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Metal Clusters as Ligands. Substitution of Fe Ions in Fe/Mo/S Clusters by Thiophilic Cu^I Ions

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The reactivity of Fe/S and Fe/Mo/S clusters, similar or analogous to those occurring in biological systems, with thiophilic metal ions has not been explored. In this Communication, we demonstrate that synthesis of heteropolynuclear clusters with different coordination geometries for different metals at different sites is possible by metal substitution or by metal addition reactions. The two clusters we report herein ($[(Cl_4\text{-cat})_2Mo_2Cu_5Fe_4S_9(P^nPr_3)_7(SP^nPr_3)_2]PF_6$ and $[(Cl_4\text{-cat})_2Mo_2Cu_6Fe_4S_{10}(P^nPr_3)_8]$) contain Fe, Mo, and Cu, which display pseudotetrahedral, pseudooctahedral, and pseudotrigonal geometries, respectively. The synthesis of these clusters is achieved by the addition of appropriate amounts of $[Cu(CH_3CN)_4]^+$ to $[(Cl_4\text{-cat})_2Mo_2Fe_8(P^nPr_3)_6]$. The formation of the different products is temperature- and solvent-dependent. The Cu^I units incorporated into the metal cluster framework, either bind to available lone pairs of the already bridging S ligands or displace the less thiophilic Fe atoms. Among the essential features of these new molecules are recognizable Fe/S fragments including an Fe_6S_9 core in the first cluster and the pentlandite $Fe_4Cu_4S_6$ core in the second cluster.

The synthesis, structures, and reactivity of high-nuclearity Mo/Fe/S clusters have received particular attention and have been fields of intense research. This interest is due to the apparent involvement of such clusters in biological dinitrogen fixation[1,2] and their possible importance in hydrodesulfurization catalysis.[3] Clusters with the $MoFe_3S_4$[4,5] and $MoFe_3S_3$[6] cuboidal subunits are known and have contributed significantly to fundamentally important chemistry relevant to that of the FeMoS center in nitrogenase. The edge-fused double cubanes $[(Cl_4\text{-cat})_2Mo_2Fe_8S_8(PR_3)_6]$ (**1**;[7] Cl_4-cat = tetrachlorocatecholate dianion) are derivatives of the $MoFe_3S_4$ cubanes and contain the $Mo_2Fe_6S_8$ core. These clusters display exceptional reactivity, and numerous derivatives have been obtained and structurally characterized.[6,8−10] Recently, we reported on the reactions of Mo/Fe/S clusters toward thiophilic metals. These reactions lead to the incorporation of Cu atoms in the Fe/Mo/S cluster. The unique trimetallic clusters $[(Cl_4\text{-cat})_2Mo_2Cu_4Fe_2S_8(P^nPr_3)_4]$ (**2**) and $[(Cl_4\text{-cat})_3Mo_3Cu_4Fe_5S_{11}(P^nPr_3)_7(pyr)]$ (**3**; pyr = pyridine) contain Fe^{III}, Mo^V or Mo^{III}, and Cu^I atoms that have pseudotetrahedral, pseudooctahedral, and pseudotrigonal geometries, respectively.[11]

In this paper, we report on the synthesis and structure of two new FeCuMoS clusters with unique and unprecedented structures. The reaction of **1** with $[Cu(CH_3CN)_4]^+$ in a mixture of THF and acetonitrile at high temperatures (90 °C) leads to the formation of $[(Cl_4\text{-cat})_2Mo_2Cu_5Fe_4S_9(P^nPr_3)_7(SP^nPr_3)_2]PF_6$ (**4**),[12] whereas the reaction of **1** with $[Cu(CH_3CN)_4]^+$ also in a mixture of THF and acetonitrile but in the presence of H_2O afforded the cluster $[(Cl_4\text{-cat})_2Mo_2Cu_6Fe_4S_{10}(P^nPr_3)_8]$ (**5**). Black crystals of **4**, and **5**, suitable for single-crystal X-ray structural determination were successfully isolated by the slow evaporation of ether solutions of these compounds at −25 °C.[13] The differences in the topology and structure in **4** and **5** indicate complex inter- and intramolecular pathways that depend on the temperature and solvent. The mechanism for the formation of all of these MoFeCuS clusters at present is not clear but remains the focus of investigation in our laboratory.

