A New Function of the (μ_3-S) Ligand in an Fe_4S_4 Cluster: Synthesis and Structure of the High-Nuclearity Mo/Fe/S Cluster, $Fe(DMF)Cl(Cl_4\text{-cat})_2$-$Mo_2Fe_2S_4(PEt_3)_2ClFe_4S_4(PEt_3)_3(CO)_6Cl$

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The active sites in metalloenzymes consist of metal centers, often with unique structural and electronic characteristics. Synthetic analogues have been obtained for many of these sites and have been instrumental in our understanding of fundamental structure−function relationships. Included among the analogues, which have remained elusive to synthesis, are the multinuclear clusters in the MoFe protein component of the nitrogenase.[1] These are the P cluster and the nitrogen-fixing FeMo-cofactor that contain Fe_8S_7 and $MoFe_7S_9$ cores, respectively. Understanding the biosynthesis and obtaining synthetic analogues for these clusters are major unfulfilled goals in bioinorganic chemistry. Explorations in the synthesis of Fe/S and Mo/Fe/S clusters have made available a large amount of basic chemistry[2] that may eventually be employed in the rational design of specific target clusters. Particularly useful approaches have been the systematic substitution and specific displacement of terminal ligands in clusters that may serve as building blocks for yet larger clusters. These techniques have made possible the synthesis of octanuclear clusters such as the singly bridged double cubanes with the $(Fe_4S_4)_2S$ frame,[3] and the doubly bridged-double cubanes with the $(Fe_3MoS_4)_2(\mu\text{-S})(\mu\text{-L})$ cores.[4,5] More recently the syntheses of fused-double cubanes with the $[Mo_2Fe_6S_8]^{4+}$, **I**,[6,7] and $[Fe_8S_8]$[8] cores have been reported.

The reactions of **I** with CO in dichloromethane (CH_2Cl_2) or tetrahydrofuran (THF) solution has led to the syntheses of a plethora of new clusters with the Roussin salt, $MoFe_3S_3$, incomplete cubane structure. These include the $(Cl_4\text{-cat})Mo(L)$-$Fe_3S_3(PR_3)_n(CO)_m$ (L = O, pyridine, or P^nPr_3, $n = 2$ or 3, $m = 4$, 5 or 6, R = Et, ^{n}Pr) clusters, **II**.[9,10] The same reaction in CH_2Cl_2 with trace amounts of dimethylformamide (DMF), in addition to **II**, affords the new, neutral, $Fe(DMF)Cl(Cl_4\text{-cat})_2Mo_2Fe_2S_4(PEt_3)_2$-$ClFe_4S_4Cl(PEt_3)_3(CO)_6$ cluster, **III**,[11] and also the tetranuclear "cubanes" $Fe_4S_4Cl(PEt_3)_3(CO)_6$, **IV**,[12] and $(Cl_4\text{-cat})_2Mo_2Fe_2S_4$-$(PEt_3)_4$, **V**.[13]

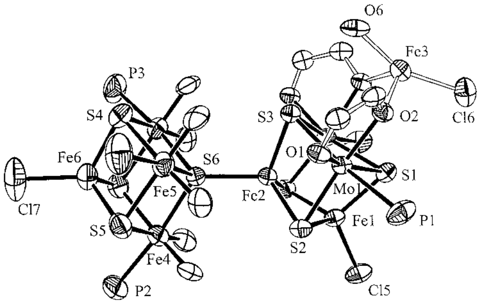

Figure 1. Molecular structure of **III**. For clarity, only the O donors of the Cl_4-cat ligand and the C atoms attached to them are shown. Similarly, only the O atoms of the DMF molecule bound to Fe(3) are shown.

