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A Trigonal-Prismatic Hexanuclear Technetium(II) Bromide Cluster: Solid-State Synthesis and Crystallographic and Electronic Structure

Erik V. Johnstone,*[†] Daniel J. Grant,[‡] Frederic Poineau,[†] Laura Fox,[‡] Paul M. Forster,[†] Longzou Ma,[†] Laura Gagliardi,[‡] Kenneth R. Czerwinski,[†] and Alfred P. Sattelberger[†,§]

[†]Department of Chemistry, University of Nevada—Las Vegas, Las Vegas, Nevada 89154, United States

[‡]Department of Chemistry, Supercomputing Institute and Chemical Theory Center, University of Minnesota, Minneapolis, Minnesota 55455, United States

[§]Energy Engineering and Systems Analysis Directorate, Argonne National Laboratory, Lemont, Illinois 60439, United States

Supporting Information

ABSTRACT: The compound Na{$[Tc_6Br_{12}]_2$Br} has been obtained from the decomposition of $TcBr_4$ under vacuum in a Pyrex ampule at 450 °C. The stoichiometry of the compound has been confirmed by energy-dispersive X-ray spectroscopy and its structure determined by single-crystal X-ray diffraction. The compound contains a trigonal-prismatic hexanuclear $[Tc_6Br_{12}]$ cluster. The cluster is composed of two triangular Tc_3Br_6 units linked by multiple Tc−Tc bonds. In the Tc_3Br_6 unit, the average Tc−Tc distance [2.6845(5) Å] is characteristic of Tc−Tc single bonds, while the average Tc−Tc distance between the two triangular units [2.1735(5) Å] is characteristic of Tc≡Tc triple bonds. The electronic structure of the $[Tc_6Br_{12}]$ cluster was studied by first-principles calculations, which confirm the presence of single and triple Tc−Tc bonds in the cluster.

Binary transition-metal halides exhibit a diverse array of structures and physicochemical properties relevant to fundamental and applied science.[1−3] For technetium, the lightest radioelement, the binary halide system had been studied only in a limited way prior to 2008, and only three binary technetium halides had been reported: TcF_6, TcF_5, and $TcCl_4$.[4] We have reinvestigated the chemistry of binary technetium halides and have reported five new compounds: $TcBr_4$, $TcBr_3$,[5] α/β-$TcCl_3$, and $TcCl_2$.[6−8] The discovery of these compounds has rapidly expanded the understanding of the synthetic chemistry and structural properties of technetium halides and the role of technetium chemistry in the periodicity of transition metals.

The preparation of binary technetium halides has been accomplished via a variety of synthetic strategies, including stoichiometric reactions of the metal and elemental halogen in a sealed ampule at elevated temperature, thermal decomposition of technetium chlorides under vacuum, and reactions between $Tc_2(O_2CCH_3)_4Cl_2$ and flowing HCl gas.

The stoichiometric reaction of the element with halogens in sealed ampules is quite effective, and $TcBr_3$, $TcBr_4$, $TcCl_4$, β-$TcCl_3$, and $TcCl_2$ were prepared using this method. Further work on the solid-state chemistry of $TcCl_4$ has shown that thermal decomposition under vacuum at elevated temperatures is another pathway for forming lower-valent binary chlorides (i.e., α-$TcCl_3$ and $TcCl_2$).[9] Because $TcCl_4$ and $TcBr_4$ are isomorphous and thermal decomposition of the tetrachloride produces $TcCl_2$, it was of interest to study the solid-state decomposition of $TcBr_4$ as possible precursor to unknown $TcBr_2$.

In this study, we investigated the thermal decomposition of $TcBr_4$ in sealed Pyrex ampules under vacuum at elevated temperatures and report the formation of the new hexanuclear technetium bromide cluster, Na{$[Tc_6Br_{12}]_2$Br}. The stoichiometry of the compound was confirmed by energy-dispersive X-ray (EDX) spectroscopy, and its structure was determined using single-crystal X-ray diffraction (SC-XRD). First-principle calculations, using density functional theory, DFT, were employed to better understand the structure and bonding of the trigonal prismatic hexanuclear $[Tc_6Br_{12}]$ cluster..

Technetium tetrabromide was prepared according to the method reported in the literature[5] (see the Supporting Information, SI). A small quantity (~64 mg) was placed in a Pyrex tube, and the tube was flame-sealed under vacuum, placed in a furnace, and reacted at 450 °C for 14 h. After the reaction, a dark-purple/black crystalline powder (~42 mg) was obtained in the hottest part of tube, and purple crystals (~2 mg) were observed on the surface of the tube adjacent to the powder. The product was annealed at 200 °C for an additional 3 days. Analysis of the crystals by optical and scanning electron microscopy revealed a “rail spike” shape (Figures S1 and S2 in the SI).