The structure of **4** (Figure 1) reveals a rather complex cluster containing three different metal atoms with diverse

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(1) (a) Einsle, O.; Tezcan, F. A.; Andrade, S. L. A.; Schmid, B.; Yoshida, M.; Howard, J. B.; Rees, D. C. *Science* **2002**, *297*, 1696. (b) Kim, J.; Rees, D. C. *Science* **1992**, *257*, 1677.

(2) (a) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965. (b) Burgess, B. K.; Lowe, D. J. *Chem. Rev.* **1996**, *96*, 2983.

(3) Curtis, D. M. In *Transition metal sulfur chemistry: biological and industrial significance*; Stiefel, E. I.; Matsumoto, K., Eds.; ACS Symposium Series 653; American Chemical Society: Washington, DC, 1996; pp 154−175 and references cited therein.

(4) (a) Wolff, T. E.; Power, P. P.; Frankel, R. B.; Holm, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 4694. (b) Coucouvanis, D.; Demadis, K. D.; Kim, C. G.; Dunham, R. W.; Kampf, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 3344.

(5) Lee, S. C.; Holm, R. H. *Chem. Rev.* **2004**, *104*, 1135.

(6) Coucouvanis, D.; Han, J.; Moon, N. *J. Am. Chem. Soc.* **2002**, *124*, 216.

(7) (a) Demadis, K. D.; Campana, C. F.; Coucouvanis, D. *J. Am. Chem. Soc.* **1995**, *117*, 7832. (b) Han, J.; Koutmos, M.; Al Ahmad, S.; Coucouvanis, D. *Inorg. Chem.* **2001**, *40*, 5985.

(8) Koutmos, M.; Coucouvanis, D. *Inorg. Chem.* **2004**, *43*, 6508.

(9) Osterloh, F.; Sanakis, Y.; Staples, R. J.; Münck, E.; Holm, R. H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2066.

(10) Koutmos, M.; Coucouvanis, D. *Angew. Chem., Int. Ed.* **2004**, *43*, 5023.

(11) Koutmos, M.; Coucouvanis, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 1971.

10.1021/ic051860p CCC: $33.50

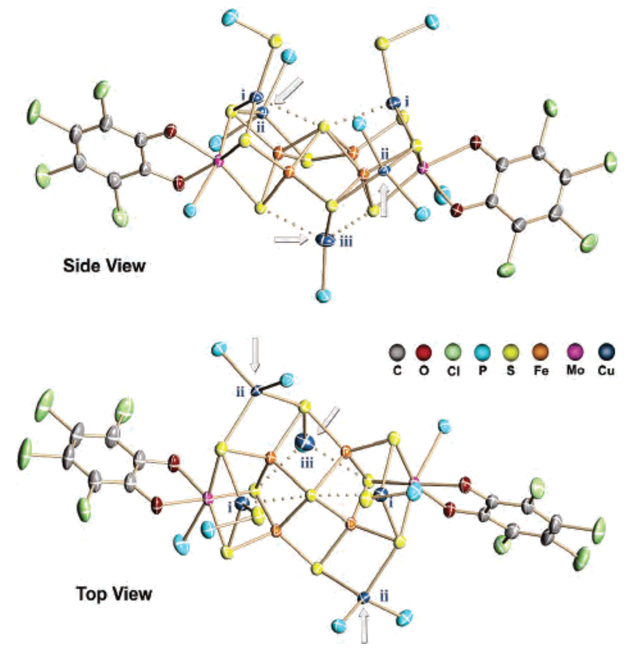

Figure 1. ORTEP diagrams of **4** showing the thermal ellipsoids at 50% probability. Two different views are presented. For clarity, the carbon and hydrogen atoms of the propyl groups of the phosphine ligands have been omitted.

