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Construction of a Novel Mo/Cu/S Cluster with a Closed Double-Cubane-like Polyhedron and a Chain Polymer of W/Cu/S Clusters

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Reaction of $[MoOS_3]^{2-}$ and $[WS_4]^{2-}$ with Cudtp (dtp = diethyl dithiophosphate) gave rise to the clusters $[Bu_4N]_2[\{MoOS_3\}_4Cu_{12}(dtp)_6]$, **1**, and $[Et_4N][\{WS_4Cu_4\}(dtp)_3]$, **2**, respectively. In cluster **1**, the dtp^- ligands act as both monodentate and bidentate ligands that bridge between Cu atoms and link together a closed double-cubane-like $[Mo_2O_2S_6Cu_6]^{2+}$ core and two incomplete cubane-like $[MoOS_3Cu_3]^+$ units. In cluster **2**, the $[WS_4Cu_4]^{2+}$ fragments were connected via bidentate and doubly bridging dtp^- bridges to give a chain polymeric anion. Cluster **1** is the first example of a Mo/Cu/S cluster that contains a closed double-cubane-like structure. Compound **2** is also rare and the first W/Cu/S polymer with dtp^- linkages.

Complexes constructed from thiomolybdates and thiotungstates with other transition metal ions have been extensively studied not only because of their relevance to biological systems but also because of the versatility of their structural types.[1−5] In addition, many of these compounds exhibit interesting properties, including semiconductivity, nonlinear optical activity, and catalytic activity.[6−8] A common synthetic strategy for the preparation of Mo(W)/Cu/S compounds is to employ neutral species CuX (X = halogen, CN, SCN), often in combination with phosphine ligands, to react with $[MO_nS_{4-n}]$ (M = Mo, W; $n = 0-2$). These reactions result in the formation of a large number of heterometallic compounds with different structural configurations such as linear, butterfly, cubane-like, and polymeric structures. Noting that the dtp^- (diethyl dithiophosphato) ligand is capable of bridging metal nuclei in different ways, we have expanded our studies of Mo(W)/Cu/S chemistry by using Cudtp to react with thiomolybdates and thiotungstates. From this reaction system, we have successfully isolated two new clusters, $[Bu_4N]_2[\{MoOS_3\}_4Cu_{12}(dtp)_6]$, **1**, and $[Et_4N][\{WS_4Cu_4\}(dtp)_3]$, **2**, in which the dtp^- ligands function as monodentate, bidentate, or doubly bridging bridges to connect the Mo(W)/Cu/S moieties.

Cluster **1** was synthesized by treatment of Cudtp with Cs_2MoOS_3 (3:1 ratio) in DMF and was isolated as the Bu_4N^+ salt. Dark-red crystals of **1** formed in 34% yield by the slow diffusion ${}^iPrOH$ into the filtered reaction mixture.[9] In the reaction of Cudtp with $[Et_4N]_2[WS_4]$ in DMF (molar ratio 2:1), the polymeric chain compound **2** was isolated as the Et_4N^+ salt. By a similar method as for **1**, orange crystals of **2** were obtained in 51% yield.[9]

Complexes **1** and **2** were characterized by X-ray crystallography.[10] The structure of **1** consists of four incomplete cubane-like $MoOS_3Cu_3$ units of which two are fused together via quadruply bridging sulfur atoms to form a closed double cubane that sits between the other two (Figure 1). The closed double-cubane-like core can be described as a ball-type polyhedron constructed from six MoS_2Cu and four CuS_2Cu quadrilateral faces, as shown in Figure 2. Each quadruply bridging S is coordinated to one Mo and three Cu atoms. Although six S−Cu bonds are relatively long [ranging from 2.562(4) to 2.646(4) Å], they are sufficiently short to be

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(9) Anal. Calcd for **1**: C 21.06, H 4.14, N 0.88. Found (%): C 21.00, H 4.01, N 0.91. Anal. Calcd for **2**: C 19.17, H 3.99, N 1.12. Found (%): C 19.44, H 4.01, N 1.25. IR (KBr pellet. cm^{-1}) for **1**: ν(Mo−O), 914, 953 vs; ν(Mo−S), 445 m. For **2**: ν(W−S), 438 m.