The powder XRD pattern of the bulk material revealed a mixture of $TcBr_3$ and technetium metal with the absence of $TcBr_4$ (see the SI). The EDX spectrum (Figure S3 in the SI) of the crystals show characteristic Na-Kα, Tc-Kα and Tc-Lα, and Br-Kα and Br-Lα lines, consistent with the presence of sodium, technetium, and bromine in the compound. A Br:Tc ratio of 2.0(3) was determined from the integrated intensities of the Tc-Kα and Tc-Lα, and Br-Kα and Br-Lα peaks.[10] Identical reactions performed in quartz tubes (absence of sodium) did not yield any crystals (see the SI). This suggests that the source of sodium in the compound originates from the Pyrex tube.[11]

A suitable crystal was picked for structural determination by SC-XRD.[12] The compound contains the trigonal-prismatic hexanuclear $[Tc_6Br_{12}]$ (Figures 1 and S4) cluster, which is capped by one Br atom. The geometry of the $[Tc_6Br_{12}]$ cluster in

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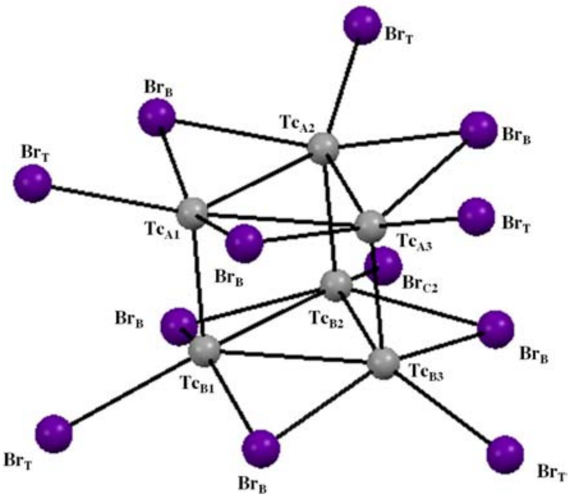

Figure 1. Ball-and-stick representation of the $[Tc_6Br_{12}]$ cluster in $Na\{[Tc_6Br_{12}]_2Br\}$. Tc atoms are in gray and Br atoms in purple. Selected distances (Å): $Tc_{A1}-Tc_{A2}$ 2.687(9), $Tc_{A2}-Tc_{A3}$ 2.667(6), $Tc_{A3}-Tc_{A1}$ 2.673(5), $Tc_{A1}-Tc_{B1}$ 2.165(1), $Tc_{A2}-Tc_{B2}$ 2.177(9), $Tc_{A3}-Tc_{B3}$ 2.177(5).

$Na\{[Tc_6Br_{12}]_2Br\}$ is similar to that found for the $[Tc_6Br_{12}]$ cluster in $(Et_4N)_2\{[Tc_6Br_{12}]Br_2\}$, the $[Tc_6Br_{12}]^-$ cluster in $(Me_4N)_3\{[Tc_6Br_{12}]Br_2\}$,[13] and the $[Re_6Br_{12}]^{2+}$ cluster in $\{[Re_6Br_{12}]Br_2\}$.[14,15] All of these clusters were prepared in an autoclave via the hydrogen reduction of $[MO_4]^-$ (M = Tc, Re) or $[TcX_6]^{2-}$ salts in concentrated HX_{aq} (X = Cl, Br) at elevated temperature.[14,16,17] To the best of our knowledge, it is the first time that a prismatic hexanuclear cluster of group VII metal has been prepared from a solid-state reaction.

The $Na\{[Tc_6Br_{12}]_2Br\}$, the $[Tc_6Br_{12}]$ cluster is composed of two identical parallel Tc_3Br_6 units linked by multiple Tc−Tc bonds. In the $[Tc_3]^{6+}$ unit, the Tc_A-Tc_A distance [av. Tc−Tc = 2.6845(5) Å] is characteristic of a Tc−Tc single bond.[18] This distance is longer than that found in the triangular $[Tc_3]^{9+}$ core in α-$TcCl_3$ [i.e., 2.444(1) Å; Tc═Tc double bond] and similar to that found (Table 1) in the $[Tc_3]^{6+}$ core of $(Et_4N)_2\{[Tc_6Br_{12}]Br_2\}$[12] [i.e., 2.66(2) Å]. The Tc_A-Tc_B distance between the Tc_3Br_6 units [av. Tc−Tc = 2.1735(5) Å] is similar to that found in the $(Et_4N)_2\{[Tc_6Br_{12}]Br_2\}$) salt [i.e., 2.188(5) Å] and is characteristic of a Tc≡Tc triple bond.[19]