geometries and coordination environments. The Mo atoms are six-coordinate distorted octahedral and retain their original coordination environment with one phosphine, one tetrachlorocatecholate, and three inorganic sulfide ligands. The mean Mo−S distance at 2.375(6,16)[14] Å and the mean M−P distance at 2.598(2,6) Å are comparable to corresponding values in **1**[15] at 2.387(3,13) and 2.575 Å, respectively. The four Fe atoms are four-coordinate and define a square array. Each one is coordinated by four inorganic sulfide ligands, one being above the plane defined by these Fe atoms and bridging all of them (μ_4-S_{cen}).[16] These Fe atoms show a short average Fe−Fe distance of 2.661 Å (range = 2.623−2.728 Å), while the average Fe−μ_4-S_{cen} distance is 2.335(4,1) Å. The central $Mo_2Fe_4S_9$ unit structurally is similar to the known $[Fe_6S_9]$[17] and $[Mo_2Fe_4S_9]$ cores.[18] The five Cu^+ ions in **4** are bound to the μ-S ligands of the core and fall into three categories:

(i) Two Cu^+ ions, each terminally bound by an $^nPr_3PS$ ligand and situated above the void of the $MoFe_2S_4$ subunits. These ions are nearly trigonal planar with only a long Cu−μ_4-S_{cen} distance of 2.714 and 2.680 Å. They deviate from planarity by $\Delta\Phi_{eq} = 2.31°$ and 3.43°.[16] The positions of these two Cu^+ ions are close to the positions of the Na^+ ions in the previously reported $(Fe_6S_9)_2Na_2$ dimer.[17b]

(ii) Two tetrahedrally coordinated Cu^+ ions, each terminally bound by two P^nPr_3 ligands [Cu−P_{aver} = 2.262(4,7) Å] and by μ_3-S and μ_2-S ligands of the core (mean Cu−S distance = 2.461 Å; range = 2.387−2.512 Å).

(iii) A unique, two-coordinate Cu^+ ion terminally coordinated to P^nPr_3 and μ_2-S ligands with distances at 2.218 and 2.251 Å, respectively. It weakly interacts with two μ_3-S ligands, one on each of the terminal subunits at 2.745 and 2.569 Å.

If three Cu atoms (categories ii and iii, designated by arrows) are removed, the cluster $[(Cl_4\text{-cat})_2(P^nPr_3)_2Mo_2Cu_2Fe_4(\mu_3\text{-}S)_6(\mu_2\text{-}S)_2(\mu_4\text{-}S)(SP^nPr_3)_2]^{2-}$ results (Figure 2A) and can be described as the fusion of two distorted $MoFe_2CuS_3$ cuboidal fragments that are sharing the μ_4-$S_{cen}{}^{2-}$ inorganic sulfide and are externally bridged by two μ_2-S^{2-} sulfides. The latter are not equivalent mainly because of their interaction with the CuP_2 and CuP units, as is evident by the mean Fe−S distances of 2.213(2,1) and 2.270(2,1) Å. This cluster structurally resembles the clusters reported by Zhang and Holm, $[(Tp)_2Mo_2Fe_6(\mu_3\text{-}S)_2(\mu_2\text{-}S)_6(\mu_4\text{-}S)(X)_2]^{3-}$ [19] (**6**; Tp = tris(pyrazolyl)hydroborate and X = SH^-), or the