(10) Crystal data for **1**: $C_{56}H_{132}Cu_{12}Mo_4N_2O_{16}P_6S_{24}$, $M = 3191.14$, monoclinic, $a = 15.4043(4)$, $b = 18.1313(5)$, $c = 21.0324(4)$ Å, $\beta = 93.8440(10)°$, $U = 5861.1(2)$ Å^3, $T = 293$ K, space group $P2_1/n$, $D_c = 1.808$ g cm^{-3}, $Z = 2$, μ(Mo Kα) = 3.094 mm^{-1}, 15887 reflections measured on a Rigaku RAXIS IIc diffractometer, 7663 were unique and 4376 [$I > 2\sigma(I)$] were used to refine the structure. The final R was 0.0653 and R_w was 0.1580. For **2**: $C_{20}H_{50}Cu_4NO_6P_3S_{10}W$, $M = 1252.13$, monoclinic, $a = 7.682(3)$, $b = 21.914(9)$, $c = 25.581(11)$ Å, $\beta = 92.698(4)°$, $U = 4302(3)$ Å^3, $T = 293$ K, space group $P2_1/n$, $D_c = 1.933$ g cm^{-3}, $Z = 4$, μ(Mo Kα) = 5.239 mm^{-1}, 20977 reflections measured on a Rigaku RAXIS IIc diffractometer, 5627 were unique and 4259 [$I > 2\sigma(I)$] were used to refine the structure. The final R was 0.0724, and R_w was 0.1541.

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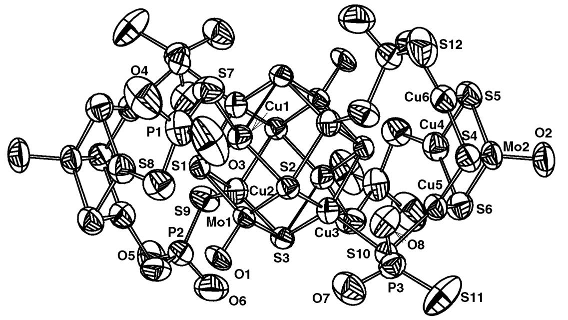

Figure 1. Molecular structure of the cluster anion of **1**, showing 50% thermal ellipsoids. The Et groups are omitted for clarity. Selected bond distances (Å) and angles (deg): Mo(1)−Cu(1), 2.719(2); Mo(1)−Cu(2), 2.728(2); Mo(1)−Cu(3), 2.720(2); Mo(2)−Cu(4), 2.662(3); Mo(2)−Cu(5), 2.653(3); Mo(2)−Cu(6), 2.672(3); Mo−S (avg), 2.273; Cu−μ3-S (avg), 2.246; Cu−μ_4-S, 2.296(4)−2.646(4); Cu−S(dtp), 2.196(5)−2.315(4); Cu(5)−S(10)−Cu(3), 99.19(15); S−P−S, 116.4(3)−119.3(3). Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y + 1$, $-z + 1$.

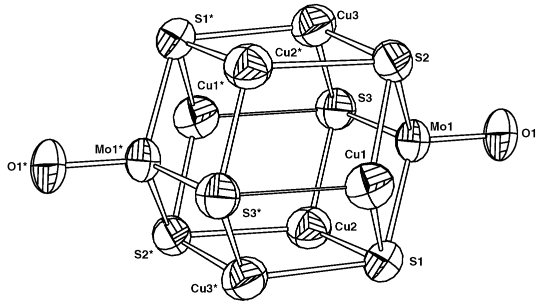

Figure 2. ORTEP drawing of the closed double-cubane-like core of **1**.

