A Novel Dodecanuclear Mo–Cu Cluster Derived from $[Mo_2S_2(edt)_2(\mu\text{-}S)_2]^{2-}$ as a Metalloligand: Preparation and Structure of $[Mo_6(edt)_4(\mu\text{-}edt)_2(\mu_3\text{-}S)_{12}Cu_6(\mu\text{-}dppe)_2]\cdot 2DMF\cdot C_6H_{14}$ (edt = $^-SC_2H_4S^-$)

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A novel dodecanuclear Mo–Cu cluster $[Mo_6(edt)_4(\mu\text{-}edt)_2(\mu_3\text{-}S)_{12}Cu_6(\mu\text{-}dppe)_2]\cdot 2DMF\cdot C_6H_{14}$ was synthesized by the reaction of $[Et_4N]_2[Mo_2S_2(edt)_2(\mu\text{-}S)_2]$ ($edtH_2$ = 1,2-ethanedithio) and $[Cu(MeCN)_4][ClO_4]$ in the presence of bidentate phosphine ligand 1,2-bis(diphenylphosphino)ethane (dppe). The molecular structure consists of one edt-linked double cubane and one single cubane which are linked by two bridging dppe ligands.

The synthesis, reactivity, and structures of high-nuclearity transition metal–sulfido clusters have been attracting much attention owing to their relevance to biological systems[1] and rich structural variations.[2] Of great interest are homo- and heterometallic cubane-type sulfido clusters because of their possible importance in industrial hydrodesulfurization catalysis.[3] Notable examples are typical Fe_4S_4 and $MoFe_3S_4$ cubane clusters as models of the active sites nitrogenase.[4] It is also interesting to note that the MCu_3S_4 and MAg_3S_4 (M = Mo and W) cubane clusters possess strong nonlinear optical absorption along with large optical limiting effects.[5] In the past two decades, a number of mixed metal–sulfido clusters have been successfully isolated by a unit-construction method that uses reactive fragments as building blocks, of which the sulfide-bridged dinuclear complexes containing M_2S_4 cores (M = Mo and W) have received much attention as precursors for the synthesis of mixed-metal clusters containing incomplete $M_2M'S_4$ cubane and complete $M_2M'_2S_4$ cubane cores (M′ = Cu, Ag, Pt, Pd, and Ir).[6,7] In the course of our research on the synthesis of high-nuclearity metal–sulfido clusters, we are interested in $[Mo_2S_2(edt)_2(\mu\text{-}S)_2]^{2-}$ (edt = $^-SC_2H_4S^-$)[8] as a metalloligand to bind metal ions in the presence of the bridging ligands. A novel dodecanuclear cluster $[Mo_6(edt)_4(\mu\text{-}edt)_2(\mu_3\text{-}S)_{12}Cu_6(\mu\text{-}dppe)_2]\cdot 2DMF\cdot C_6H_{14}$ was isolated therefore. In this paper, we report the synthesis and structural characterization of the title cluster compound.

To 5 mL of $[Et_4N]_2[Mo_2S_2(edt)_2(\mu\text{-}S)_2]$ (91 mg, 0.12 mmol) DMF solution was added a solution of $[Cu(MeCN)_4][ClO_4]$ (245 mg, 0.75 mmol) and dppe (150 mg, 0.38 mmol) in CH_2Cl_2 (10 mL), a brown solution formed immediately. After the mixture was stirred for 45 min, little black precipitates were filtered off. The clear brown-red filtrate was carefully layered with hexane to harvest dark red block crystals, suitable for single-crystal X-ray structural determination, in a yield of 74% (based on Mo) after three days. The dinuclear molybdenum compound $[Et_4N]_2[Mo_2S_2(edt)_2(\mu\text{-}S)_2]$ has two terminal and two μ-bridging sulfido ligands and four active sulfur atoms from the two edt moieties. In the present reaction, the $Mo_2S_2(\mu\text{-}S)_2$ core is bound to two copper atoms to form a typical cubane fragment, whereas sulfur-participated coordination of two edt moieties further resulted in formation of an edt-linked double cubane fragment. Two fragments are linked by two bridging dppe ligands to give dodecanuclear Mo–Cu cluster $[Mo_6(edt)_4(\mu\text{-}edt)_2(\mu_3\text{-}S)_{12}Cu_6(\mu\text{-}dppe)_2]$ with sulfide-bridged dinuclear Mo_2S_4 cores.

