The First Hexanuclear Tungsten Telluride Clusters $[W_6Te_8L_6]^{n-}$ as Amine Complexes with L = Piperidine ($n = 0$) and L = Pyridine ($n = 1$)

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The chemistry of molecular tungsten chalcogenide complexes with W_6Y_8 (Y = chalcogen atom) cluster units has attracted great interest. These compounds are closely related to the well-known molybdenum chalcogenide Chevrel phases, $M_xMo_6Y_8$, which exhibit diverse interesting physical and chemical properties, including superconductivity with high H_{c2},[1] ordered magnetic behavior,[2] fast ion conductivity,[3] and catalytic activity for hydrodesulfurization (HDS).[4] The coordination chemistry of molecular molybdenum sulfide and selenide complexes has been well-developed.[5] Also recently, the preparations of molecular tungsten analogues for both the sulfide[6] and selenide[7] complexes were reported. However, no example of the corresponding telluride molecular complexes, such as $M_6Te_8L_6$ (M = Mo, W), has been reported. Furthermore, we have become especially interested in the possible low-temperature conversion of these $W_6Y_8L_6$ complexes into the W_6Y_8 or $M_xW_6Y_8$ analogues of the Chevrel phase structure. However, this conversion has not yet been possible with the W_6S_8[8] and W_6Se_8[9] clusters. We wished to examine the W_6Te_8 complexes for this purpose with the idea that the W_6Te_8 binary compound might be more stable toward disproportionation than the W_6S_8[6a] and W_6Se_8 examples. In this paper, we report the synthesis and structures of the first two molecular telluride complexes with $M_6Te_8^-$ and M_6Te_8 (M = Mo, W) cluster cores.

These tungsten telluride complexes $[W_6Te_8(py)_6]^-$ (py = pyridine) and $W_6Te_8(pip)_6$ (pip = piperidine) were obtained by the reaction of W_6Cl_{12} with Na_2Te (W_6Cl_{12}:Na_2Te = 1:8) in pyridine and piperidine, respectively. A mixture of W_6Cl_{12} (0.150 g, 0.098 mmol), Na_2Te (0.136 g, 0.783 mmol), and 35 mL of the amine solvent was refluxed under a nitrogen flow for 3 days. The mixture was then filtered while hot, and a black solid was separated from the dark solution. Solvent was removed from the filtrate under dynamic vacuum. Single crystals of $[Na(py)_6][W_6Te_8(py)_6]\cdot py$ (**1**) or $W_6Te_8(pip)_6\cdot 6pip$ (**2**) were obtained by allowing the filtrate solution to stand at room temperature or −20 °C for several days, respectively.

The structures of **1** and **2** were determined by single-crystal X-ray diffraction.[10,11] Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with one molecule per unit cell. An ORTEP drawing of $[Na^+(py)_6][W_6Te_8(py)_6]\cdot py$ in the unit cell is shown in Figure 1. The cluster anion $[W_6Te_8(py)_6]^-$ has a slightly distorted octahedral core of six tungsten atoms with eight face-capping tellurium atoms and with one terminal pyridine molecule coordinated to each tungsten. This anion is centered on the origin of the unit cell (1a site symmetry), whereas the Na^+ cation is located at the center of the unit cell (1h site symmetry) with six pyridine molecules pseudooctahedrally coordinated to it, and one free pyridine solvent molecule is centered on the face center of the *bc* plane (1g site symmetry). In the $[W_6Te_8(py)_6]^-$ unit, the main component of the distortion of the metal octahedron is a pseudotetragonal elongation along the W(1)−W(1A) axis: the W(1)−W(1A) distance of 3.895(1) Å is longer than the other two metal−metal distances across the center of the cluster by 0.054(1) and 0.041(1) Å, respectively. This reduced complex formally has 21 electrons involved in the metal−metal bonding. The distortion may be driven by the Jahn−Teller effect resulting from the HOMO e_g^1 electron configuration and ^2E_g ground state in O_h symmetry. The average W−W and W−Te distances are 2.732(1) and 2.763(1) Å, respectively. In comparison, the neutral complex **2** has a slightly longer average W−W bond distance, 2.742(2) Å, and a slightly shorter average W−Te bond distance, 2.753(2) Å. The shortening of the W−W bond distances and the elongation of the W−Te bond distances in the reduced complex confirm that the HOMO e_g orbital is metal−metal bonding and metal−tellurium antibonding in nature. EHMO calculations[9] on this tungsten telluride compound lead to a similar conclusion. In contrast, for molybdenum clusters ($[Mo_6Y_8(PEt_3)_6]^{n-}$, Y = S or Se, n = 0 or 1),[5b] the reduced anionic complexes had slightly longer metal−metal bond distances than those of the neutral complexes, which indicated that the e_g MO's in these systems were slightly antibonding with respect to the metal−metal bonding. This