The structure of **III** has been determined (Figure 1).[14] It is best described as a complex of the $[Fe(DMF)Cl]^+$ monomer and the $[(Cl_4\text{-cat})_2Mo_2Fe_2S_4(PEt_3)_2ClFe_4S_4(PEt_3)_3(CO)_6Cl]^-$ anionic cluster. A mirror plane that contains Cl(7), Fe(6), Fe(4), S(4), S(6), Fe(2), S(3), S(1), Fe(1), Fe(3), O(6), and C(16) bisects the nonanuclear cluster. The anion consists of the neutral $[Fe_4S_4$-$(PEt_3)_3(CO)_6Cl]$ cluster bound via one of its $\mu_3\text{-}S^{2-}$ ligands to one of the Fe atoms in the $[(Cl_4\text{-cat})_2Mo_2Fe_2S_4(PEt_3)_2Cl]^-$ cubane. *The function of a cubane as a terminal ligand using an already triply bridging sulfido ligand is unprecedented and demonstrates the basicity of the sulfido ligands in the electron-rich $[Fe_4S_4Cl$-$(PEt_3)_3(CO)_6]$ cluster*. The $[Fe_4S_4(PEt_3)_3(CO)_6Cl]$ subunit in **III** is a site-differentiated cubane and structurally nearly identical to **IV**. It has approximate C_{3v} symmetry with the three-fold axis along the cube-diagonal containing the μ_4-sulfido ligand, Fe(6), and the terminal chloride ligand. The unit contains three six-coordinate (distorted octahedral) Fe^{II} ions ($S_3Fe(CO)_2PR_3$) and a four-coordinate (distorted tetrahedral) Fe^{III} ion (S_3FeCl). The Fe_4S_4 cores in **III**, and **IV**[15] are considerably larger (Fe−Fe 3.030(6) Å, 3.026(17) Å[16] and 3.489(3) Å, 3.528(2) Å[17]) than those in the ferredoxin-like cubanes[18] and their synthetic analogues[19] (Fe−Fe, ~2.75 Å). In **III** and **IV**, the Fe(II)−Fe(II) distances are similar to those in the $[Fe^{II}{}_4S_4]^0$ core of the electron precise

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(1) (a) Howard, J. B.; Rees, D. C. *Chem. Rev.* **1996**, *96*, 2965. (b) Rangaraj P.; Ryle M. J.; Lanzilotta W. N.; Ludden P. W.; Shah V. K. *J. Biol. Chem.* **1999**, *274*, 19778. (c) Allen R. M.; Roll J. T.; Rangaraj P.; Shah V. K.; Roberts G. P.; Ludden P. W. *J. Biol. Chem.* **1999**, *274*, 15869. (d) Rawls, R. L. *Chem. Eng. News* **2000**, *78*(47), 43.

(2) (a) Malinak, S. M.; Coucouvanis, D. *Prog. Inorg. Chem.* **2001**, *49*, 599. (b) Holm, R. H. Simhon, E. D. In *Molybdenum Enzymes*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1985; pp 1−87.

(3) Challen, P. R.; Koo, S.-M.; Dunham, W. R.; Coucouvanis, D. *J. Am. Chem. Soc.* **1990**, *112*, 2455.

(4) (a) Coucouvanis, D.; Challen, P. R.; Koo, S.-M.; Davis, W. M.; Butler, W.; Dunham, W. R. *Inorg. Chem.* **1989**, *28*, 4181. (b) Challen, P. R.; Koo, S.-M.; Kim, C.-G.; Dunham, W. R.; Coucouvanis, D. *J. Am. Chem. Soc.* **1990**, *112*, 8606.

(5) (a) Huang, J.; Mukerjee, S.; Segal, B. M.; Akashi, H.; Zhou, J.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 8662. (b) Huang, J.; Goh, C.; Holm, R. H. *Inorg. Chem.* **1997**, *36*, 356. (c) Huang, J.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 2247.

(6) Demadis, K. D.; Campana, C. F.; Coucouvanis, D. *J. Am. Chem. Soc.* **1995**, *117*, 7832.