Each of the Tc_3Br_6 units contains three terminal Br_T atoms [av. $Tc-Br_T$ = 2.4966(8) Å] and three bridging Br_B atoms [av. $Tc-Br_B$ = 2.4738(7) Å]. In the $[Tc_6Br_{12}]$ cluster, one of the two Tc_3Br_6 units is capped by a Br atom (Br_C). The capping Br atom lies above the center of the triangular face. The distances between the Br_C and Tc atoms of the Tc_3Br_6 unit [i.e., 3.1952(5), 3.0994(4), and 2.9636(5) Å] are significantly longer than those in other technetium(II) complexes (i.e., Tc−Br ~ 2.50−2.60 Å) and indicate that the Tc and Br atoms are coupled by a weak electrostatic interaction.[4,19−21] The distances between the Br_C atom and the three bridging Br_B atoms (i.e., 3.472, 3.482, and 3.625 Å) of the Tc_3Br_6 unit indicate that those Br atoms are in van der Waals contact (sum of the van der Waals radii = 3.70 Å).[21] The distances between Br_C and Br_T (i.e., 4.067, 4.300, and 4.447 Å) are larger than the sum of the van der Waals radii.

The environment of the $[Tc_6Br_{12}]$ cluster in $Na\{[Tc_6Br_{12}]_2Br\}$ differs from that of $[Tc_6Br_{12}]$ in $(Et_4N)_2\{[Tc_6Br_{12}]Br_2\}$. In the latter compound, both Tc_3Br_6 units are capped by Br atoms.

The packing of the $[Tc_6Br_{12}]$ cluster in $Na\{[Tc_6Br_{12}]_2Br\}$ is presented in Figure S7 in the SI. The shortest interatomic distance between the $[Tc_6Br_{12}]$ clusters (Br···Br = 3.935 Å) exceeds the sum of the bromine van der Waals radii (3.70 Å), indicating that there are no direct interactions between the $[Tc_6Br_{12}]$ clusters. The Na atoms are located in the cavities between the clusters and hexagonally coordinated to three of the terminal Br atoms between two of the clusters (Na−Br = 2.96−3.26 Å)

In comparison to $Na\{[Tc_6Br_{12}]_2Br\}$, $TcCl_2$ crystallizes as a pure binary halide and consists of infinite chains of eclipsed face-sharing $[Tc_2Cl_8]$ rectangular prisms running along the c axis. Similarly, within these $[Tc_2Cl_8]$ units, the Tc−Tc separation of 2.127(2) Å also suggests the formation of a Tc≡Tc triple bond.

In order to better understand the structure and bonding in the $[Tc_6Br_{12}]$ cluster, density functional theory (DFT) calculations were performed. The interatomic distances found by DFT in $[Tc_6Br_{12}]$ are in excellent agreement with the crystallographic data (Table 1). The largest discrepancy (0.036 Å) was found for the Tc_A-Tc_A distance in the Tc_3Br_6 unit.

The calculated Tc_A-Tc_B distance (i.e, 2.173 Å) is identical with that found by SC-XRD (2.1735 Å). The calculated $Tc-Br_T$ and $Tc-Br_B$ distances are respectively 0.018 Å shorter and 0.020 Å longer than the experimental ones. The calculated $Tc_A-Tc_A-Tc_A$, $Br_{Bri}-Tc_A-Br_{Bri}$, and $Tc_A-Br_{Bri}-Tc_{face}$ angles are within 0.5° (see Table S2 in the SI) of the crystal data.

Shortly after the structural determination of $[Tc_6Cl_{12}]^{2-}$,[22] Wheeler and Hoffman performed electronic structure calculations, revealing the "magic cluster electron count" to contain multiple metal−metal bonds that alter the preferred electron count for trigonal-prismatic clusters.[23] Employing skeletal electron pair counting rules,[24] we found that $[Tc_6Br_{12}]$ has 30 bonding electrons within the metal framework, differing from the typical magic number of 18 electrons for trigonal prisms.[25] The molecular orbital analysis reveals bonding in $[Tc_6Br_{12}]$ to be electron-rich Tc≡Tc bonds along the edge and Tc−Tc single bonds in the triangles with an overall electronic configuration of $(\sigma^{12}\pi^{10}\delta^4\delta^{*4})$.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) plots of $[Tc_6Br_{12}]$ are depicted in Figure 2. The HOMO consists of two degenerate δ^* antibonding orbitals within the edge and σ Tc−Tc bonds within the triangle. The LUMO is a three-center, two-electron (3c-2e) π^* bond on the triangular face. The predicted HOMO−LUMO

