Mixed-Metal Clusters

Metal Clusters as Ligands: Substitution of Fe ions in Fe/Mo/S Clusters by Thiophilic Cu^I Ions To Give Clusters with $[Cu_4Mo_2Fe_2S_8]^{4+}$ and $[Cu_5Mo_3Fe_4S_{11}]^{6+}$ Cores**

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The edge-fused double cubanes $[(Cl_4\text{-cat})_2(PR_3)_2Mo_2Fe_8S_8(L')_4]$ (**1**; Cl_4-cat = tetrachlorocatecholate dianion) contain the $Mo_2Fe_6S_8$ core and have been obtained with various terminal ligands on the Fe atoms ($L' = PR_3$,[1] BH_4^-,[2] Cl^-,[3] and N^{3-}[3]). More recently analogues of these clusters with tris(pyrazolyl) borate as a molybdenum-bound terminal ligand also have been reported.[4] The exceptional reactivity of **1** and its pronounced tendency to undergo core rearrangement has made possible the synthesis of various derivative clusters that are relevant as partial analogues for the FeMo-cofactor[5] or the P-clusters of nitrogenase.[6]

Herein we report on the reaction of $[(Cl_4\text{-cat})_2Mo_2Fe_8(PnPr_3)_6]$ (**2**; Figure 1), with $[Cu(CH_3CN)_4]^+$ ions and the subsequent substitution of for iron centers by for copper

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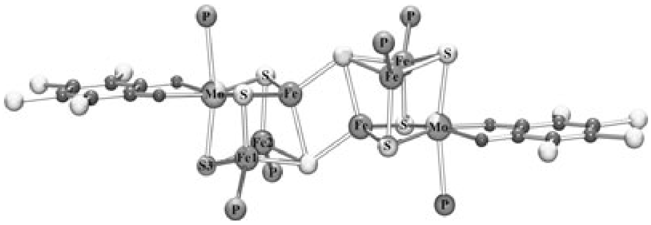

Figure 1. Structure of **2**. The carbon and hydrogen atoms of the propyl groups of the phosphine ligands are omitted for clarity.

centers to give a structure that retains the basic, edge-fused, M_8S_8 cubane structure and contains three different metal ions in three different coordination geometries. The reaction of **2** with $[Cu(CH_3CN)_4]^+$ in a CH_2Cl_2/CH_3CN solution at low temperature (−40 °C) affords the cluster $[(Cl_4\text{-cat})_2Mo_2Cu_4Fe_2S_8(PnPr_3)_4]$ (**3**), in 65 % yield.[7] A byproduct of this reaction has been isolated and crystallographically characterized as a rather complex but unique cluster with the formulation $[(Cl_4\text{-cat})_3Mo_3Cu_4Fe_5S_{11}(PnPr_3)_7(pyr)]$ (**4**; pyr = pyridine). These products are the first two examples of heterotrimetallic-sulfur compounds that have a cubane-like structure. Compounds that contain Mo/Fe/Cu and S atoms are rare and the only two examples known are the linear $(Et_4N)_2[(PPh_3)_2CuS_2MoS_2FeS_2Cl_2]$[8] and a $[CuS_2MoS_2Cu]^{2+}$ complex[9] that coordinates through the copper atoms to a diphenylphosphinoferrocene ligand.

The structure of **3**[10] was determined (Figure 2) and can be described in terms of a ferredoxin-type $[Fe_2S_2]^{2+}$ center bound

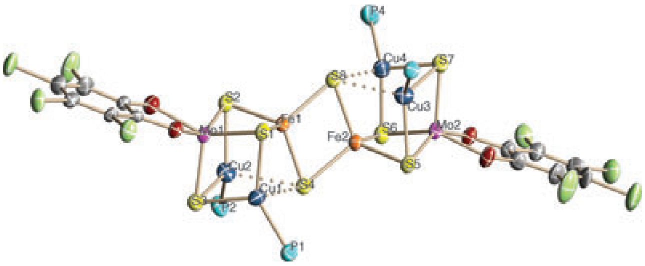

Figure 2. ORTEP diagram of **3** (thermal ellipsoids set at 50 % probability). The carbon and hydrogen atoms of the propyl groups of the phosphine ligands are omitted for clarity.