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(12) (a) Synthesis of **4**: A total of 0.3 g (0.13 mmol) of $[(Cl_4\text{-cat})_2Mo_2Cu_4Fe_2S_8(P^nPr_3)_4]$ was dissolved in 25 mL of THF in a three-necked, 150-mL round-bottomed flask that was brought out of the glovebox and placed in an oil bath. A total of 0.195 g (0.52 mmol) of $Cu(CH_3CN)_4PF_6$ was dissolved in 10 mL of acetonitrile. This solution was added to the THF solution via a syringe under vigorous stirring over a period of 10 min. The reaction mixture was set to reflux for 5 h at 90 °C. The reaction mixture was then filtered (almost no precipitate). The filtrate was subsequently taken to dryness under a N_2 flow. A total of 60 mL of acetonitrile was added to the resulting black material, and the suspension was stirred for 15 min followed by filtration. The acetonitrile filtrate was taken to dryness under a N_2 flow. The black residue was washed with hexanes, and 50 mL of ether was added. The ether extract after filtration was kept in the freezer (−25 °C) for several days. A total of 120 mg of black crystals was isolated (yield 29%, based on Mo). Elem microanal. Calcd for **4**: C, 35.30; H, 6.02; S, 11.15; Cu, 10.04. Found: C, 35.80; H, 6.21; S, 10.97; Cu, 9.8. (b) Synthesis of **5**: A total of 0.3 g (0.13 mmol) of $[(Cl_4\text{-cat})_2Mo_2Cu_4Fe_2S_8(P^nPr_3)_4]$ was dissolved in 20 mL of THF followed by the addition of 0.195 g (0.52 mmol) of $Cu(CH_3CN)_4PF_6$ dissolved in 15 mL of acetonitrile. The reaction mixture was stirred for 1.5 h before 0.2 mL of H_2O was added dropwise through the septum via a syringe. The reaction mixture was stirred for another 1 h before it was filtered (a white pink powder was isolated and discarded). The solvents were then stripped under a N_2 flow, and the resulting material was dried under vacuum for several hours. A total of 80 mL of acetonitrile was added to the black material, and the suspension was stirred for 15 min followed by filtration. The acetonitrile filtrate was taken to dryness under a N_2 flow. The black residue was washed with hexanes, and 50 mL of ether was added. The ether extract after filtration was kept in the freezer (−25 °C) for several days. A total of 80 mg of black crystals was isolated (yield 21%, based on Mo). Elem microanal. Calcd for **5**: C, 34.90; H, 5.86; S, 11.09; Cu, 13.19. Found: C, 34.80; H, 5.73; S, 11.16; Cu, 13.3.

(13) Diffraction data were collected on a Bruker CCD-based X-ray diffractometer at 150(2) K, at The University of Michigan X-ray facility ($2\theta_{max}$ = 52.98° and 52.96° for **4** and **5**, respectively). The space groups ($P\bar{1}$, triclinic, and $P2(1)/n$, monoclinic) were determined based on systematic absences and intensity statistics. Cell dimensions are $a = 15.860(3)$ Å, $b = 18.159(3)$ Å, and $c = 28.410(5)$ Å with $\alpha = 84.443(3)°$, $\beta = 66.400(3)°$, and $\gamma = 90.00°$ and $V = 7256(2)$ Å^3 for **4** ($z = 2$) and $a = 13.695(2)$ Å, $b = 27.611(4)$ Å, $c = 16.045(2)$ Å with $\beta = 96.286(2)°$ and $V = 6031(2)$ Å^3 ($z = 2$) for **5**. Full matrix least-squares refinement based on F^2 converged to R1 [$I > 2\sigma$] values of 0.0381 and 0.0493 and wR2 values of 0.0979 and 0.1018 (GOF = 1.020 and 1.020) for **4** and **5**, respectively.

(14) The first number in the parentheses indicates the number of distances that are averaged, while the second number indicates the standard deviation.

(15) Because of the lack of good structural data for compound **2**, $[(Cl_4\text{-cat})_2\ Mo_2Fe_6S_8(P^nBu_3)_6]$ has been used for comparison of the two structures. Compounds $[(Cl_4\text{-cat})_2Mo_2Fe_6S_8(PR_3)_6]$ (where R = Et, ^nPr, and ^nBu) have identical core structures and exhibit minimal differences in bond distances.

(16) We define $\Delta\Phi_{eq}$ as $\Delta\Phi_{eq} = 360 - \sum\Phi_{eq}$, where $\sum\Phi_{eq}$ is the sum of the angles in the triangular base to which the longest Cu−S_{ax} distance (in the case of cluster **4**, it is Cu−μ_4-S_{cen}) is normal.