Table 1. Selected Bond Distances (Å) in the $[Tc_6Br_{12}]$ Cluster in $Na\{[Tc_6Br_{12}]_2Br\}^a$ and $(Et_4N)_2\{[Tc_6Br_{12}]Br_2\}^b$ (Experimental Values in Boldface and Calculated Values in Italics)

compound	Tc_A-Tc_A	Tc_A-Tc_B	$Tc-Br_T$	$Tc-Br_B$
$Na\{[Tc_6Br_{12}]_2Br\}$	**2.6845(5)**	**2.1735(5)**	**2.4966(8)**	**2.4738(7)**
$(Et_4N)_2\{[Tc_6Br_{12}]Br_2\}^b$	**2.66(2)**	**2.188(5)**	**2.50(1)**	**2.49(1)**
$[Tc_6Br_{12}]$	*2.720*	*2.173*	*2.479*	*2.494*

[a] Represents an average value. [b] Reference 13.

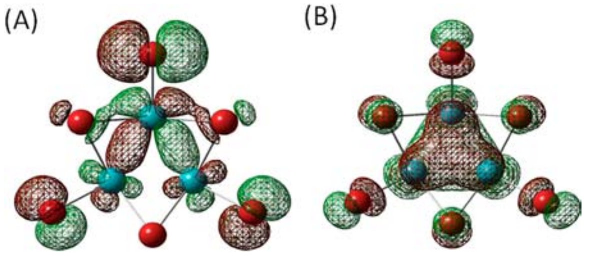

Figure 2. HOMO (A) and LUMO (B) plots of [Tc_6Br_{12}]. Color code: Tc, blue-green; Br, burgundy.

gap for the cluster is 1.281 eV. Natural bond orbital (NBO) calculations were performed to characterize the metal−metal bonding in the cluster (Figure S8 in the SI). The NBO occupancy along the edge of [Tc_6Br_{12}] is 5.4e, close to that of an ideal covalent triple bond (i.e., NBO = 6.0) and further confirms the presence of a Tc≡Tc triple bond in the cluster. The NBO occupancy along the face is 1.5e, consistent with a Tc−Tc single bond.

In summary, the compounds Na{[Tc_6Br_{12}]$_2$Br} and $TcBr_3$ were obtained from the decomposition of $TcBr_4$ under vacuum in a glass ampule. The Br:Tc stoichiometry in Na{[Tc_6Br_{12}]$_2$Br} was confirmed using EDX spectroscopy and its structure determined using SC-XRD. The compound contains the trigonal-prismatic hexanuclear [Tc_6Br_{12}] cluster. It is the first group VII trigonal-prismatic hexanuclear cluster to be synthesized from a solid-state reaction. DFT calculations have been used to investigate the geometrical and electronic structure of the [Tc_6Br_{12}] cluster. The calculated structural parameters are in excellent agreement with the experimental data. NBO analyses indicate the presence of six Tc−Tc single and three Tc≡Tc triple bonds within the [Tc_6]$^{12+}$ core. Interestingly, the decomposition of $TcBr_4$ in quartz did not yield any isolable crystals and suggests that the sodium probably derives from the glass. It is still of question whether $TcBr_2$ is achievable by thermal decomposition and whether its structure will be similar to $TcCl_2$. Current work is focused on alternative methods for the synthesis of $TcBr_2$ and the mechanism of formation of binary technetium halides.

■ ASSOCIATED CONTENT

Supporting Information

Additional synthetic details, computational chemistry, crystallographic tables, and X-ray crystallographic data in CIF format for Na{[Tc_6Br_{12}]$_2$Br}. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: erikvjohnstone@gmail.com.

Notes

The authors declare no competing financial interest.

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(10) Lighter Z elements are difficult to accurately quantify by EDX.

(11) Pyrex composition: SiO_2, 83.34%, B_2O_3, 11.19%, Na_2O, 4.08%, Al_2O_3, 1.33%, K_2O, 0.04%.

(12) Crystal data for Na{[Tc_6Br_{12}]$_2$Br}: $P\bar{1}$ [a = 9.5173(5) Å, b = 10.5233(6) Å, and c = 11.1412(6) Å; α = 3.6700(10)°, β = 73.7290(10)°, and γ = 84.844(10)°], R1 2.52%, GOF 1.079, 6456 peaks > 2σ, 175 refined parameters. Full refinement details are included in the SI.

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