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The First Complex with an M_3Te_7 Cluster Core: Synthesis and Molecular and Crystal Structure of $Cs_{4.5}[Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3(CN)_6]I_{2.5}\cdot 3H_2O$

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The coordination chemistry of molybdenum and tungsten sulfides and also selenides is well-developed with extensive descriptive chemistry and detailed spectroscopic and mechanistic investigations.[1] Studies of the corresponding tellurides are quite undeveloped and most have occurred in the last 10 years.[2] Many of the traditional reagents in sulfide/selenide chemistry, such as H_2Y or MY_4^{2-} (M = Mo, W; Y = S, Se), are not simply transferable to molybdenum/tungsten telluride chemistry.[2a] Our recent efforts therefore focused on the development of a high-temperature technique to synthesize solid-state molybdenum/tungsten tellurido halides as starting materials for the preparation of molecular complexes by extrusion. This approach has been developed for sulfur and selenium analogs. For instance, polymeric chain compounds $M_3Y_7X_2X_{4/2}$ (M = Mo, W; Y = S, Se; X = Cl, Br, I) were prepared by direct combination of the elements.[3] Procedures have been developed for the conversion of the latter into molecular complexes with $M_3(\mu_3\text{-}Y)(\mu_2\text{-}Y_2)_3^{4+}$ and $M_3(\mu_3\text{-}Y)(\mu_2\text{-}Y)_3^{4+}$ cluster cores.[4] Recently, the preparations of the first triangular cluster complexes containing Re_3S_7, V_3S_7, and also Ti_3OS_6 cores were reported.[5] There are no examples of compounds with M_3Te_7 cluster cores. The number of known solid-state molybdenum/tungsten tellurido halides is limited; examples are (i) $Mo_4Te_7X_8$ (X = Cl, Br) with $Mo_2(Te_2)_3(TeX)$ chains, (ii) $W_2O_2Te_4Br_5$ with $(WOTe_4Br)_n$ chains,[6] and (iii) octahedral cluster compounds $[Mo_6X_7Te]X_{6/2}$ (X = Cl, Br, I)[7] and $[Mo_6Te_{8-x}X_x]$ ($x = 1-3$).[8]

In this paper, we have used a simple method starting from the elements for the synthesis of tellurium-rich triangular cluster compounds of molybdenum with the $Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3^{4+}$ cluster core. The novel tellurium-rich compounds $Cs_{2.5}K_2[Mo_3Te_7(CN)_6]I_{2.5}\cdot 3H_2O$ (**1**), $Cs_3[Mo_3Te_7(CN)_6]I\cdot 3H_2O$ (**2**), and $Cs_{4.5}[Mo_3Te_7(CN)_6]I_{2.5}\cdot 3H_2O$ (**3**) were obtained by the reaction of aqueous cyanide with a solid-state product of the high-temperature reaction of molybdenum, tellurium, and iodine (Mo:Te:I = 3:7:4) at 380 °C.[9]

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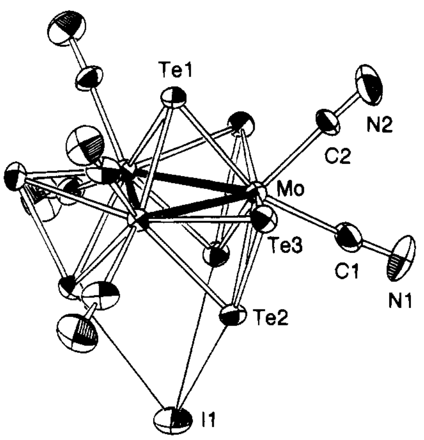

Figure 1. ORTEP drawing of the $\{[Mo_3Te_7(CN)_6]I\}^{3-}$ anion showing the atom-labeling scheme for selected atoms. All atoms are represented by 50% probability thermal ellipsoids.

The structure of **3** was determined by single-crystal X-ray diffraction.[10] The cluster anion $[Mo_3(\mu_3\text{-}Te)(\mu_2\text{-}Te_2)_3(CN)_6]^{2-}$ (Figure 1) has C_{3v} symmetry with the three Mo atoms (Mo−Mo = 2.891(2) Å) defining an equilateral triangle and with the Te(1) atom apical (Mo−Te(1) = 2.696(1) Å). Each molybdenum is coordinated by two carbon atoms of the cyanide ligands. The Te(2)−Te(3) distance of 2.688(2) Å is comparable to those of other η^2-Te_2 complexes,[11] and on the basis of Te−Te distances in Te_2 (2.59(2) Å)[12] and elemental tellurium (2.835 Å),[13] the Te−Te bond order in **3** is between 1 and 2. The three μ_2-Te_2 ligands are coordinated asymmetrically in such a way that three Te(3) atoms lie in the Mo_3 plane (equatorial position) (Mo−Te(3) = 2.816(1) and 2.806(1) Å) and three Te(2) atoms lie on the side of the Mo_3 triangule that is opposite the apical Te(1) atom (axial position) (Mo−Te(2) = 2.738(1) and 2.756(1) Å). Moreover, Te_2 ligands are strongly tilted toward the Mo_3 plane and three axial tellurium atoms form a cavity. The short contacts between axial Te(2) atoms and I(1) (Te(2)−I(1) = 3.576(1) Å) result in the formation of the ion pairs $\{[Mo_3Te_7(CN)_6]I\}^{3-}$.[14] Short contacts also take place between equatorial Te(3) atoms and I(2) (Te(3)−I(2) = 3.4995(8) Å) (supplementary Figure S1). These short contacts lead to the formation of practically linear fragments I(1)···Te(2)−Te(3)···I(2)···Te(3)−Te(2)···I(1), with angles I(1)Te(2)Te(3) = 169.32(3)°, Te(2)Te(3)I(2) = 166.76(3)°, and Te(3)I(2)Te(3) = 178.86(5)°. It is worth noting that the short contacts are realized despite the electrostatic repulsion between the anions. The Te−I distances are substantially shorter than the sum of van der Waals radii (4.35 Å).[15] These rather strong interactions play an important role in the crystal packing and lead to the formation of quasi-two-dimensional layers. The adjacent layers, formed from anionic fragments, are held together by ionic interactions with the cations. There are also rather short interlayer Te(2)−Te(2) contacts at 3.832(1) Å.