(7) Han, J.; Koutmos, M.; Al-Ahmad, S.; Coucouvanis, D. Submitted for publication.

(8) (a) Goh, C.; Segal, B. M.; Huang, J.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 11844. (b) Cai, L.; Segal, B. M.; Long, J. R.; Scott, M. J.; Holm, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 8863.

(9) (a) Han, J.; Beck, K.; Ockwig, N.; Coucouvanis, D. *J. Am. Chem. Soc.* **1999**, *121*, 10448. (b) Tyson, M. A.; Coucouvanis, D. *Inorg. Chem.* **1997**, *36*, 3808.

(10) Coucouvanis, D.; Han, J.; Moon, N. To be submitted.

(11) $Fe(DMF)Cl(Cl_4\text{-cat})_2Mo_2Fe_2S_4(PEt_3)ClFe_4S_4(PEt_3)_3(CO)_6Cl$ (**III**). Isolation yield 0.9%. IR(KBr, cm^{-1}) ν(CO) 2019(s), 2003(vs), 1975(s), 1970(s, sh). ν(CO of DMF) 1618(m). ν(Cl_4-cat) 1455(m), 1437(m), 1405(m), 1385(m). UV(CH_2Cl_2) 310 nm. FAB$^+$-MS(NBA, *m/z*) 2119($[[M] - SPEt_3]^+$). ^1H NMR (300 MHz, Benzene-d_6) 4.22(Fe−PCH_2, 12H), 3.54(Fe−PCH_2, 6H), 1.38(Mo−PCH_2, 4H), 1.19(Mo−PCH_2CH_3, 18H), 0.83(Fe−CH_2CH_3, 27H), 0.92(d, DMF−Me, 6H), 0.56(Mo−PCH_2, 8H).

(12) $Fe_4S_4(PEt_3)_3(CO)_6Cl$ (**IV**) Isolation yield 22%. Anal. Calcd for $C_{24}H_{45}$-$ClFe_4O_6P_3S_4$ (MW: 909.628): C, 31.69; H, 4.99. Found: C, 30.87, H, 4.34. Mid-IR(KBr, cm^{-1}) ν(CO) 2023(s), 1995(vs), 1959(s), 1948(s). FAB$^+$-MS (NBA, *m/z*) 909.8($[M]^+$), 817.9($[M - FeCl]^+$), 740.9($[M - FeCl(CO)_2]^+$). ^1H NMR(300 MHz, $CDCl_3$) 5.29(Fe−PCH_2, 12H), 3.74(Fe−PCH_2, 6H), 0.88(Fe−PCH_2CH_3, 27H). UV(CH_2Cl_2, nm) 315(3700), 380(2000), 490(1000). Cyclic voltammetry (1,2-dichloroethane, vs SCE, V) −1.32(irr), −1.73(irr). (DMF, vs SCE, V) −0.92(irr), −1.37(irr). EPR(CH_2Cl_2, 25K, g) 6.8, 6.6, 5.9, 4.7, 4.3, 3.25, 1.98. At 15 K, $g = 4.7, 4.3, 3.25$. Mössbauer (125 K) $\delta = 0.077$ mm s^{-1} and $\Delta E_Q = 0.368$ mm s^{-1}.

(13) $(Cl_4\text{-cat})_2Mo_2Fe_2S_4(PEt_3)_4$ (**V**) Isolation yield 28%. Analysis, Calcd [M•MeCN] MW: 1437.26. C, 31.76; H, 4.42; N, 0.97. Obsd: C, 31.27; H, 4.95; N, 0.89. Mössbauer (125 K) $\delta = 0.398$ mm s^{-1}, $\Delta E_Q = 0.934$ mm s^{-1}.

(14) Black needle-shaped crystals of **III** are in the monoclinic space group $P2_1/m$ with $Z = 2$. The cell dimensions (Å, deg) are $a = 11.2718(19)$, $b = 23.256(4)$, $c = 17.637(3)$, and $\beta = 98.109(3)$. Full matrix refinement of 478 parameters on 6817 unique data ($2\theta = 46.66°$, $I > 2\_(I)$) converged to final R (wR2) values of 0.0650 (0.1851) and GOF of 1.028.