(17) (a) Christou, G.; Holm, R. H.; Sabat, M.; Ibers, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 6269. (b) Henkel, G.; Strasdeit, H.; Krebs, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 201.

(18) Zhou, H. C.; Su, W. P.; Achim, C.; Rao, V. P.; Holm, R. H. *Inorg. Chem.* **2002**, *41*, 3191.

(19) Zhang, Y. G.; Holm, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 3910.

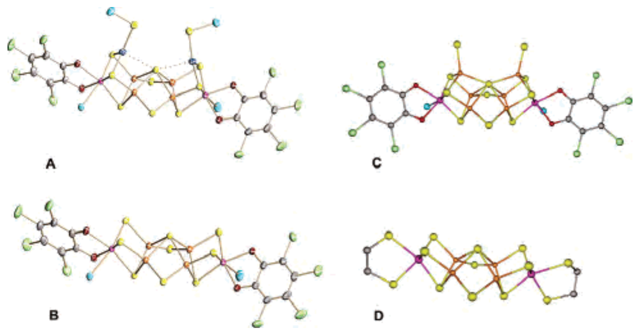

Figure 2. Visual comparison of **A** and **B** (fragments of cluster **4** after sequential removal of Cu atoms) with fragments of cluster $[(Cl_4\text{-cat})_6(PEt_3)_6Mo_6Fe_{20}S_{30}]^{4-}$, **C**,[9] and cluster $[(edt)_2Mo_2Fe_4(\mu_3\text{-}S)_6(\mu_2\text{-}S)_2(\mu_4\text{-}S)]^{4-}$, **D**.[17]

$Mo_2Fe_6S_9$ fragment **7** of cluster $(Bu_4N)_2(Et_4N)_2[(Cl_4\text{-cat})_6(PEt_3)_6Mo_6Fe_{20}S_{30}]$.[9] Fragment **7** (Figure 2C) represents a close synthetic analogue of the topology of the P^N cluster of the nitrogenase. Both of these clusters (Figure 2C) have almost the same core stoichiometry and exhibit similar features. The cluster in Figure 2A also is similar, with $S_2Cu[SP^nPr_3]$ units in place of the S_3FeX units in Figure 2C. The two nearly planar $S_2Cu[SP^nPr_3]$ units in Figure 2A interact only weakly with the bridging sulfide in the middle of the cluster. As a result, the latter is best described as a μ_4-S^{2-} ligand rather than a μ_6-S^{2-} ligand.

Further removal of the $Cu[SP^nPr_3]$ units results in the $[(Cl_4\text{-cat})_2(P^nPr_3)_2Mo_2Fe_4(\mu_3\text{-}S)_6(\mu_2\text{-}S)_2(\mu_4\text{-}S)]^{4-}$ fragment (Figure 2B) with a structure very similar to that found in $[(edt)_2Mo_2Fe_4(\mu_3\text{-}S)_6(\mu_2\text{-}S)_2(\mu_4\text{-}S)]^{4-}$ (**8**; edt = ethane-1,2-dithiolate; Figure 2D).[18] The resemblance is evident in the comparable Fe−Fe and Fe−S distances. The only difference between the two clusters is the Mo environment (five-coordinate in **8** versus six-coordinate in **4**).

The molecular structure of **5**, revealed by X-ray analysis, exhibits a unique topology that can be best described as the face-sharing fusion of a $[Cu_4Fe_4S_6]$ "pentlandite"-like central core with two $[MoCuS_2]$ dimers (Figure 3).

