Synthesis of a Molybdenum Cluster Complex $[Mo_{12}(\mu_3\text{-}S)_{14}(\mu_4\text{-}S)_2(PEt_3)_{10}]$ with Chevrel Phase Type Intercluster Bondings

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The reaction of $[Mo_6S_8(PEt_3)_6]$ with elemental sulfur in toluene at reflux temperature formed a dodecanuclear cluster complex $[Mo_{12}S_{16}(PEt_3)_{10}]$ with the Chevrel phase type intercluster bonding.

The chemistry of octahedral cluster complexes with chalcogenide ligands has been studied in relation to the superconducting Chevrel phases $M_xMo_6E_8$ (M = Cu, Sn, Pb, La, etc.; x = 0 - 4; E = S, Se, Te).[1-4] The Chevrel type solid state compounds are known only for molybdenum in spite of intensive efforts to prepare the analogues of other metals, especially of chromium and tungsten.[5-6] One of the most intriguing problems in the studies of the Chevrel compounds is whether the intercluster electronic and magnetic communications between the Mo_6E_8 cluster units are transmitted through the Mo-Mo or Mo-μ_4-E intercluster bondings which are considered to be responsible for the unique superconductivity.[7] If molecular cluster complexes composed of the octahedral M_6E_8 cluster units linked together with the intercluster bondings are prepared, the intercluster interactions in the solid Chevrel compounds will be understood more clearly. As the smallest cluster complexes to meet the requirement, three M_{12} molecular cluster compounds composed of two M_6E_8 cluster units (M = Co, Cr, Re) linked by M_2E_2 bridges have been reported. The cobalt complex $[Co_{12}S_{16}(PEt_3)_{10}](TCNQ)_2$ was obtained as a byproduct in the synthesis of $[Co_6S_8(PEt_3)_6](TCNQ)$.[8] The chromium complex $[Cr_{12}S_{16}(PEt_3)_{10}]$ was prepared by the removal of one of six triethylphosphines in $[Cr_6S_8(PEt_3)_6]$ by elemental sulfur.[9] The rhenium complex was synthesized by the thermal dimerization of $[Re_6Se_8(PEt_3)_5(CH_3CN)]$ which took place by the loss of coordinated acetonitrile.[10] The present communication describes the synthesis and structure of the first dodecanuclear cluster complex of molybdenum in which the linking mode is similar to those in the Chevrel phases.

After the reaction of $[Mo_6S_8(PEt_3)_6]$ **1**[11] with sulfur in toluene at reflux temperature for 6 h, toluene was removed and the residue was washed with acetone and extracted with hexane. Hexane was removed under reduced pressure and the residue was dissolved in chloroform and chromatographed on a Sephadex LH-20 column. The first brown band was collected, ethanol was added and the solution was left standing for 5 days to form dark brown crystals in 8% yield. The elemental analysis agreed with the formula $[Mo_{12}S_{16}(PEt_3)_{10}]$ **2**. UV-Vis (toluene, λ/nm (ε/M^{-1}cm^{-1})); 492 (8400), 744 (1390), 1017 (1910), 1210 (sh).

The structure was determined by the single crystal X-ray crystallography.[12] Figure 1 shows the ORTEP drawing of the structure of **2** with selected interatomic distances. The dodecanuclear cluster complex comprises two octahedral cluster units $[Mo_6S_8(PEt_3)_5]$ linked by two μ_4-S-Mo bondings. The Mo-Mo distances in each monomeric cluster unit range from 2.642 Å to 2.694 Å and the cluster shape is somewhat distorted from a regular octahedron but the average distance 2.665 Å is almost the same with that (2.663 Å) of the starting compound **1** which has a very regular octahedral structure.[11] Negligible elongation in the mean Mo-Mo distance indicates that there is little intercluster Mo-Mo bonding interaction in **2** with the same number (20 e$^-$) of metal cluster electrons for each octahedral unit as that in **1**. The bond order of n = 0.05 calculated for the intercluster Mo-Mo by using the Pauling's equation[13] $d(n) = d(1) - 0.6 \log n$, where $d(n)$ = 3.419 Å and $d(1)$ = 2.619 Å, also suggests that the direct bonding interaction between the molybdenum atoms is insignificant. It is interesting to compare the Mo-Mo distance 3.419 Å with the corresponding one 3.084 Å in the solid state Chevrel compound Mo_6S_8 which has elongated intracluster Mo-Mo bondings (2.698 Å - 2.862 Å).[4]

The visible spectrum of **2** shows an extra weak and broad band centered at 744 nm and the shift of the band at 991 nm in **1** to 1017 nm, but otherwise the spectral features are similar to those of **1** suggesting that the electronic states of the cluster do not change remarkably upon dimerization.