(15) Black crystals of **IV**, obtained by slow evaporation of solvent at 5 °C, are in the monoclinic space group $P2_1/c$ with $Z = 16$. The cell dimensions (Å, deg) are $a = 32.992(6)$, $b = 12.609(2)$, $c = 39.048(7)$, and $\beta = 110.069(3)$. Full matrix refinement of 1513 parameters on 31295 unique data ($2\theta = 52.86°$, $I > 2\_(I)$) converged to final R (wR2) values of 0.0611 (0.1195), GOF = 1.125.

(16) Fe(III)−Fe(II) distances.

(17) Fe(II)−Fe(II) distances.

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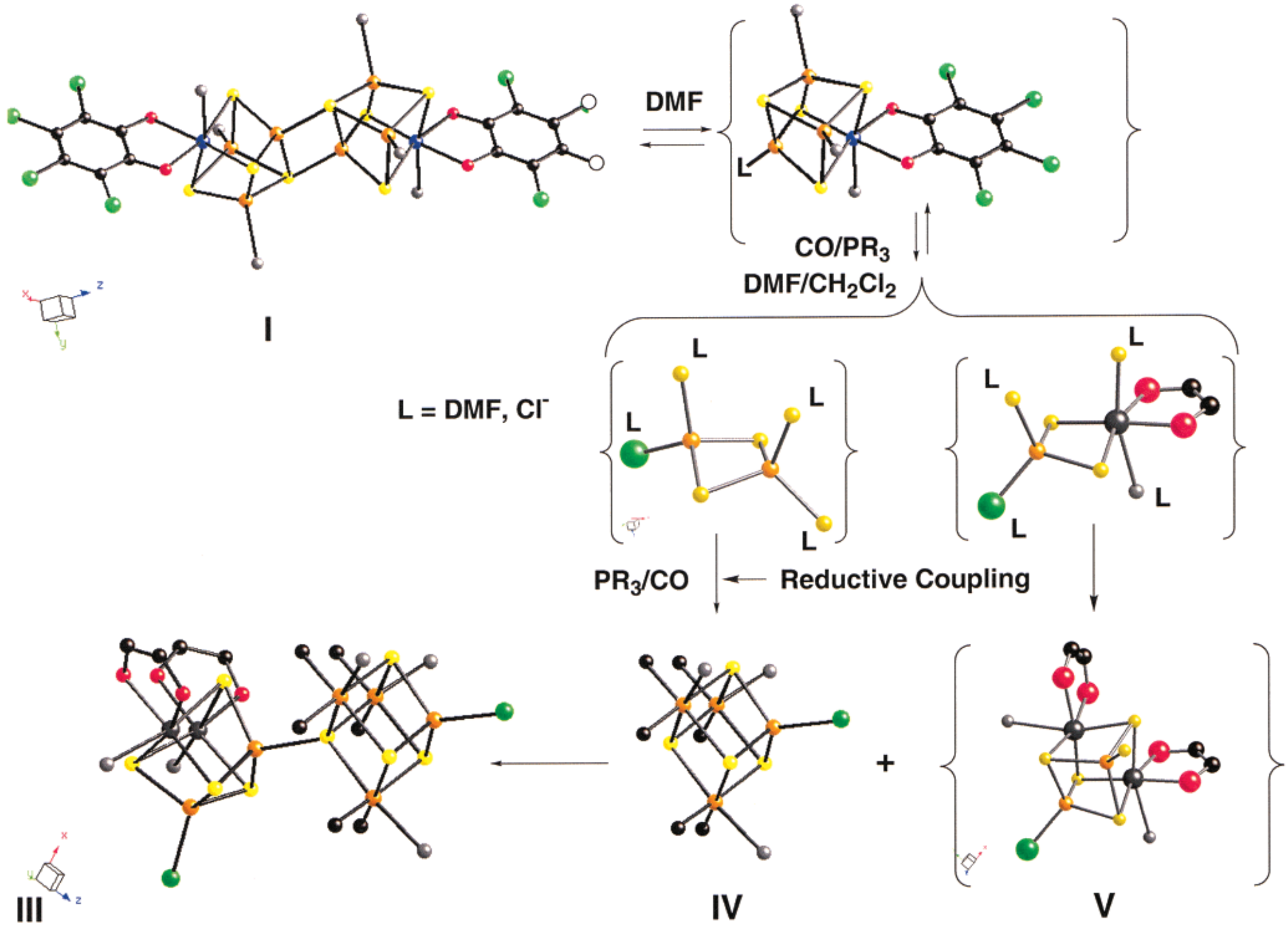
Scheme 1[a]