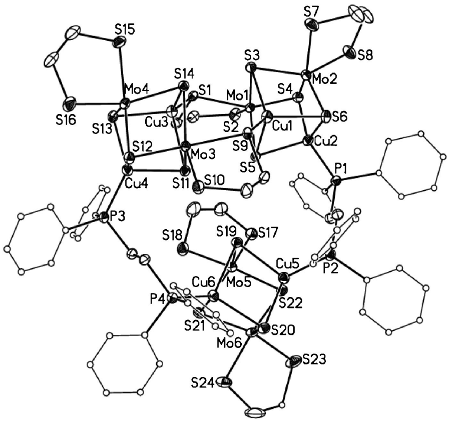

Figure 1. A perspective view of $[Mo_6(edt)_4(\mu\text{-}edt)_2(\mu_3\text{-}S)_{12}Cu_6(\mu\text{-}dppe)_2]$ with the ellipsoids drawn at 40% probability level.

The structure of the title cluster was confirmed by an X-ray diffraction study.[9] The structure consists of one well-separated neutral $[Mo_6(edt)_4(\mu\text{-}edt)_2(\mu_3\text{-}S)_{12}Cu_6(\mu\text{-}dppe)_2]$ cluster molecule shown in Figure 1, two DMF, and one disorder hexane solvents, which is supported by satisfactory microanalytical results.[10] The peak at 1641 cm^{-1} for $\nu(C{=}O)$ in the IR spectrum indicates the presence of DMF in the title cluster. The characteristic bands at 517 cm^{-1} for $\nu(Mo{=}S)$ and 466 cm^{-1} for $\nu(Mo\text{–}\mu\text{-}S)$ of the precursor $[Et_4N]_2[Mo_2S_2(edt)_2(\mu\text{-}S)_2]$[8] are replaced by a medium strength band at 504 cm^{-1} and a weaker band at 475 cm^{-1} in the IR spectrum of the title cluster. The cluster molecule contains one single cubane $[Mo_2(edt)_2(\mu_3\text{-}S)_4Cu_2]$ and one edt-linked double cubane $[Mo_4(edt)_2(\mu\text{-}edt)_2(\mu_3\text{-}S)_8Cu_4]$ which are linked by two bridging dppe ligands. The formal oxidation states for each Mo and Cu of the title cluster remain +5 and +1, respectively. The single cubane fragment contains one $[Mo_2(edt)_2(\mu_3\text{-}S)_4]$ moiety and two copper atoms. The $Mo_2S_4Cu_2$ cubane core is closely related to those found in $[Mo_2(edt)_2(\mu_3\text{-}S)_4(CuPPh_3)_2]$,[11] $[Mo_2(dtc)_2(\mu_3\text{-}S)_4(CuBr)_2]$,[12] and $[Mo_2(dtc)_2(\mu_3\text{-}S)_4M'_2(cod)_2]$ (M = Pd, Pt, Rh, and Ir).[7] The edt-linked double cubane fragment contains two single cubane $[Mo_2(edt)_2(\mu_3\text{-}S)_4Cu_2]$ linked by two unprecedented

Mo(μ-edt)Cu bridges.[13] Although related sulfur-linked double cubane thiobimetallic clusters such as $[Et_4N]_4[Mo_2Fe_6S_8(S\text{-}p\text{-}C_6H_4Cl)_6(cat)_2]$ and $[Et_4N]_4[Mo_2Fe_6S_8(SEt)_6(Pr_2cat)_2]$ (cat = catecholate) have been previously reported by Holm and co-workers,[14] the present edt-linked double cubane is the first example of a molybdenum–copper–sulfur cluster with dinuclear complex $[Mo_2S_2(edt)_2(\mu\text{-}S)_2]$ unit as a building block.