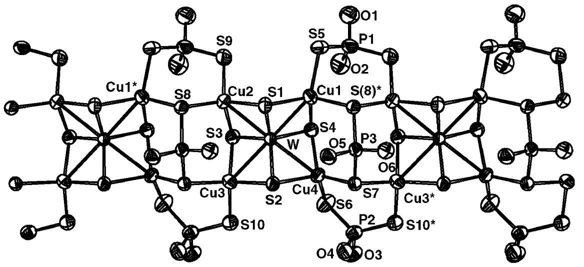

Figure 3. Molecular structure of the polymeric anion of **2**, showing 50% thermal ellipsoids. The Et groups are omitted for clarity. Selected bond distances (Å) and angles (°): W−Cu(1), 2.707(2); W−Cu(2), 2.753(2); W−Cu(3), 2.731(2); W−Cu(4), 2.741(2); W−S (avg), 2.228; Cu−S(WS_4) (avg) 2.321; Cu−S(dtp) (avg), 2.346; Cu(2)−S(8)−Cu(1)*, 102.46(16); Cu(4)−S(7)−Cu(3)*, 100.37(16); S(9)−P(1)−S(5), 119.9(3); S(6)−P(2)−S(10)*, 120.9(3); S(7)−P(3)−S(8)*, 121.7(2). Symmetry transformations used to generate equivalent atoms: #1 $x - 1$, y, z; #2 $x + 1$, y, z.

considered as bonding. For the known Mo(W)/S/Cu clusters with double-cubane-like structures, the two incomplete cubane-like fragments are usually linked via thiolato, halogen anions and SCN^- bridging ligands.[11−13] Therefore, cluster **1** is the first example of a Mo/Cu/S cluster that contains a closed double-cubane-like structure. The six bridging dtp^- ligands are of two types: four of them connect Cu atoms via two S atoms, and the other two use only one S atom, leaving the other one uncoordinated. In the latter coordination mode, the P−S bond distance for the nonbonded sulfur is significantly shorter than that of the sulfur bonded to copper [1.905(7) vs. 2.012(6) Å]. Such a coordination mode of the dtp^- ligand is not commonly observed.[14] Comparing the single incomplete cubane-like $[MoOS_3Cu_3]^+$ core and the closed $\{[MoOS_3Cu_3]_2\}^{2+}$ polyhedron, one can see that the average Mo−Cu distance for the former is slightly shorter than that for the latter (2.662 vs. 2.722 Å). This provides evidence that bond distances for the three-coordinate Cu are somewhat shorter than those for the four-coordinate Cu. Moreover, there are weak interactions between Cu atoms (avg 2.907 Å) in the double-cubane polyhedron that are comparable to those found in $[Cu_8(\mu_8\text{-}S)\{S_2P(OC_2H_5)_2\}_6]$.[15]

A structure determination shows that complex **2** is composed of polymeric chains of $[WS_4Cu_4(dtp)_3]^-$ anions. A portion of the single-chain structure is shown in Figure 3. The W atom displays an approximately tetrahedral coordination to four sulfur atoms. Four edges of this WS_4 tetrahedron are bridged by Cu atoms with W•••Cu distances ranging from 2.707(2) to 2.753(2) Å. Four essentially coplanar Cu atoms are also bonded to the WS_4 core, with the Cu−S bond lengths in the range 2.298(4)−2.348(4) Å. Each Cu adopts a distorted tetrahedral geometry (coordinated by two S^{2-} from tetrathiotungstate and two S^- from different dtp^- ligands). Three dtp^- ligands bridge between WS_4Cu_4 units to form an infinite chain. Two coordination types of dtp^- ligands are observed: two of them serve as a bidentate bridge connecting two Cu atoms of adjacent WS_4Cu_4 fragments, whereas the other acts as a doubly bridging ligand to bridge four Cu atoms. Examples of complexes containing doubly bridging dtp^- ligands are rare.[15] Although a number of polymeric W/Cu/S complexes with thiocyanates or halogen anions have been reported previously,[16,17] involvement of all dtp^- ligands as bridges has no precedent. The incorporation of dithiolato moieties such as dithiocarbamate (dtc) to the W/Cu/S system has been reported. However, the dtc^- ligands acted as either a chelating or a bidentate ligand to coordinate to Cu atoms, and no polymers were obtained.[18] It is therefore possible that, by taking advantage of the versatile coordination modes of dtp^-, more polymeric complexes with different structures can be obtained from this reaction system.

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Supporting Information Available: Crystallographic data for compounds **1** and **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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