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Synthesis of $[Mo_4S_6(SH)_2(PMe_3)_6]$ and $[Mo_6S_{10}(SH)_2(PEt_3)_6]$ Consisting of Fused $Mo_3(\mu_3\text{-}S)$ Cluster Units

Kiyoshi Tsuge, Hideo Imoto, and Taro Saito*

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

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In order to build extended metal clusters, empty coordination sites must be generated for new metal–metal bondings. The abstraction of a sulfur atom by trialkylphosphine from the S_2 ligand in $(NH_4)_2[Mo_3S(S_2)_6]$ (**1**)[1] may be a candidate for such a reaction to prepare larger molybdenum sulfide clusters. However, as having been reported in the previous communication, the reaction of **1** with trimethylphosphine gave unexpectedly a reduced trinuclear cluster complex $[Mo_3S_5(PMe_3)_6]$ with a bicapped Mo_3 triangle core.[2] In the subsequent study of the reactions of **1** with trialkylphosphines, we have found that extended clusters also can be formed by the two-step reactions. The products reported here have been found to contain raft-type cluster units, which are structurally related to those found in the solid compounds, especially in the reduced molybdenum oxides. Such a structural relation between the molecular and the solid cluster compounds is one of the recent topics in cluster chemistry.[3]

The reaction of a solution of **1** in butylamine with trimethylphosphine in THF at room temperature gave a brown precipitate. Refluxing the mixture of this precipitate with trimethylphosphine in THF yielded a black solution, and the filtered solution was left at room temperature to yield a tetranuclear cluster complex $[Mo_4S_6(SH)_2(PMe_3)_6]$ (**2**) (yield 14%) as a black crystalline material. Similarly the treatment of **1** with triethylphosphine in THF produced a black precipitate, and the reaction of the precipitate with triethylphosphine in THF gave a black hexanuclear complex $[Mo_6S_{10}(SH)_2(PEt_3)_6]$ (**3**) (yield 11%).

The X-ray structure analysis[4] of **2** has shown that the cluster contains four molybdenum atoms arranged in a rhombus (a flat butterfly) geometry (Figure 1). The structure of the whole molecule is very close to C_{2h} symmetry with a 2-fold axis passing through the hinge molybdenum atoms. The two Mo_3 triangles are capped by a sulfur ligand, and the capping atoms are on the opposite sides of the Mo_4 plane. Each of the four peripheral Mo–Mo edges of the Mo_4 rhombus is bridged by a sulfur atom. Thus, the molecule has an arrangement in which two Mo_3S_3 units are fused along one edge. The molybdenum atoms at the wing-tip positions are bound to a trimethylphosphine and a SH ligand (ν(SH) 2516 cm^{-1}) with a Mo–S distane of 2.41 Å which is close to the reported Mo–SH distances.[5] It has a deformed trigonal bipyramidal coordination sphere. The hinge molybdenum atom is octahedrally coordinated with two trimethylphosphine ligands together with four sulfur atoms.

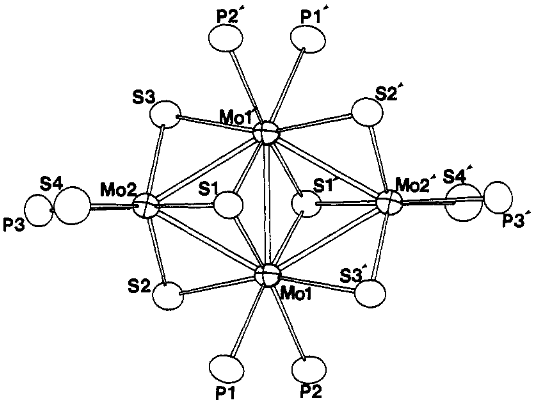

Figure 1. ORTEP drawing of $[Mo_4S_6(SH)_2(PMe_3)_6]$ (**2**). The molecule has a crystallographically imposed inversion center. Selected bond distances (Å) are as follows: Mo1–Mo1' = 2.845 (1), Mo1–Mo2 = 2.825 (1), Mo1–Mo2' = 2.825 (1), Mo1–S1 = 2.369 (2), Mo1–S1' = 2.368 (2), Mo1–S2 = 2.430 (2), Mo1–S3' = 2.437 (2), Mo2–S1 = 2.394 (2), Mo2–S2 = 2.269 (2), Mo2–S3 = 2.260 (2), Mo2–S4 = 2.410 (2), Mo1–P1 = 2.595 (2), Mo1–P2 = 2.601 (2), Mo2–P3 = 2.508 (2).

