to d^5 (Tc(II)) is accompanied by the formation of metal–metal bonds in the coordination polyhedra. There is no metal–metal interaction in TcX_4, a $Tc{=}Tc$ double bond is present in α/β-$TcCl_3$, and a $Tc\equiv Tc$ triple bond is present in α/β-$TcCl_2$.

We investigated the thermal behavior of these binary halides in sealed tubes under vacuum at elevated temperature. Technetium tetrachloride decomposes stepwise to α-$TcCl_3$ and β-$TcCl_2$ at 450 °C, while β-$TcCl_3$ converts to α-$TcCl_3$ at 280 °C. The technetium dichlorides disproportionate to Tc metal and $TcCl_4$ above ~600 °C. At 450 °C in a sealed Pyrex tube, $TcBr_3$ decomposes to $Na\{[Tc_6Br_{12}]_2Br\}$, while TcI_3 decomposes to Tc metal.

We have used technetium tribromide in the preparation of new divalent complexes; we expect that the other halides will also serve as starting materials for the synthesis of new compounds (e.g., complexes with a Tc_3^{9+} core, divalent iodide complexes, binary carbides, nitrides, and phosphides, etc.). Technetium halides may also find applications in the nuclear fuel cycle; their thermal properties could be utilized in separation processes using halide volatility. In summary, we hope that these new insights on technetium binary halides will contribute to a better understanding of the chemistry of this fascinating element.

Introduction

Technetium is the lightest radioelement and the last transition metal to be discovered. The study of simple Tc binary halides is essential to a thorough understanding of the chemistry of this element; it is also relevant to nuclear and medical applications, for example, the development of waste form materials for safe long-term disposal and imaging agents for nuclear medicine.[1,2] Prior to 2008, only

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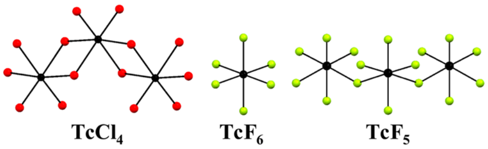
CHART 1. Technetium Binary Halides Reported prior to 2008[a]



[a] Color of atoms: Tc in black, Cl in red, and F in yellow.

three Tc binary halides were well characterized: TcF_6, TcF_5, and $TcCl_4$ (Chart 1); today, ten phases are known. Historically, the first technetium binary halide to be reported was $TcCl_4$ in 1957.[3] Its structure was solved in 1965, and $TcCl_4$ was the first tetrahalide of group 7 to be structurally characterized.[4] The discovery of $TcCl_4$ was followed by that of TcF_6 in 1961[5] and TcF_5 in 1963;[6] both fluorides were obtained from the reaction of Tc metal and F_2 gas. The structure of the hexafluoride consists of molecular TcF_6 octahedra, while TcF_5 consists of infinite chains of corner-sharing TcF_6 octahedra.

The absence of Tc(III) binary chlorides, bromides, and iodides in the literature was surprising considering the existence of such compounds for all of the elements surrounding technetium.[7] The trichloride had been observed in the gas phase (as Tc_3Cl_9) but its preparation in weighable amounts was unsuccessful.[8] Technetium tribromide[9] and $TcBr_4$[10] were reported, but their structures were not elucidated. The synthetic strategies commonly used to obtain binary halides of neighboring elements, for example, stoichiometric reaction between the elements in a sealed tube and flowing gas reactions between a preformed dimer and HX gas (X = Cl, Br, or I) had not been reported for technetium.[11] Using these strategies, we investigated the synthesis of technetium chlorides, bromides, and iodides; over the past five years, we have reported seven new technetium phases, $TcBr_4$, $TcBr_3$, α/β-$TcCl_3$, α/β-$TcCl_2$, and TcI_3, and prepared several additional compounds (e.g., $Na\{[Tc_6Br_{12}]_2\}Br$) derived from these phases. Here, we review the preparation, structure, and properties of technetium binary halides and compare their chemistry to neighboring element analogues.

Technetium Chlorides

Tetrachloride. Technetium tetrachloride can be prepared in a sealed glass tube from the elements (Tc/Cl, 1:6) at 450 °C.[12] The structure of $TcCl_4$ consists of infinite chains of edge-sharing $TcCl_6$ octahedra (Figure 1). The large Tc···Tc separation within the chain (i.e., 3.6048(3) Å) precludes any metal–metal interaction. Technetium was the first element where the "$TcCl_4$ structure-type" was observed. Similar to technetium, the tetrachlorides of Zr,[13] Hf,[14] and Pt[15] adopt the $TcCl_4$ structure-type. In those tetrachlorides, the M–M separations within the chains suggest little or no interaction between neighboring metal ions. Concerning technetium's nearest neighbors, β-$ReCl_4$ consists of infinite chains of Re_2Cl_9 bioctahedra,[16] α-$MoCl_4$[17] consists of infinite chains of $MoCl_6$ edge-sharing octahedra, and β-$MoCl_4$[18] consists of infinite layers of $MoCl_6$ edge-sharing octahedra; $RuCl_4$ is unknown.