Finally, we note that comparison of the reactivities of the complexes isoelectronic and isostructural with $M_3Y_7^{4+}$ (M = Mo, W; Y = S, Se, Te) cluster cores is of considerable interest. Previous results demonstrate a tendency for the $M_3Y_4^{4+}$ (Y = S, Se) cluster compounds to form by the reaction of $M_3Y_7^{4+}$ cluster compounds with cyanide and phosphines (chalcogen-transfer reactions).[16] In contrast, the $Mo_3Te_7^{4+}$ cluster fragment demonstrates an extraordinary stability in aqueous cyanide under heating to 130 °C (in a sealed tube) or with water-soluble phosphine PR_3^{3-} (R = 3-sulfonatophenyl) and with PEt_3 (in CH_3OH).

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Supporting Information Available: Tables of structure determination data, atomic coordinates, bond distances and angles, and anisotropic thermal parameters and a figure of the structure projected onto the 100 plane (9 pages). Ordering information is given on any current masthead page.

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(9) A mixture of Mo (2.87 g; 0.030 mol), Te (9.19 g; 0.072 mol), and I_2 (5.58 g; 0.022 mol) was heated (380 °C; 96 h) in a sealed Pyrex tube. A portion (2.00 g) of the X-ray-amorphous product was added to an aqueous solution of KCN (3.0 g in 30 mL of water), and the mixture was refluxed for 3 h. After addition of CsI (2.0 g) and filtration, the solution was kept at 80 °C. During this time, the volume was decreased to 10 mL. After the mixture was allowed to stand at 20 °C for 1 day, the dark red precipitated crystals of $Cs_{2.5}K_2[Mo_3Te_7(CN)_6]I_{2.5}\cdot 3H_2O$ (**1**) were isolated by filtration and dried in air. Yield: 1.46 g (61%). Anal. Calcd for $C_6H_6N_6Cs_{2.5}I_{2.5}K_2Mo_3O_3Te_7$: C, 3.40; H, 0.29; N, 3.97; Mo, 13.58; Te, 42.15. Found: C, 3.21; H, 0.23; N, 3.75; Mo, 13.40; Te, 42.16. IR (as KBr pellet): ν(CN) 2100 cm^{-1} (s). The product has a featureless UV−vis spectrum. Addition of CsCl to the reaction solution led to the formation of $Cs_3[Mo_3Te_7(CN)_6]I\cdot 3H_2O$ (**2**). Anal. Calcd for $C_6H_6N_6Cs_3IMo_3O_3Te_7$: C, 3.76; H, 0.32; N, 4.38. Found: C, 3.75; H, 0.23; N, 4.26. The ^{125}Te NMR spectrum of **2** in D_2O contains three resonances at 114, −815, and −1816 ppm (referenced externally to $Te(OH)_6$ in H_2O). The ^{13}C spectrum contains two main resonances at 154.6 and 149.5 ppm. This is consistent with the crystal structure, which has each Mo atom coordinated by two inequivalent CN ligands, one triply bridging Te, and two different species of doubly bridging Te atoms in the molybdenum−tellurium cage. Single crystals of $Cs_{4.5}[Mo_3Te_7(CN)_6]I_{2.5}\cdot 3H_2O$ (**3**) were obtained by recrystallization of **1** from an aqueous solution of CsI at 80 °C. Anal. Calcd for $C_6H_6N_6Cs_{4.5}I_{2.5}Mo_3O_3Te_7$: C, 3.12; H, 0.26; N, 3.64; Mo, 12.48; Te, 38.73. Found: C, 3.20; H, 0.26; N, 3.46; Mo, 11.90; Te, 38.34. The salts **1**−**3** are diamagnetic and dissolve in H_2O. Use of Br_2 instead of I_2 in the reaction leads to a mixture of liquid and solid products. The latter does not react with an aqueous solution of KCN.

(10) Crystal data: $C_6H_6Cs_{4.5}I_{2.5}Mo_3N_6O_3Te_7$, $M_r = 2306.5$, space group $P3c1$, $a = 13.2952(9)$ Å, $c = 24.9053(14)$ Å, $V = 3812.5(6)$ Å^3, $Z = 4$, $D_c = 4.02$ g cm^{-3}. A Rigaku AFC-5R diffractometer with Mo Kα radiation ($\lambda = 0.7107$ Å) and a graphite monochromator was used to collect 15 794 reflections ($4 < 2\theta < 60°$) from a red prism crystal of dimensions 0.08 × 0.08 × 0.10 mm^3 at 296 K. Of these, 4184 were unique and 2730 observed ($F_o > 3\sigma(F_o)$). An empirical absorption correction based on azimithal scans of several reflections was applied. The structure was solved by direct methods and refined by full-matrix least-squares procedures with $R = 0.048$, $R_w = 0.035$.

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