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(10) Crystal data for **1**: $C_{65}H_{65}N_{13}NaTe_8W_6$, M_r = 3175.2, space group $P\bar{1}$, a = 12.433(3) Å, b = 12.760(2) Å, c = 12.882(2) Å, α = 96.78(1)°, β = 100.03(1)°, γ = 98.58(1)°, V = 1968(1) Å^3, Z = 1, D_c = 2.679 g cm^{-3}. A Rigaku AFC6R diffractometer with Mo Kα radiation (λ = 0.710 69 Å) and a graphite monochromator was used to collect 9508 reflections (3° < 2θ < 55°, $+h,\pm k,\pm l$) at −70 °C from a dark rectangular crystal of dimensions 0.20 × 0.20 × 0.40 mm^3. Of these, 9101 were unique (R_{int} = 0.055) and 4575 were observed with $I > 4\sigma(I)$. An empirical absorption correction using the DIFABS program was applied. The structure was solved by direct methods and refined by full-matrix least-squares procedures with R = 0.034, R_w = 0.030.

(11) Crystal data for **2**: $C_{60}H_{132}N_{12}Te_8W_6$, M_r = 3145.7, space group $R\bar{3}$, a = 17.738(6) Å, c = 24.318(10) Å, V = 6638(2) Å^3, Z = 3, D_c = 2.361 g cm^{-3}. A Rigaku AFC6R diffractometer with Mo Kα radiation (λ = 0.710 69 Å) and a graphite monochromator was used to collect 3294 reflections (4° < 2θ < 45°, $\pm h,+k,\pm l$) at −70 °C from a dark chunky crystal of dimensions 0.20 × 0.30 × 0.35 mm^3. Of these, 1938 were unique (R_{int} = 0.068) and 1203 were observed with $I > 3\sigma(I)$. An empirical absorption correction using the DIFABS program was applied. The structure was solved by direct methods and refined by full-matrix least-squares procedures with R = 0.045, R_w = 0.041.

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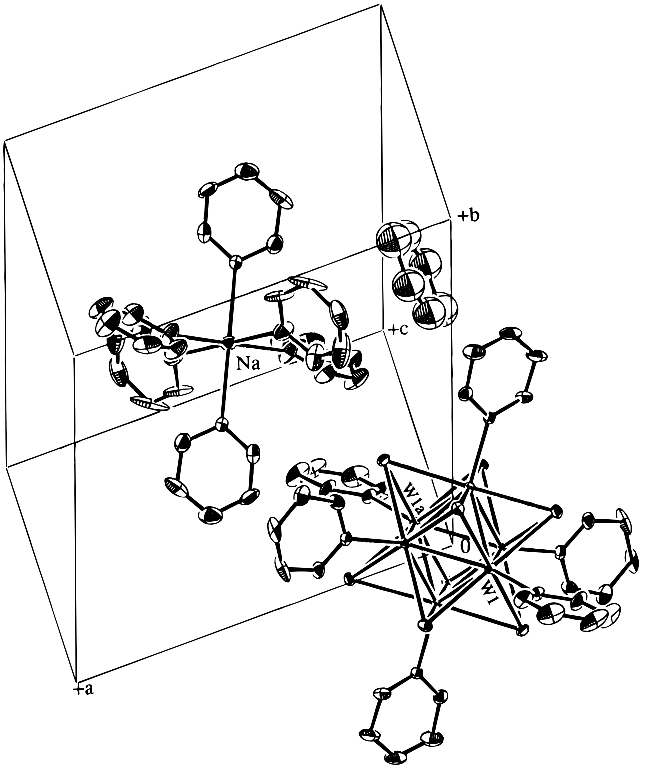