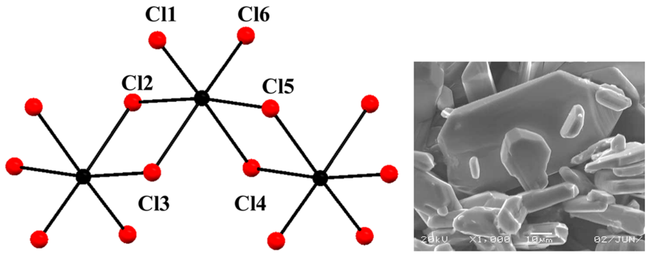


FIGURE 1. (left) Ball and stick representation of the structure of $TcCl_4$. Color of atoms: Tc in black and Cl in red. Selected distances (Å): Tc–Cl1 = 2.2379(6); Tc–Cl2 = 2.3786(6); Tc–Cl3 = 2.4825(6); Tc–Cl4 = 2.4791(6); Tc–Cl5 = 2.3806(6); Tc–Cl6 = 2.2355(6). (right) Scanning electron microscopy (SEM) image of $TcCl_4$.

Technetium tetrachloride is a red, slightly hygroscopic solid; it can be kept for a week in air without noticeable decomposition. The compound is soluble in THF and CH_3CN and hydrolyzes to TcO_2 in water. The compound has been used as a precursor in the synthesis of molecular Tc(IV) chloro complexes.[19]

The magnetic properties of $TcCl_4$ have been measured, and its effective moment (3.76 μ_B) is similar to that expected for an isolated $Tc^{IV}Cl_6$ octahedron (3.87 μ_B) and consistent with the absence of a significant metal–metal interactions within the chains.

The thermal behavior of $TcCl_4$ was studied under flowing argon and in a sealed tube under vacuum. Experiments under flowing argon at 250–500 °C only resulted in the volatilization of the starting material. Experiments in sealed tubes under vacuum at 450 °C indicate that $TcCl_4$ successively decomposes to α-$TcCl_3$ and β-$TcCl_2$.[12]

The Trichloride System: α-$TcCl_3$ and β-$TcCl_3$. The compound α-$TcCl_3$ can be obtained by thermal decomposition of $TcCl_4$ under vacuum or by reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and flowing HCl(g) at 300 °C.[20] The reaction of $Tc_2(O_2CCH_3)_4Cl_2$ with HCl(g) is the method of choice for production of weighable amounts of α-$TcCl_3$; during this reaction, a color change from pink to green (~100 °C) and then black (~250 °C) was noted. Analyses of the green compound showed the product to be $Tc_2(O_2CCH_3)_2Cl_4$ while the black amorphous compound was

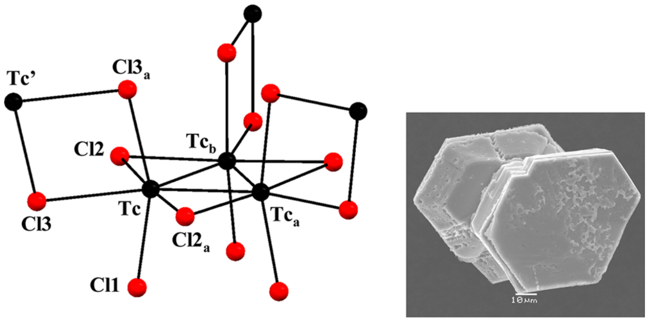


FIGURE 2. (left) Ball and stick representation of the structure of α-$TcCl_3$. Color of atoms: Tc in black and Cl in red. Selected distances (Å): Tc–Cl1 = 2.238(2); Tc–$Cl2_a$ = Tc–$Cl3_a$ = 2.373(2); Tc–Cl3 = 2.585(2); Tc–$Tc_{(a,b)}$ = 2.444(1); Tc–Tc′ = 3.852(1). (right) SEM image of α-$TcCl_3$.

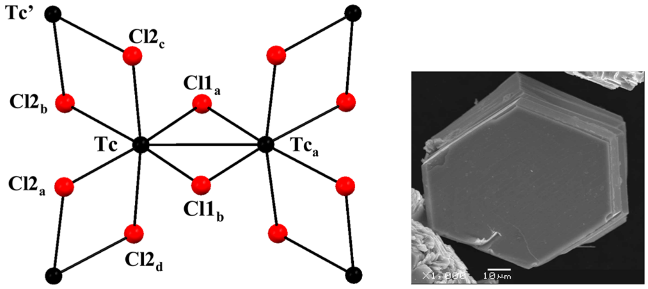


FIGURE 3. (left) Ball and stick representation of the structure of β-$TcCl_3$. Color of atoms: Tc in black and Cl in red. Selected distances (Å): Tc–Tc_a = 2.861(3); Tc–Tc′ = 3.601(2); Tc–$Cl1_{(a,b)}$ = 2.316(3); Tc–$Cl2_{(a,b)}$ = 2.434(3); Tc–$Cl2_{(c,d)}$ = 2.403(2); $Cl1_a$–$Cl1_b$ = 3.642(4). (right) SEM image of β-$TcCl_3$.

identified as α-$TcCl_3$.[21] The mechanism of formation of α-$TcCl_3$ mimics the one described for rhenium;[22] the dimers $M_2(O_2CCH_3)_2Cl_4$ (M = Tc or Re) are formed as intermediates in the early stage of the reaction, after which rhenium and technetium trichlorides are formed at 340 and 300 °C, respectively.