The average oxidation state of the molybdenum atoms in **2** is +3.50, and there are 10 cluster valence electrons to form five Mo–Mo bonds. Since the Mo–Mo distances are in a narrow range (2.83–2.85 Å), it is reasonable to assign a pair of electrons for each Mo–Mo bond (an electron-precise cluster[6]). This leads to the assignment of the oxidation number of +3 to the hinge

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(4) Crystallographic details for **2** and **3** are as follow. The intensity data were collected by a Rigaku AFC-5R diffractometer with Mo Kα radiation at 298 K for **2** and at 295 K for **3**. In the crystal structure analyses, the positions of the molybdenum atoms were determined by direct methods and the Patterson method (SHELXS86), and other non-hydrogen atoms were located on the Fourier maps (SHELX76). The full-matrix refinements were performed with programs SHELXS76 and ANYBLK. Crystallographic data are as follow. **2**: space group $P2_1/n$ with α = 11.374 (2) Å, b = 14.103 (2) Å, c = 16.227 (2) Å, β = 104.77 (2)°, V = 2516.8 (5) Å^3, Z = 2, R = 0.053, and R_w = 0.024 for 3735 reflections ($|F_o| > 3\sigma(|F_o|)$; $2\theta < 55°$). **3**: space group $P\bar{1}$ with a = 12.529 (3) Å, b = 13.661 (4) Å, c = 12.464 (5) Å, α = 109.47 (3)°, β = 107.13 (2)°, γ = 69.16 (2)°, V = 1841.8 (10) Å^3, Z = 1, R = 0.066, and R_w = 0.043 for 6117 reflections ($|F_o| > 4\sigma(|F_o|)$; $2\theta < 60°$).

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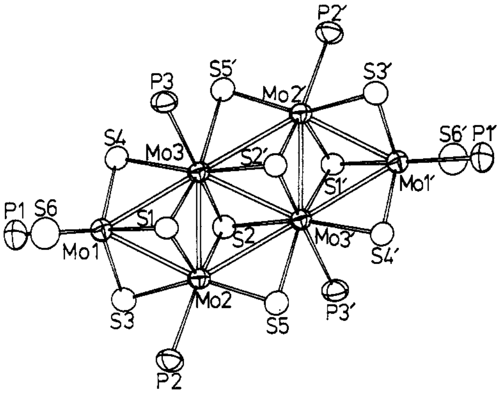

Figure 2. ORTEP drawing of [Mo$_6$S$_{10}$(SH)$_2$(PEt$_3$)$_6$] (**3**). The molecule has a crystallographically imposed inversion center. Selected bond distances (Å) are as follows: Mo1–Mo2 = 2.818 (2), Mo1–Mo3 = 2.908 (2), Mo2–Mo3' = 3.057 (2), Mo2–Mo3 = 2.733 (2), Mo3–Mo3' = 2.948 (2), Mo1–S1 = 2.385 (4), Mo1–S3 = 2.284 (4), Mo1–S4 = 2.227 (4), Mo1–S6 = 2.379 (5), Mo2–S1 = 2.294 (4), Mo2–S2 = 2.365 (4), Mo2–S3 = 2.392 (4), Mo$_2$–S5 = 2.250 (4), Mo3–S1 = 2.358 (4), Mo3–S2 = 2.412 (4), Mo3–S2' = 2.418 (4), Mo3–S4 = 2.452 (4), Mo3–S5' = 2.554 (4), Mo1–P1 = 2.558 (5), Mo2–P2 = 2.621 (4), Mo3–P3 = 2.672 (4).

atoms having three Mo–Mo bonds and +4 to the wing-tip atoms having two Mo–Mo bonds.