by two $\{(R_3PCu^I)_2Mo(Cl_4\text{-cat})S_3\}$ units. These units contain MoS_3Cu_2 cores structurally similar to those found in the $[Cu_3Cl_3MoS_3O]^{2-}$[11] and $[Cu_3(NCS)_3MoS_3O]^{2-}$[12] clusters. The Cu^I sites in the $\{(R_3PCu^I)_2Mo(Cl_4\text{-cat})S_3\}$ units are three-coordinate, distorted pyramidal (one of them (Cu1) is almost trigonal planar, deviating from planarity by $\Delta\Phi_{eq} = 4.6°$),[13] and only weakly interact with the μ_2-S ligands in the $[Fe_2S_2]^{2+}$ center. The intercubane Fe1–Fe2 separation in **3**, at 2.630 Å, is not much different than that of **2**, at 2.645 Å. There is a distinct shortening of the Fe–S separations by almost 0.1 Å on average.[14] Specifically, the separations Fe1–S8 (2.198 Å), Fe1–S4 (2.250 Å), Fe2–S8 (2.261 Å), and Fe2–S4 (2.197 Å) in **3** give $Fe\text{–}S_{av} = 2.226$ Å. The corresponding separations in cluster **2** (Fe–S4 and Fe–S8) are 2.379 Å, and 2.268 Å and give $Fe\text{–}S_{av} = 2.324$ Å. These $Fe\text{–}S_{av}$ separation in **3** is comparable albeit slightly longer than that found for the $[Fe_2S_2Cl_4]^{2-}$ dimer[15] at 2.200 Å.

In **3** the molybdenum atoms are five-coordinate rather than six-coordinate as in **2** and the $MoFeCu_2S_4$ cuboidal subunits are "opened-up" in **3** whereas the $MoFe_3S_4$ subunits in **2** are "closed". The axial and mean equatorial Mo–S bonds in **3** at 2.227 Å and 2.325 Å, respectively, are not very similar to those in either the $[(S_4)_2Mo^{IV}S]^{2-}$ complex[16] (2.128(1) Å, 2.359 Å) or the $S{=}Mo^V(S_4)$ unit in the $[Mo_2S_{10}]^{2-}$ ion[17] (2.123 Å, 2.413 Å).

An assignment of the +4 oxidation state to the molybdenum atoms in **3** leads to the unrealistic electronic description $[Mo^{IV}Cu^I_4Fe^{IV}_2S_8]^{4+}$. With Mo^V, the description $[Mo^V\text{-}Cu^I_4Fe^{III}_2S_8]^{4+}$ appears more satisfactory. The magnetic properties of **3** (μ_{eff}^{corr}: 4.91 μ_B, 300 K; 1.01 μ_B, 4.2 K (H = 5000 G)) suggest antiferromagnetic coupling between the two Fe^{III} ions. It appears that the substitution of the iron atoms by copper atoms in compound **2** results in the removal of the axial bound phosphine unit of the molybdenum atom with a concomitant oxidation of the molybdenum atom from +3 to +5.

The μ_3-S3–Mo separation in **2** (2.397 Å) is shortened to 2.230 Å when the μ_3-S3 ligand assumes the role of an axial ligand in the square-pyramidal Mo^V in **3**. This change is accompanied by an increase in the Fe1,2–S4 separation in **2** (2.250 Å and 2.267 Å) to separations in **3** (Cu1,2–S4 and Cu3,4? no Cu5,6–S8) that are nearly non-bonding and range from 2.562 Å to 2.726 Å. The Cu1–Cu2 and Cu3–Cu4 separations in **3** at 3.106(1) Å and 3.131(1) Å, respectively, are much longer than the corresponding Fe–Fe separations in **2** (2.631(1) Å).

The THF/hexanes filtrate collected during the isolation of **3** was kept and after removal of the solvents under a N_2 stream part of the resulting black material was extracted with diethyl ether. Slow evaporation of the solvent resulted in the formation of a few milligrams of single crystals that were structurally, characterized as **4**.[18]

The X-Ray crystal structure revealed[19] a cluster with unprecedented features (Figure 3). The structure is best described when it is separated into two fragments. The first fragment exhibits an unusual $[MoCuFe_2S_4]$ "cubane" like core that is depicted in Figure 4. The molybdenum retains its original coordination environment with one phosphine, one Cl_4-catecholate, and three μ_3-S ligands. The copper atom again has an almost trigonal planar coordination environment ($\Delta\Phi_{eq}$ 6.1°, $Cu\text{–}S_{ax}$ 2.591 Å) with one phosphine and 2 μ_3-S ligands. The two Fe atoms are distorted tetrahedral and one (Fe1) has only a sulfur coordination environment (with two μ_3-S and μ_4-S ligands (S1, S2, and S4 in Figure 3)) while the other (Fe2) has three S ligands with its coordination completed by a pyridine atom.