Figure 1. Unit cell of $[Na(py)_6][W_6Te_8(py)_6]\cdot py$ **(1)** depicted with thermal ellipsoids at the 35% probability level. The cation, anion, and disordered pyridine solvent molecule are each located at a center of inversion. Ranges for some important selected bond distances (Å): W−W, 2.718(1)−2.746(1); W−Te, 2.745(1)−2.777(1); W−N, 2.29(1)−2.31(1); Na−N, 2.52(2)−2.63(2).

contrasting result for the Mo_6Y_8 clusters is not accounted for in more sophisticated calculations by the DV−Xα method.[12]

It is worth noting that the W−W bond distance of 2.742(2) Å in the piperidine telluride complex **2** is much longer than those of 2.689(2) and 2.659(1) Å in the corresponding selenide and sulfide compounds,[7,9] respectively. The average trans Te−W−Te bond angle is 179.24(5)°, as compared to 176.1(1) and 173.0(1)° for the average trans Se−W−Se and S−W−S bond angles, respectively. Thus, while each tungsten atom is almost coplanar with four tellurium atoms, it resides in the interior slightly below the plane formed by these four Te atoms. However, in the selenide and sulfide cases, the tungsten atoms reside on the outside above the planes formed by the neighboring four chalcogen atoms. Both the size of the chalcogen atom and electronic effects must be involved in determining these observed structural differences among the W_6Y_8 cluster units.

In the interesting and novel $[Na(py)_6]^+$ cation unit, the average Na−N bond distance is 2.56(2) Å. The summation of the ionic radius for Na^+ and the van der Waals radius for N $[r(Na)_{ion} + r(N)_{vdW} = 0.95 + 1.55 = 2.50$ Å] produces a value that is very close to the experimental value, 2.56 Å. This suggests that the pyridine molecules are loosely bonded to the sodium cation. The $[Na(NC_5H_5)_6]^+$ cation is to our knowledge the first documented example of a sodium ion octahedrally coordinated with six pyridine molecules. The average Na−N distance of 2.56(2) Å in this cation is much longer than the Na−N distances of 2.464(4) and 2.463(5) Å in the compounds $\{[Na(py)_4]_2[Fe_2(CO)_8]\}$[13a] and $(C_5Me_5)Na(py)_3$,[13b] respectively. The overall configuration of the $Na(py)_6^+$ cation is close to that of $Fe(py)_6^{2+}$ (with T_h symmetry)[14] but very unlike that of $Ru(py)_6^{2+}$, which has no symmetry.[15] After overnight drying *in vacuo* at room temperature, the pyridine molecules associated with the sodium ion in complex **1** were lost. The recovered black powder has a formula close to $NaW_6Te_8(py)_x$ $(x = 6-7)$. An EPR spectrum of this powdered sample at 110 K showed a very broad EPR signal. Further magnetic susceptibility measurements clearly demonstrated that the material is paramagnetic.

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Supporting Information Available: Listings of complete crystallographic parameters, atomic coordinates, bond distances, bond angles, and anisotropic temperature factors, ORTEP diagrams of the anion and cation in **1**, and a packing diagram of **1** (13 pages). Ordering information is given on any current masthead page.

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