This assignment is consistent with the coordination geometries of the hinge and wing-tip molybdenum atoms. The atomic orbitals used for the Mo–Mo bonding in **2** must be those which are extended toward the edges of the coordination polyhedron because the neighboring molybdenum atoms are in those directions. The hinge atom in the octahedral environment has three such d orbitals (t_{2g} orbitals), and it can make three Mo–Mo bonds. On the other hand, the wing-tip molybdenum atom in the trigonal-bipyramidal environment has just two low-lying d orbitals, and it can accommodate only two d electrons for the Mo–Mo bondings. A tetranuclear niobium cluster compound [Nb$_4$Cl$_{10}$(PMe$_3$)$_6$] has also 10 cluster valence electrons that form five Nb–Nb bonds.[7] However, all niobium atoms are octahedrally coordinated.

The structure of **3** determined by X-ray structure analysis[4] is shown in Figure 2. The six molybdenum atoms in the molecule are in a raft geometry where four Mo$_3$ triangles are aligned linearly sharing their edges. The positions of the molybdenum atoms are not exactly on a plane. Due to the inversion symmetry, the two terminal triangles are on the parallel planes and the distance between the planes is 0.46 Å. Each Mo$_3$ triangle is capped by a sulfur ligand, and each peripheral Mo–Mo edge is bridged also by a sulfur ligand. These capping and bridging atoms form two close-packing layers, and the molybdenum atoms are between them. The central molybdenum atom (Mo3) is octahedrally coordinated. While Mo1 has a deformed trigonal-bipyramidal coordination with an axis of S1–P1, the coordination geometry of the Mo2 atom is intermediate between trigonal-bipyramidal (axis S2–P2) and square-pyramidal (top S1). The cluster **3** also has two SH ligands bonded with Mo1 (ν(SH) 2497 cm^{-1}; Mo–S = 2.38 Å).

The average oxidation number of molybdenum in **3** is +3.67, and there are 14 cluster valence electrons, which are 4 electrons short of the "electron-precise" cluster if we regard the cluster as having nine Mo–Mo bonds. Since the distances between the molybdenum atoms are scattered over a wide range (2.73–3.06 Å), it is difficult to assign a simple bond order like 1 or 0.5 to each Mo–Mo bond. The Mo–S distances also deviate over a wide range (2.23–2.39 Å). These irregularities of the bond distances must be the reflection of the complex electronic structure of this molecule. However, it is possible to make a simplified picture of the bonding between the molybdenum atoms if we neglect the bonds longer than 3 Å (Mo3–Mo2' = 3.06 Å). Then there are seven Mo–Mo bonds for 14 electrons, and the cluster can be regarded electron precise. The neglected weak bonding between Mo3 and Mo2' may modify this picture so that the opposite Mo1–Mo3 bond becomes longer (2.91 Å) because they share the same molybdenum d orbital. In a similar way discussed for **2**, the oxidation number of +3 is assigned to the central molybdenum atoms (Mo3 and Mo3') and +4 for other molybdenum atoms. The molybdenum atom in the +3 oxidation state is again in the octahedral environment.

It is not clear right now how the tetranuclear cluster is formed from a trinuclear cluster. On the other hand, it is tempting to assume that the hexanuclear cluster **3** is produced by reductive dimerization of the triangular cluster **1**. If this is the case, the reaction is a rare example of a horizontal condensation of M$_3$ units in contrast to the vertical one to form octahedral cluster complexes.[8,9]

The raft-type framework is not common in the nonmolecular sulfide clusters.[3] However, CsNb$_4$Cl$_{11}$[10] and Ba$_{1.13}$Mo$_8$O$_{16}$[11] have tetranuclear raft cluster units similar to that of **2**, and the molybdenum oxide NaMo$_2$O$_4$[12] has an infinitely extended raft cluster of molybdenum atoms with the oxidation number of +3.5. The last compound suggests that the extension of the raft structure beyond that of compound **3** is structurally possible.

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Supplementary Material Available: Listings of crystallographic data, atomic parameters, anisotropic thermal parameters, and bond distances and angles (Table SI–SVII) (14 pages). Ordering information is given on any current masthead page.

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