The second fragment (with a $[Mo_2Cu_2Fe_3S_6]$ core) is best described as the edge fusion (along an Fe–S edge (Fe3–S5)) of a sulfur voided $[MoCuFe_2S_3]$ cuboidal subunit with a $[MoCuFe_2S_4]$ cubane where the Fe–S edge is shared (Figure 5). The molybdenum atoms have the same coordination environment as the previous fragment. The two copper centers have also almost trigonal planar coordination environments ($\Delta\Phi_{eq}$ 5.4°, $\Delta\Phi_{eq}$ 7.8°, with $Cu\text{–}S_{ax}$ of 2.924 Å and 2.723 Å). The two fragments shown in Figure 4 and Figure 5,

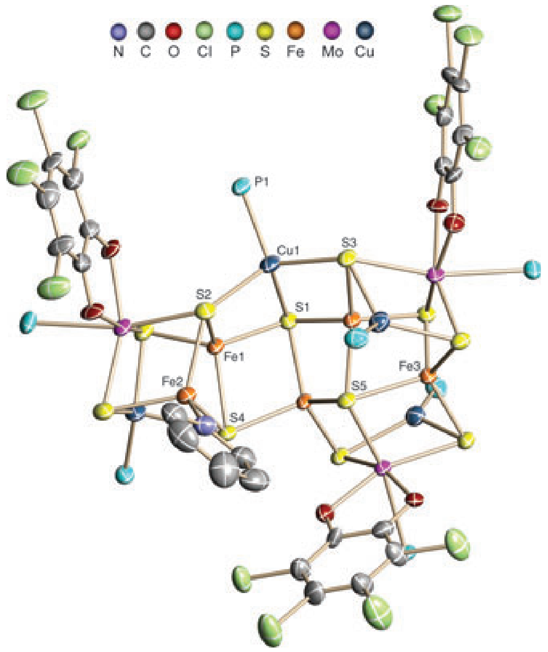

Figure 3. ORTEP diagram of the [(Cl$_4$-cat)$_3$Mo$_3$Cu$_4$Fe$_5$S$_{11}$(P*n*Pr$_3$)$_7$(pyr)] cluster **4** (thermal ellipsoids set at 50% probability). The carbon and the hydrogen atoms of the *n*Pr groups of the phosphine ligands are omitted for clarity.

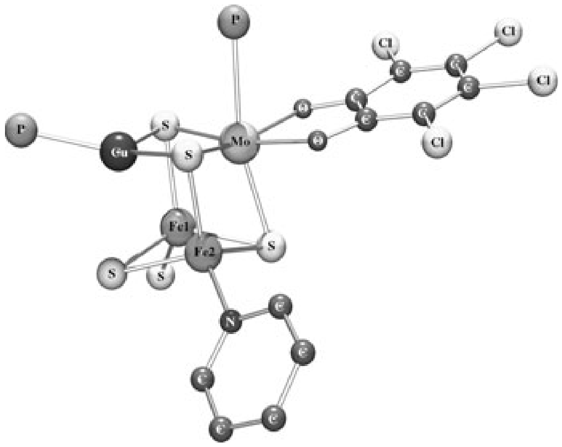

Figure 4. Schematic representation of the {MoCuFe$_2$S$_4$} fragment of cluster **4**.

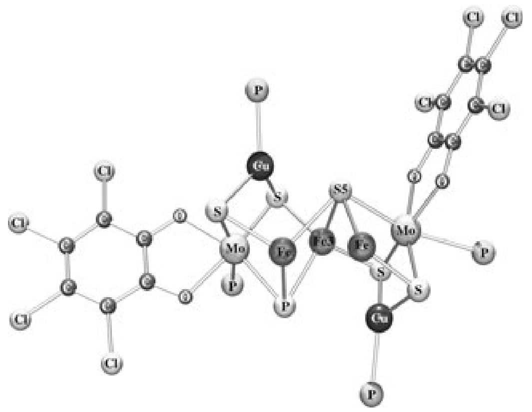

Figure 5. Schematic representation of the {Mo$_2$Cu$_2$Fe$_3$S$_6$} fragment of cluster **4**.

are connected through a μ$_4$-S ligand (S1 in Figure 3) and a CuP*n*Pr$_3$ unit (Cu1,P1). In the CuP*n*Pr$_3$ unit the copper atom has a distorted tetrahedral coordination environment and is coordinated by 3 μ$_4$-S ligands (S1, S2, S3; Figure 3) however, the Cu–S separations at 2.411, 2.435, and 2.437 Å are unusually long, and indicate weak bonding.

Mo/Fe/S and Mo/Cu/S clusters have been extensively studied over the past years; the Mo/Fe/S clusters, mainly because of their relevance to the FeMo cofactor of nitrogenase,[20] the Mo/Cu/S clusters because of their optical properties and their potential importance in the sequestering and regulation of copper in biological systems.[21] The reactivity of Mo/Fe/S clusters prompt us to the exploration of their reactions with monomeric copper complexes. Our studies have led to the discovery of a new class of trimetallic sulfur compounds.