α-$TcCl_3$ consists of infinite layers of Tc_3Cl_9 units and is isostructural to $ReCl_3$. In the Tc_3Cl_9 unit (Figure 2), 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 in $ReCl_3$ and is indicative of a Tc=Tc double bond. The Tc_3Cl_9 units are linked by the Cl atoms and the Tc···Tc′ distance between Tc_3Cl_9 units (3.852(1) Å) precludes any metal–metal interaction. Chemical bonding in the Tc_3Cl_9 cluster has been analyzed, and the results confirms the presence of a Tc=Tc double bonds within the Tc_3^{9+} core.[23] Occupation number calculations of the Tc=Tc bond indicated the presence of 1.99 electrons in both the σ and π orbitals, which indicates an effective bond order of 2.

The compound β-$TcCl_3$ was obtained from the sealed tube reaction between Tc metal and chlorine (Tc/Cl ratio, 1:2.5) at 450 °C for 24 h.[24] Following the reaction, a dark powder containing technetium metal and $TcCl_2$ was obtained in the hottest part of the tube, β-$TcCl_2$ needles in the center portion, and a dark colored product (containing $TcCl_4$ and β-$TcCl_3$) in the coldest end. To the best of our knowledge, technetium is the only transition metal where three binary chloride phases in different oxidation states (i.e., $TcCl_4$, $TcCl_3$, and $TcCl_2$) are formed congruently from the reaction of the elements. Individual reactions of the neighboring second-row elements, molybdenum and ruthenium, with one equivalent of chlorine at 450 °C provide the trivalent chloride and unreacted metal. For rhenium, the pentachloride is the main reaction product of Re metal and chlorine at 500–700 °C.[7a] The absence of measurable amounts of α-$TcCl_3$ or β-$TcCl_3$ is due to the instability of theses phases at 450 °C (*vide infra*).

β-$TcCl_3$ consists of infinite layers of edge-sharing $TcCl_6$ octahedra (Figure 3) and is isostructural to α-$MoCl_3$.[25] Within a layer, coupling of Tc atoms into Tc_2^{6+} pairs occurs and two sets of Tc–Tc distances are observed (i.e., Tc–Tc = 2.861(3) Å, Tc···Tc′ = 3.601(2) Å). The Tc–Tc distance in the Tc_2^{6+} pair indicates a significant metal–metal bonding interaction, while the Tc···Tc′ distance is similar to the nonbonded one in $TcCl_4$ (i.e., 3.6048(3) Å). The calculated effective bond order of the Tc–Tc bond in the Tc_2^{6+} unit (i.e., 1.38) is consistent with the presence of a weak double bond; the Tc=Tc bond is clearly stronger in α-$TcCl_3$ than in β-$TcCl_3$.

In the other layered trichlorides, strong coupling between metal atoms occurs in α-$MoCl_3$ but not in α-$RuCl_3$.[26] The disparity (ΔMM, in Å) between paired and nonpaired metal–metal distances in layered MCl_3 (M = Mo, Tc, or Ru) follows the order ΔMoMo (0.957(4)) > ΔTcTc (0.740(3)) > ΔRuRu (0.01(1)), and a Peierls distortion is likely the origin of formation of M_2^{6+} units.

Amorphous α-$TcCl_3$ is readily soluble in concentrated aqueous HCl and in acetone; the compound is stable in air for a week without decomposition. The thermal properties of α/β-$TcCl_3$ have been investigated in a sealed tube under vacuum. Both trichlorides are unstable; β-$TcCl_3$ is converted to α-$TcCl_3$ after 16 days at 280 °C, while α-$TcCl_3$ decomposes to β-$TcCl_2$ and Tc metal after 12 h at 450 °C. The conversion of β-$TcCl_3$ to α-$TcCl_3$ is consistent with calculations that predict β-$TcCl_3$ to be energetically less stable than α-$TcCl_3$.[24]

Among second- and third-row transition metal trichlorides, polymorphism has been observed for molybdenum, ruthenium, and rhodium.[27] Technetium and ruthenium are the only elements where one trichloride phase can be converted to another in the solid state.[28] The behavior of the

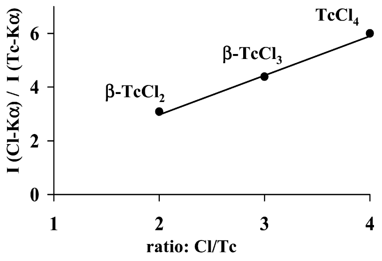


FIGURE 4. Plot of the intensity [Cl Kα]/intensity [Tc Kα] for β-$TcCl_2$, β-$TcCl_3$, and $TcCl_4$.

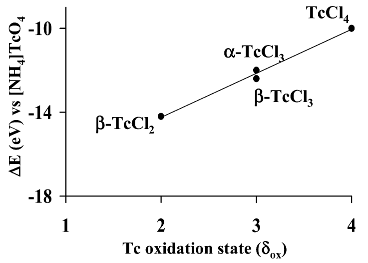


FIGURE 5. Chemical shift, ΔE (eV), of Tc K-edge relative to NH_4TcO_4 versus formal oxidation state for β-$TcCl_2$, α/β-$TcCl_3$, and $TcCl_4$.

technetium trichlorides contrasts with that of Re_3Cl_9 and α-$MoCl_3$. Rhenium trichloride volatilizes as the Re_3Cl_9 cluster, and no decomposition has been reported.[29] α-$MoCl_3$ disproportionates to the dichloride and the tetrachloride.