Among the essential features of cluster **5** are the presence of three different types of bridging inorganic sulfides including two μ_5-S^{2-} and two μ_4-S^{2-}, which are located in the $[Cu_4Fe_4S_6]$ core fragment, and four μ_3-S^{2-}, which are present in the $[MoCuS_2]$ fragment. The bond lengths decrease in the expected order $M{-}\mu_3\text{-}S^{2-} < M{-}\mu_4\text{-}S^{2-} < M{-}\mu_5\text{-}S^{2-}$, as is evident by the mean M−S distances of 2.303(6,10), 2.322(4,11), and 2.380(10,17) Å respectively. The μ_5-S bridging mode is unsymmetrical, and although infrequent, it has been identified in at least two occasions: one in the P^N cluster of nitrogenase[20] and the other in the naturally occurring minerals of the pentlandite family.[21]

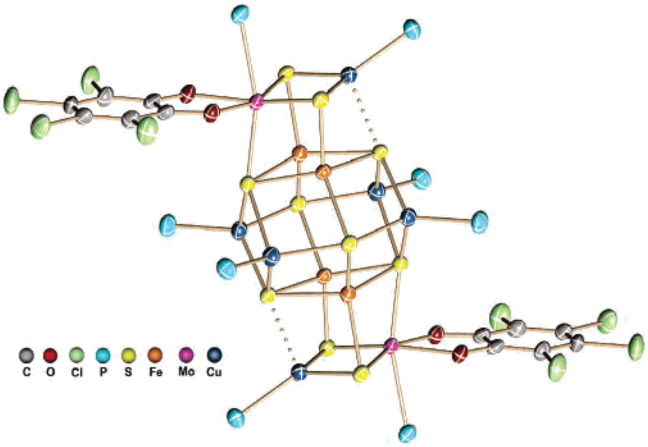

Figure 3. ORTEP diagram of **5** showing the thermal ellipsoids at 50% probability. For clarity, the carbon and hydrogen atoms of the propyl groups of the phosphine ligands have been omitted ($Mo{-}S_{aver}$ = 2.347 Å; Mo−P = 2.594 Å; Fe−Fe and Cu−Cu body diagonals at 4.448, 4.478 and 5.347, 5.384 Å, respectively).

The four Cu atoms within the $Cu_4Fe_4S_6$ "pentlandite" core are four-coordinate distorted tetrahedral and are bound by three bridging sulfides and one phosphine group. The $Cu{-}S_{aver}$ and $Cu{-}P_{aver}$ distances are 2.331(6,31) and 2.206(2,1) Å, respectively. The two Cu atoms of the external $[MoFeCuS_2]$ units can be viewed as three-coordinate distorted (deviating from planarity; $\Delta\Phi_{eq} = 5.81°$) and show a $Cu{-}S_{aver}$ distance of 2.288(2,6) Å and a Cu−P distance of 2.238 Å. A trigonal-pyramidal description also should be considered given the short $Cu{-}S_{ax}$ interactions at 2.456 Å. The four Fe atoms exhibit a distorted tetrahedral geometry and are coordinated by four inorganic sulfides with a mean Fe−S distance of 2.335(8,14) Å.

The $[Cu_4Fe_4S_6]$ or $[MoCuFe_2S_4]$ structural motifs are uncommon, albeit not unprecedented. The latter is a recognizable fragment of cluster **3**,[11] whereas the former has a core composition similar to that of cluster $[Cu_4Fe_4S_6(P^nPr_3)_4Cl_4]$ (**9**), which was recently isolated and characterized.[22]

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Supporting Information Available: The X-ray crystallographic files in CIF format for $[(Cl_4\text{-cat})_2Mo_2Cu_5Fe_4S_9(P^nPr_3)_7(SP^nPr_3)_2]PF_6$ (**4**) and $[[(Cl_4\text{-cat})_2Mo_2Cu_6Fe_4S_{10}(P^nPr_3)_8]$ (**5**).

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(20) Peters, J. W.; Stowell, M. H. B.; Soltis, S. M.; Finnegan, M. G.; Johnson, M. K.; Rees, D. C. *Biochemistry* **1997**, *36*, 1181.

(21) Rajamani, V.; Prewitt, C. T. *Can. Mineral.* **1975**, *13*, 75.

(22) Koutmos, M.; Kalyvas, H.; Sanakis, Y.; Simopoulos, A.; Coucouvanis, D. *J. Am. Chem. Soc.* **2005**, *127*, 3706.