The dodecanuclear cluster complexes, $[Co_{12}S_{16}(PEt_3)_{10}]^{2+}$,[8] $[Cr_{12}S_{16}(PEt_3)_{10}]$,[9] $[Re_{12}Se_{16}(PEt_3)_{10}]^{4+}$,[10] and $[Mo_{12}S_{16}(PEt_3)_{10}]$ **2** demonstrate an interesting variation of the intercluster M-M distances. The cobalt cluster has a short intercluster Co-Co distance (2.64 Å), and the chromium one has a longer Cr-Cr

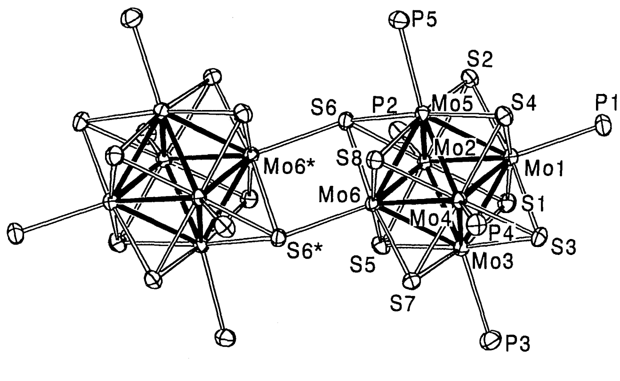

Figure 1. ORTEP drawing of $[Mo_{12}S_{16}(PEt_3)_{10}]$ **2**. Ethyl groups are omitted for clarity. Selected interatomic distances are: Mo3-Mo6 2.642(1) Å; Mo2-Mo5 2.694(2) Å; Mo6-Mo6* 3.419(2) Å; Mo1-S3 2.447(3) Å; Mo1-S4 2.448(3) Å; Mo6-S6 2.486(3) Å; Mo6-S6* 2.554(3) Å; Mo1-P1 2.537(3) Å; Mo5-P5 2.561(3) Å.

distance (2.95Å). The rhenium and molybdenum clusters have a much longer M-M distance (3.42 Å) indicating essentially no bonding interaction. As previously discussed by Saito,[1] these distances are related to the position of the bridging metal atom above the E_4 plane of the four surrounding chalcogen atoms, and to the μ_4-E-M distance. In the cobalt and chromium clusters, the bridging metal atoms protrude from the S_4 plane but in the rhenium and molybdenum clusters, they are almost on the E_4 plane reflecting the strong M-M bonding interaction within the octahedral cluster units.[11] The μ_4-S-M distances (M = Co, 2.148 Å; M = Cr, 2.373 Å) are shorter than the μ_4-E-M distances (M = Re, E = Se, 2.638 Å; M = Mo, E = S, 2.554 Å). These two geometrical features make necessarily the intercluster M-M distances of the rhenium and molybdenum clusters longer than those of the cobalt and chromium clusters. The antiferromagnetic coupling interaction between the paramagnetic centers in the octahedral cobalt and chromium clusters should exert additional influence upon shortening of the intercluster distances as discussed by Mealli.[14]

This seems to be also the case in the solid state Chevrel phases with different chalcogen atoms and with different oxidation states (and thus different magnetism). For example, the intercluster Mo-Mo distance in Mo_6Te_8 (3.674 Å) is much longer than that in the isoelectronic Mo_6S_8 (3.084 Å), and a 22 e^- cluster $SnMo_6S_8$ (3.232 Å) and a 23 e^- cluster $LaMo_6S_8$ (3.238 Å) have almost equal distances,[4] suggesting the importance of the geometric positions of molybdenum and chalcogen atoms to determine the intercluster distances.

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12 Crystal data for $[Mo_{12}S_{16}(PEt_3)_{10}].3CHCl_3$: formula $C_{63}H_{153}Cl_9Mo_{12}P_{10}S_{16}$, fw = 3204.0, space group $P\bar{1}$, a = 14.859(5) Å, b = 15.868(4) Å, c = 14.200(7) Å, α = 100.58(3)°, β = 117.58(3)°, γ = 79.53(2)°, V = 2899(1) Å^3, Z = 1, D_{calcd} = 1.84 g/cm^3, R = 0.056, R_w = 0.045 for 9016 observed reflections ($|F_o| > 4\sigma(|F_o|)$; $6° < 2\theta < 60°$). The intensity data were collected by a Rigaku AFC7R diffractometer with MoKα (λ = 0.71069 Å) radiation at 173 K. The intensity data were corrected for Lorentz-polarizatiion and absorption. In the crystal structure determination, the positions of molybdenum were determined by Patterson method,[15] and other non-hydrogen atoms were located on Fourier maps. The full-matrix refinements were performed with the teXsan programs.[15] Two kinds of chloroform molecules were found in the structure, both of which were disordered in two sites. The non-hydrogen atoms except for those of the solvent molecule were refined anisotropically. Hydrogen atoms were not included in the refinements.

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