The Dichloride System: α-$TcCl_2$ and β-$TcCl_2$. Technetium dichloride can be obtained by reaction between the elements at elevated temperature or by thermal decomposition of $TcCl_4$ or α-$TcCl_3$ under vacuum at 450 °C.[30,31] For the first route, single crystals of β-$TcCl_2$, β-$TcCl_3$, and $TcCl_4$ were congruently obtained (*vide supra*). The β-$TcCl_2$ needles that were located in the center part of the tube were used for the structure determination. The dark powder containing technetium metal and $TcCl_2$ was sealed in a tube with $AlCl_3$, and α-$TcCl_2$ single crystals were obtained after four days at 450 °C.

The composition of β-$TcCl_2$ was analyzed by energy dispersive X-ray (EDX) spectroscopy, and its structure and oxidation state were analyzed by X-ray absorption fine structure spectroscopy.[32] During our study on Tc binary halides, these two techniques have proven very useful in determining stoichiometries and the oxidation state of the Tc atoms, respectively. The correlation between the Cl/Tc ratio and the intensity of [Cl Kα]/intensity of [Tc Kα] can be plotted from the EDX data (Figure 4), while the oxidation state of the Tc atom can be correlated to the shift of Tc absorption edge[33] (Figure 5).

Both β-$TcCl_2$ and α-$TcCl_2$ exhibit new structure-types that consist of infinite chains of eclipsed $[Tc_2Cl_8]$ units (Figure 6). In the $[Tc_2Cl_8]$ units, the average Tc–Cl distances for β-$TcCl_2$ (i.e., 2.398(3) Å) are slightly larger than that for α-$TcCl_2$ (i.e., 2.372(9)) and the Tc–Tc separations (2.136(3) for β-$TcCl_2$ and 2.127(2) for α-$TcCl_2$) are indicative of a Tc≡Tc triple bond (*vide infra*).[34]

In a β-$TcCl_2$ chain, two orientations of the Tc≡Tc bonds in the $[Tc_2Cl_8]$ unit are observed: the Tc≡Tc bonds of two adjacent $[Tc_2Cl_8]$ units are either parallel or perpendicular (Figure 6), and the orientation of the Tc≡Tc bonds changes every two $[Tc_2Cl_8]$ units. The distances between Tc≡Tc bonds of parallel (i.e., 3.425(2) Å) and perpendicular $[Tc_2Cl_8]$ units (i.e., 3.744(2) Å) preclude any metal–metal interaction between adjacent units.

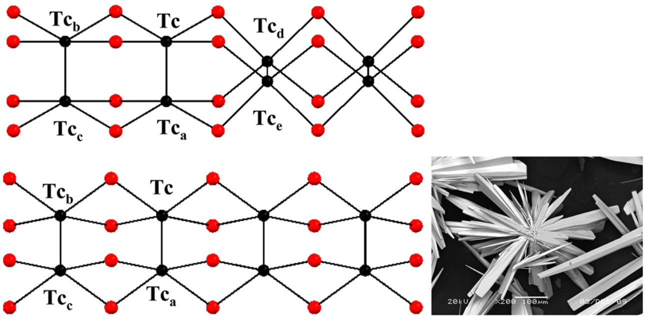


FIGURE 6. Ball-and-stick representation of portions of β-$TcCl_2$ (top) and α-$TcCl_2$ (bottom) chains. Color of atoms: Tc in black and Cl in red. Selected distances (Å) in β-$TcCl_2$: Tc–Tc_a = 2.136(3); Tc–Tc_b = 3.425(2); Tc–Tc_c = 4.037(3); Tc–$Tc_{(d,e)}$ = 3.744(2). Selected distances (Å) in α-$TcCl_2$: Tc–Tc_a = 2.127(2); Tc–$Tc_{b,}$ = 3.417(2); Tc–Tc_c = 4.025(2). (right) SEM image of β-$TcCl_2$.

In α-$TcCl_2$, only one orientation of the Tc≡Tc bonds is observed, and the Tc≡Tc vectors of adjacent units are parallel. The distances between Tc atoms of the adjacent units (i.e., 3.417(2) Å) also preclude any metal–metal interaction.

The metal–metal separations in α/β-$TcCl_2$ are similar to those observed in a number of Tc(II) dinuclear complexes and are consistent with the presence of a metal–metal triple bond.[35] Further quantification of the metal–metal bonding is provided by first-principles calculations of the natural bond orbital (NBO) occupancy of the Tc–Tc bond; the results indicate a NBO of 5.30, which is close to the value expected for a triple bond (i.e., 6.00). In β-$TcCl_2$, the Tc≡Tc triple bond should exhibit the $\sigma^2\pi^4\delta^2\delta^{*2}$ configuration, which is in agreement with the experimental diamagnetism of the compound (*vide infra*).