The coordination geometry at the Mo centers remains nearly tetragonal-pyramidal: the angles range from 77.20(5) to 149.65(6)°. The angles around Cu atoms range from 93.90(5) to 124.33(5)°, suggesting that the coordination geometry of the Cu atoms is highly distorted tetrahedral. The variety from terminal sulfur in the staring $[Et_4N]_2[Mo_2S_2(edt)_2(\mu\text{-}S)_2]$ (av. Mo=S: 2.101(4) Å)[8] to bridging μ_3-sulfido in the title cluster makes slight elongation of Mo–S bond lengths (av Mo–μ_3-S: 2.200(1) Å). The Cu–S bond lengths similarly fall into three categories: the average bond length of the copper atoms to those terminal sulfur atoms is 2.3955(14) Å, the average bond length of the copper atoms to those μ_2-sulfur atoms of original $[Mo_2S_2(\mu\text{-}S)_2]$ cores is 2.2735(14) Å, and the average bond length of the copper atoms to μ_3-sulfur atoms (S1 and S9) of edt moieties is 2.2228(13) Å. By comparison of normal Mo–S(edt) bonds, obvious elongation of two Mo–μ_3-S(edt) bonds (Mo(1)–S(1) = 2.4272(13) Å and Mo(3)–S(9) = 2.4505(13) Å) is due to the sulfur-participated coordination to copper atoms in the title cluster. The average Mo–Cu and Mo–Mo distances in the title cluster are 2.8001(7) and 2.8571(6) Å, respectively, which are comparable to the according values in $[Mo_2(edt)_2(\mu_3\text{-}S)_4(CuPPh_3)_2]$ (2.813(1) and 2.8576(7) Å).[11] The average Cu–P bond distance of 2.2134(14) Å in the title cluster is normal and also compares excellently with those in other related clusters.[11,15] It is interesting to note that two subcubanes in the edt-linked double cubane are joined by the bridges Mo(1)–S(1)–Cu(3) (111.08(5)°) and Mo(3)–S(9)–Cu(1) (109.96(5)°) with the specified angles. These six atoms (Mo(1), S(1), Cu(3), Mo(3), S(9), and Cu(1)) are approximately coplanar with a maximum deviation of 0.23 Å from the least-squares plane. This character is also found in Mo–Fe–S cluster $[Et_4N]_4[Mo_2Fe_6S_8(S\text{-}p\text{-}C_6H_4Cl)_6(cat)_2]$ with sulfur-linked double cubane structure.[14]

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9 Crystal data: crystal dimensions $0.21 \times 0.16 \times 0.10\,\text{mm}^3$, $C_{64}H_{72}N_2O_2P_4S_{24}Mo_6Cu_6$, $M_r = 2923.78$, monoclinic, space group $P\bar{1}$, $a = 16.8816(4)$, $b = 17.2053(4)$, $c = 19.7613(5)$ Å, $\alpha = 81.255(1)$, $\beta = 83.295(1)$, $\gamma = 71.486(1)°$, $V = 5365.0(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.810\,\text{g·cm}^{-3}$, $\mu = 2.406\,\text{mm}^{-1}$, $2\theta_{max} = 55.42°$, Mo Kα radiation ($\lambda = 0.71073$ Å), $T = 293$ K, $R1 = 0.0428$, $wR2 = 0.1047$, and $S = 1.021$ for 24769 independent reflections with $I \geq 2.0\sigma(I)$ and 1042 variables.

10 Anal. Found: C, 30.9; H, 3.38; N, 0.91%. Calcd for $C_{64}H_{72}P_4S_{24}Mo_6Cu_6{\cdot}2(C_3H_7NO){\cdot}(C_6H_{14})$: C, 31.2; H, 3.45; N, 0.96%. IR (KBr disc, cm^{-1}): ν(C=O) 1641 (vs), ν(Mo=S) 504 (s), ν(Mo–μ-S) 475 (m). UV–vis (CH_2Cl_2) λ_{max}, nm: 318, 496.

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