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[7] For the synthesis of **3** see Supporting Information. Elemental analysis (%) calcd for **3**: C 29.61, H 4.35; found: C 29.82, H 4.42. FT-IR (KBr): $\tilde{\nu}$ = 2958(s), 2928(s), 28699(s), 1419(vs), 989(s), 812(s), 789(s), 575(s), 555(m), 443 cm^{-1} (m). ^{1}H NMR (CD$_2$Cl$_2$): δ = 1.08 (C*H*$_3$-CH$_2$-CH$_2$-P), 1.64 (CH$_3$-C*H*$_2$-CH$_2$-P), 2.18 (CH$_3$-CH$_2$-C*H*$_2$-P). Cyclic voltammetry (CH$_2$Cl$_2$) shows two reversible reduction process at −1.07 V and −0.64 V and one irreversible oxidation at 1.15 V (experiments were carried out with Pt working and Ag/AgCl reference electrodes with 0.1 M of *n*Bu$_4$NPF$_6$ electrolyte and the redox potentials are reported versus the saturated calomel electrode (SCE). Electron microprobe analysis for both **3** and **4** (The University of Michigan Electron Microbeam Analysis Laboratory) confirmed the ratio of Mo/Fe/Cu/S thus supporting the assignment based on crystallographic and chemical criteria (phosphine should bind preferentially to Cu^{I} since Cu^{I} is more electron rich than Fe^{III}).

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[10] a) Suitable crystals for X-ray structure determination were isolated from THF/hexanes at −23 °C. Diffraction data were collected on a Bruker SMART CCD-based X-ray diffractometer equipped with an LT-2 low-temperature device and normal focus Mo-target X-ray tube ($\lambda = 0.71073$ A) operated at 150(2) K, at the University of Michigan X-ray facility ($2\theta_{max} = 44.22$). The space group ($P2(1)/c$, monoclinic) was determined based on systematic absences and intensity statistics. A successful direct-methods solution was calculated using the software package SHELXTL v.6.1 that revealed the locations of most non-hydrogen atoms. Several full-matrix least-squares refinements followed by difference Fourier calculations were performed using SHELXTL, which located the remainder of the non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal-displacement parameters unless stated otherwise. All hydrogen atoms were placed in ideal positions and refined as riding atoms with individual isotropic thermal-displacement parameters. From the 51 518 reflections that were collected, 9884 were independent while the number of parameters was 746. The data were processed with SADABS for absorption correction. Cell dimensions $a = 20.525(4)$, $b = 19.832(4)$, $c = 19.928(4)$ Å with $\beta = 96.630(4)°$, $V = 8057(3)$ Å^3. Full-matrix least-squares refinement based on F^2 converged to an $R1$ [$I > 2\sigma$] value of 0.0524 and a wR2 value of 0.1173, GOF 0.999; b) CCDC-255596 (**3**) and CCDC-255597 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[13] We define $\Delta\Phi_{eq}$ as: $\Delta\Phi_{eq} = 360 - \Sigma\Phi_{eq}$, where $\Sigma\Phi_{eq}$ is the sum of the angles in the triangular base to which the longest Cu–S separation (Cu–S_{ax}) is normal. The $\Delta\Phi_{eq}$ values for the other three atoms are for 9.2° (Cu2), 15.9° (Cu3), and 20.3° (Cu4). These values increase as the Cu–S_{ax} separations for the corresponding copper centers decrease: Cu1–S4 (2.728 Å), Cu2–S4 (2.648 Å), Cu3–S8 (2.565 Å), and Cu4–S8 (2.560 Å).

[14] Owing to the lack of good structural data for compound **2**, [$(Cl_4$-cat$)_2Mo_2Fe_6S_8(PnBu_3)_6$] has been used for the comparison of the two structures. Compounds [(Cl4-cat)$_2Mo_2Fe_6S_8(PR_3)_6$] (were R = Et, *n*Pr, and *n*Bu) have identical core structures and exhibit minimal differences in bond lengths.

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[18] Elemental analysis (%) calcd for **4**·2$(CH_3)_2O$, $C_{91}H_{172}Cl_{12}Cu_4Fe_5Mo_3NO_9P_7S_{11}$: C 33.73, H 5.35, N 0.43; found: C 33.86, H 5.47, N 0.38.

[19] Crystals suitable for X-ray diffraction were grown for compound **3** from a diethyl ether solution at −30 °C. Data were collected at 150 K, ($2\theta_{max} = 48.2$). The space group ($P\bar{1}$, triclinic) was determined based on systematic absences and intensity statistics. From the 52 838 reflections that were collected, 23 685 were independent while the number of parameters was 1377. Cell dimensions are $a = 15.906(3)$, $b = 19.922(4)$, $c = 24.978(5)$ Å, with $\alpha = 87.11(3)$, $\beta = 71.89(3)$ $\gamma = 89.15(3)°$ and the volume is $V = 7513(3)$ Å^3. Full-matrix least-squares refinement based on F^2 converged to an $R1$ [$I > 2\sigma$] value of 0.0677 and a $wR2$ value of 0.1776, GOF 0.993.[10b]

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