Among the second- and third-row transition metals, α-$TcCl_2$ and β-$TcCl_2$ are, respectively, the 11th and 12th dichloride phases to be structurally characterized. Transition metal dichlorides can be classified into one of four

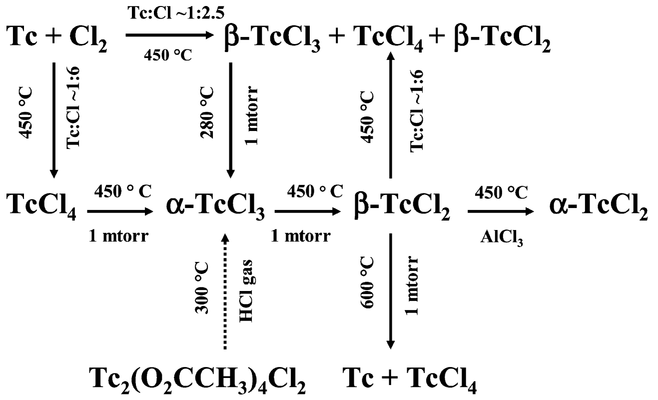


FIGURE 7. Mechanism of formation of technetium binary chlorides. Solid arrow, sealed tube reaction; dotted arrow, flowing gas reaction.

categories, namely, those composed of $[M_2Cl_8]$ units (α/β-$TcCl_2$ and β-$MoCl_2$), those composed of square planar MCl_4 units ($\alpha/\beta/\gamma/\delta$-$PdCl_2$[36] and α/β-$PtCl_2$[37]), those containing $[M_6Cl_8]^{4+}$ hexanuclear clusters (α-$MoCl_2$ and WCl_2),[25] and $ZrCl_2$.[38] We note that $ReCl_2$ and $RuCl_2$ have yet to be synthesized, although both elements form a variety of divalent mononuclear or dinuclear compounds.[7b]

Technetium dichloride crystals are stable in air and can be kept for a year without any evidence of decomposition. The β-$TcCl_2$ needles are insoluble in common organic solvents and aqueous HCl at ambient temperature. No reactions occur between $TcCl_2$ powder and neat PMe_3. The compound is thermally unstable and disproportionates to Tc metal and $TcCl_4$ in a sealed tube at or above 600 °C. The formation mechanism of the various technetium binary chloride phases as well as their decomposition products is summarized in Figure 7.

The magnetic and transport properties of technetium dichloride were investigated.[31] Magnetic susceptibility measurements indicate $TcCl_2$ is diamagnetic, which is consistent with the presence of $Tc{\equiv}Tc$ triple bonds. The transport properties were studied by diffuse reflectance spectroscopy and electrical resistivity measurements. The diffuse reflectance measurement yields a band gap of 0.12(2) eV, which suggests that the compound is a narrow band gap semiconductor. Resistivity and Seebeck measurements indicate β-$TcCl_2$ to be a p-type semiconductor. The experimental results are in agreement with the calculated band structure of β-$TcCl_2$, which predicts semiconductor behavior with an indirect gap of ~0.5 eV.

Technetium Bromides

Tetrabromide. Technetium tetrabromide single crystals were obtained in a sealed glass tube from the elements at 400 °C (Tc/Br ratio, 1:4) for 6 h.[39] After the reaction, an XRD analysis of the powder showed the presence of Tc metal, $TcBr_4$, and $TcBr_3$. Two subsequent treatments of the resulting powder with excess bromine (Tc/Br, 1:6) at 400 °C were required to isolate single-phase, crystalline $TcBr_4$.[40] Technetium tetrabromide (Figure 8) has the $TcCl_4$ structure-type and is isostructural to $PtBr_4$[41] and $OsBr_4$.[42] In a $TcBr_4$ chain, the metal–metal separation (i.e., 3.7914(4) Å) precludes metal–metal interaction.

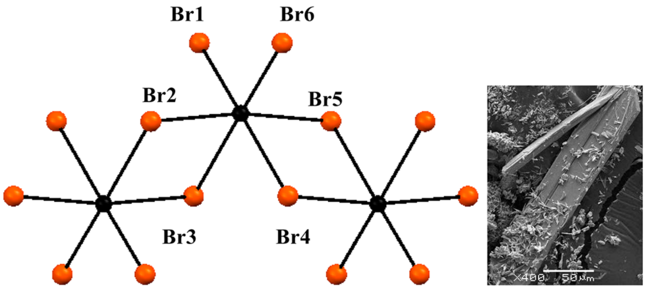


FIGURE 8. (left) Ball and stick representation of the structure of $TcBr_4$. Color of atoms: Tc in black and Br in orange. Selected distances (Å): Tc–Br1 = 2.3966(3); Tc–Br2 = 2.5253(4); Tc–Br3 = 2.6263(3); Tc–Br4 = 2.6205(3); Tc–Br5 = 2.5259(4); Tc–Br6 = 2.3941(4); Tc–Tc = 3.7914(4). (right) SEM image of $TcBr_4$.

The coordination chemistry of transition metal tetrabromides is less well developed than that of the tetrachlorides. Among the second-row transition metals, only $ZrBr_4$, $NbBr_4$, and $TcBr_4$ have been structurally characterized. Concerning Tc neighboring elements, $ReBr_4$[43] and $MoBr_4$[44] have been reported but not structurally characterized, while $RuBr_4$ is unknown.

Technetium tetrabromide is slightly hygroscopic; it can be kept in dry air for weeks without degrading. It is slightly soluble in tetrahydrofuran and dichloromethane. The magnetic properties of $TcBr_4$ have been measured, and the compound is paramagnetic (3.4 μ_B). The thermal behavior of $TcBr_4$ was investigated in a sealed tube under vacuum at 450 °C. The compound is unstable under these conditions and yields two products, namely, $TcBr_3$ and single crystals of an unusual technetium(II) cluster with the composition $Na\{[Tc_6Br_{12}]_2Br\}$ (*vide infra*).

Tribromide. Technetium tribromide can be obtained by the reaction of Tc metal and Br_2 (Tc/Br ratio, ~1:3) in a sealed tube at 400 °C or via the reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and flowing HBr gas at 300 °C.[39,45] Technetium tribromide obtained from the reaction of $Tc_2(O_2CCH_3)_4Cl_2$ and HBr(g) has the same structure (TiI_3 structure-type) as the material obtained by direct combination of the elements. It was hoped that the reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and HBr(g) would mimic the rhenium system and provide Tc_3Br_9.[46]

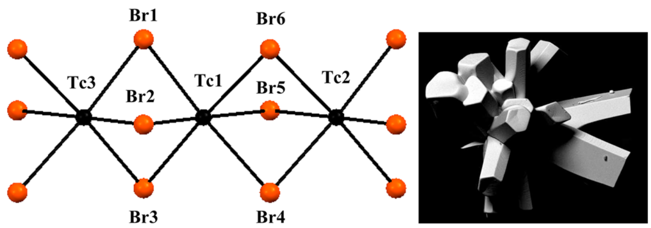


FIGURE 9. (left) Ball and stick representation of the structure of $TcBr_3$. Color of atoms: Tc in black and Br in orange. Selected distances (Å): Tc(1,3)−Br1 = 2.4869(6); Tc(1,3)−Br2 = 2.4945(8); Tc(1,3)−Br3 = 2.4869(6); Tc(1,2)−Br4 = 2.5197(6); Tc(1,2)−Br5 = 2.5300(8); Tc(1,2)−Br6 = 2.5197(6); Tc1−Tc2 = 3.1434(4); Tc1−Tc3 = 2.8283(4). (right) SEM image of $TcBr_3$.

Technetium tribromide (Figure 9) consists of infinite chains of face-sharing $TcBr_6$ octahedra and is isostructural with $RuBr_3$ and $MoBr_3$.[47] In a $TcBr_3$ chain, 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. The disparity between paired and nonpaired metal−metal distances is comparable to the observed couplings for $MoBr_3$ (d^3) or $RuBr_3$ (d^5); the disparity (ΔMM in Å) between the M−M and M···M distances follows the order $\Delta RuRu = 0.395(4) > \Delta TcTc = 0.3151(6) > \Delta MoMo = 0.329(4)$.

Technetium tribromide is air stable and can be kept for several years without decomposition. It is soluble in tetrahydrofuran and has been used as a precursor in the preparation of two new divalent compounds, *trans*-$TcBr_2(PMe_3)_4$ and $[Tc_2Br_4(PMe_3)_4]$.[48] The magnetic properties of $TcBr_3$ have been measured, and the compound is paramagnetic. Technetium tribromide is thermally unstable and decomposes to Tc metal and $Na\{[Tc_6Br_{12}]_2Br\}$ in a sealed tube under vacuum at 450 °C.

In Search of Technetium Dibromide. Because technetium tri- and tetrachloride decompose to $TcCl_2$, it was expected that $TcBr_2$ would result from the thermal decomposition of $TcBr_4$ and $TcBr_3$, which is not the case. Rather, $TcBr_4$ and $TcBr_3$ both decompose to $Na\{[Tc_6Br_{12}]_2Br\}$ in a sealed Pyrex tube under vacuum at 450 °C.[40] In $Na\{[Tc_6Br_{12}]_2Br$, the hexanuclear $[Tc_6Br_{12}]$ cluster exhibits a trigonal prismatic geometry and is composed of two identical parallel Tc_3Br_6 units linked by multiple Tc≡Tc bonds (Figure 10). Thermal decomposition of $TcBr_4$ and $TcBr_3$ performed in a quartz tube did not provide a crystalline product, which suggests that the source of the sodium in the compound originates from the Pyrex tube. Questions remain on whether $TcBr_2$ is accessible by thermal decomposition and whether its structure is a "naked" Tc_6Br_{12} cluster or one similar to $TcCl_2$. The formation mechanism of the various technetium bromide phases as well as their decomposition products is summarized in Figure 11.

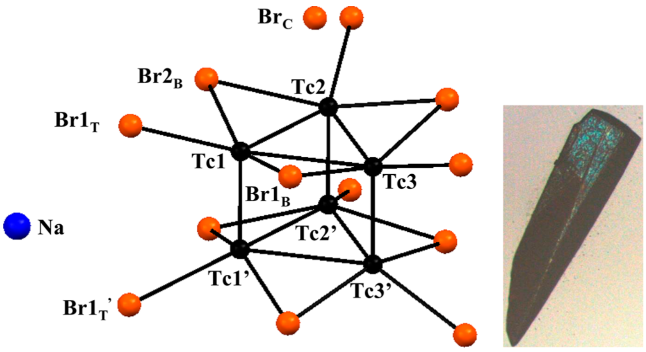


FIGURE 10. (left) Ball and stick representation of $Na\{[Tc_6Br_{12}]_2Br\}$. Color of atoms: Tc in black, Br in orange, and Na in blue. Selected distances (Å): Tc1−Tc2 = 2.6879(5); Tc1−Tc3 = 2.6735(5); Tc2−Tc3 = 2.6776(5); Tc1−Tc1′= 2.1651(5); Tc2−Tc2′ = 2.1779(5); Tc3−Tc3′= 2.1776(5); Tc1−Br1$_T$ = 2.5216(8); Tc1−Br2$_B$ = 2.4819(7); Tc1−Br$_C$ = 3.0994(4). (right) Optical image of a single crystal of $Na\{[Tc_6Br_{12}]_2Br\}$.

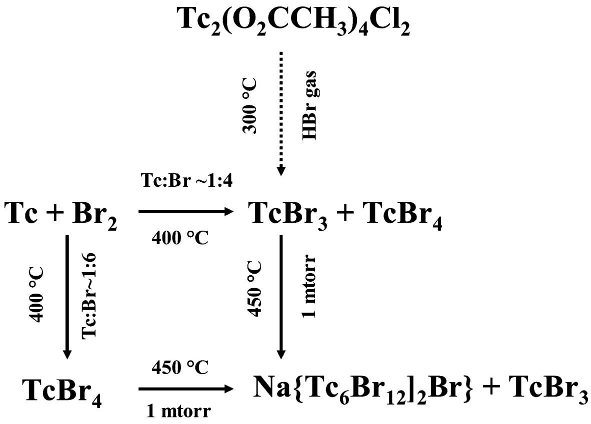


FIGURE 11. Mechanism of formation of binary technetium bromides. Solid arrow, sealed tube reaction; dotted arrow, flowing gas reaction.

Technetium Iodides

Triiodide. Technetium triiodide has been obtained by two methods: the reaction between $Tc_2(O_2CCH_3)_4Cl_2$ and flowing HI gas and the reaction between the elements in sealed tubes.[45] Concerning the first method, technetium triiodide was obtained from the reaction of $Tc_2(O_2CCH_3)_4Cl_2$ with HI at 150 and 300 °C. In the second method, the reaction of Tc metal and I_2 (Tc/I ratio, 1:3) was investigated in sealed tubes at 250 and 400 °C. The reaction products were studied by powder XRD, which revealed that no reaction occurred at 250 °C, while TcI_3 was observed after 2 weeks at 400 °C. The XRD powder pattern of TcI_3 obtained in the sealed tube reaction at 400 °C matches the one obtained from the flowing gas reactions.

The technetium triiodide powder obtained from the flowing gas reaction is semicrystalline; attempts to grow single

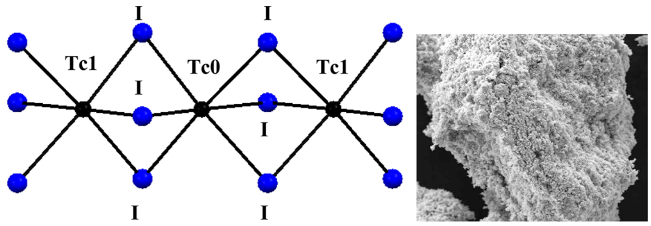


FIGURE 12. (left) Ball and stick representation of the structural motif in TcI_3. Color of atoms: Tc in black and I in blue. Selected distances (Å): Tc0−Tc1 = 3.10(3) and Tc0−I = 2.67(3). (right) SEM image of TcI_3.

crystals were unsuccessful, and the structure of TcI_3 was analyzed by extended X-ray absorption fine structure (EXAFS) spectroscopy. Our analysis of the EXAFS data on TcI_3 (Figure 12) is consistent with the presence of face-sharing TcI_6 octahedra, indicating that TcI_3 adopts the TiI_3 structure-type. Concerning Tc neighboring elements, MoI_3 and RuI_3 also exhibit the TiI_3 structure-type, while ReI_3 consists of Re_3I_9 clusters. This finding shows that the heavier halides of Tc(III) tend to mimic their Mo(III) and Ru(III) homologues.[49]

Technetium triiodide is not hydroscopic but slowly releases iodine at room temperature. It is insoluble in acetone, dichloromethane, HCl_{aq}, ether, hexane, and water. Attempts to prepare TcI_2 from the thermal decomposition of TcI_3 were unsuccessful; the decomposition of TcI_3 in a sealed tube under vacuum at 450 °C produced Tc metal.

Conclusion

Technetium binary halides can now be regarded as one the most prolific systems in transition metal binary halide chemistry. Ten phases exhibiting eight different structure-types are now known. The structure-types include a molecular solid (TcF_6), chains (TcF_5, $TcCl_4$, $TcBr_4$, $TcBr_3$, TcI_3, and α/β-$TcCl_2$), layers (β-$TcCl_3$), and bidimensional networks containing metal−halide clusters (α-$TcCl_3$). These halides can also be categorized as those having the structure of platinum tetrachloride ($TcCl_4$ and $TcBr_4$), those having the structure of its Re counterpart (TcF_6, TcF_5, and α-$TcCl_3$) or Mo/Ru (TcI_3, $TcBr_3$, and β-$TcCl_3$), and those with a new structure-type (α-$TcCl_2$ and β-$TcCl_2$). In the chloride system, the change of the electronic configuration of the metal atom from d^3 (Tc(IV)) to d^5 (Tc(II)) is accompanied by formation of metal−metal bonds in the coordination polyhedra. In the tetrahalide, there is no appreciable metal−metal interaction, a Tc═Tc double bond is observed in α/β-$TcCl_3$, and a Tc≡Tc triple bond is observed in α/β-$TcCl_2$. In the trivalent state, the heavier halides (Br and I) of technetium are isostructural to their Mo and Ru homologues. Technetium halides exhibit a rich thermo-chemistry; depending on temperature and gaseous atmosphere, they can volatilize, decompose to lower valent halides (or to the metal), disproportionate, or interconvert to another polymorph (i.e., β-$TcCl_3 \rightarrow \alpha$-$TcCl_3$).

Technetium halides will find applications as precursors in synthetic chemistry. Technetium tribromide has already been used in the preparation of new divalent complexes, and it is expected that similar complexes will be obtained from TcI_3. Rhenium and molybdenum trichlorides have been used in the synthesis of complexes with the triangular Re_3^{9+} core and in the preparation of Mo binary carbides, nitrides, or phosphides, respectively; it is expected that α-$TcCl_3$ and β-$TcCl_3$ should also lead to the formation of similar compounds. Technetium halides are also candidates for applications in the fuel cycle and for the development of Tc waste forms (i.e., $TcCl_2$); their thermal properties could potentially be utilized in separation processes via halide volatility.

Unknown binary Tc halides are certainly waiting to be discovered: those might include TcF_n ($n = 4, 7$), $TcCl_n$ ($n = 5, 6$), and $TcBr_5$. Calculations predict TcF_4[50] and TcF_7[51] to be stable; these compounds could be obtained by the methods used for the preparation of ReF_4[52] and ReF_7.[53] Technetium hexachloride, $TcCl_5$, and $TcBr_5$ could be obtained using similar synthetic routes for preparing $ReCl_6$,[54] $OsCl_5$,[55] and $ReBr_5$,[56] respectively. However, in view of the unpredictable nature of Tc halide chemistry (sometimes a mimic for Re, Mo, or Ru, or sometimes unique), it is risky to make predictions on the nature and structure of these yet-to-be-discovered compounds. It is also surprising and encouraging for chemists that new binary halides are still being discovered in the 21st century.

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BIOGRAPHICAL INFORMATION

Frederic Poineau is a research professor in the Radiochemistry Program at the University of Nevada Las Vegas (UNLV). From 2001 to 2004, he performed his doctoral studies at the laboratory Subatech (Nantes, France) on technetium chemistry. In 2005, he moved to UNLV where he conducted his postdoctoral research. His current research interests include synthesis and coordination chemistry of technetium complexes with multiple metal−metal bonds, technetium binary materials, and speciation of technetium complexes. He is also interested in the chemistry of technetium for nuclear fuel cycle applications, that is, separations and development of waste forms.

Erik V. Johnstone attended the College of Charleston from 2004 to 2009 where he received two Bachelor of Science degrees in biochemistry and chemistry. In 2009, he began graduate studies in Radiochemistry at UNLV under the supervision of Professors Kenneth R. Czerwinski, Alfred P. Sattelberger, and Frederic Poineau. The focus of his graduate thesis has been on the synthesis and characterization of binary technetium halides, which has also included studies on multiple metal−metal bonded complexes and metal alloys of transition metals and actinides.

Kenneth R. Czerwinski obtained his Ph.D. in nuclear chemistry from the University of California, Berkeley, in 1992. He was a research scientist at the Institute for Radiochemistry in Munich and then a faculty member in nuclear engineering at the Massachusetts Institute of Technology. Since 2004, he has directed the UNLV Radiochemistry Program. His current research is centered on understanding the chemical speciation and coordination of actinides and technetium compounds for exploratory and applied studies. His fundamental research focuses on coordination chemistry and evaluating electronic structure.

Alfred P. Sattelberger was educated at Rutgers College (B.A., Chemistry, 1970) and obtained a Ph.D. in Inorganic Chemistry from Indiana University in 1975. He was the recipient of an NSF Postdoctoral Fellowship at Case Western Reserve University, where he worked with Professor John P. Fackler, Jr. (1975−1977). After serving in positions in the Chemistry Department at the University of Michigan (1977−1984) and at Los Alamos National Laboratory (1984−2006), he joined Argonne National Laboratory as an Associate Laboratory Director in 2006. He holds adjunct faculty appointments in Chemistry at both UNLV and Northwestern University and his research interests include actinide and fission product chemistry.

FOOTNOTES

The authors declare no competing financial interest.

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