[a] The formation of Fe(DMF)Cl(Cl$_4$-cat)$_2$Mo$_2$Fe$_2$S$_4$(PEt$_3$)$_2$ClFe$_4$S$_4$(PEt$_3$)$_3$(CO)$_6$Cl, **IV** by Mo/Fe/S cluster transformations. Molecules in brackets are hypothetical, and those in frames have been isolated and structurally characterized. The larger black spheres represent the Mo atoms, the orange spheres, the Fe atoms, and the yellow bridging spheres, the S atoms.

$Fe_4S_4(CO)_{12}$ cluster (mean Fe−Fe, 3.466(5) Å).[20] The overall oxidation state of the $[Fe_4S_4]^+$ cores in **III** and **IV,** however, is identical to that in the neutral $Fe_4S_4(PR_3)_3Cl$ cluster, **VI**,[21] (Fe−Fe, 2.768(12) Å) and contains three Fe^{II} and one Fe^{III} atoms. The latter also is a site differentiated cubane, but has fewer valence electrons than **III** and **IV**, and contains only high-spin, tetrahedrally coordinated Fe(II) and Fe(III) sites. The relative importance of M−M bonding vs ligand crowding in determining the Fe−Fe distances in **III**, **IV**, and **VI** is difficult to ascertain. The EPR spectrum of **IV** at temperatures <30 K shows resonances at g = 6.8, 6.6, 5.9, 4.7, 4.3, 3.25, and 1.98 consistent with an $S = {}^5/_2$ ground state. The spectrum could be interpreted as due to a valence-localized high-spin Fe^{III} site in a structure that contains three additional low-spin Fe^{II} diamagnetic sites. This valence localization, suggested by the EPR spectrum, is not obvious in the Mössbauer spectrum of **IV**. In the latter a sharp quadrupole doublet is fitted by one Fe site with an I.S. of 0.077 mm s^{-1} and a quadrupole splitting 0.368 mm s^{-1}. A magnetic study of **IV** (the independently isolated component of **III**) as a function of temperature clearly showed the presence of the high-spin Fe^{III} center.[22] On the basis of the Mössbauer and EPR spectra and the stoichiometry of **III**, the formal oxidation states of the metal atoms are tentatively described as: $[Fe^{II}(DMF)Cl]^+\{[Cl_4\text{-cat}]_2Mo^{IV}_2Fe^{II}_2S_4(PEt_3)_2Cl\}^-$ $[Fe^{II}_3Fe^{III}S_4(PEt_3)_3(CO)_6Cl]^0\}$.

The four-coordinate Fe^{II} ion in the $[Fe(DMF)Cl]^+$ cation, shows a severely distorted tetrahedral coordination geometry with extremes of very large angles, O(6)−Fe(3)−Cl(6), at 156.9(3)° and small angles, O(2)−Fe(3)−O(6), at 87.5(2)°.

The formation of **III**, **IV**, and **V** from **I** under CO pressure (in CH_2Cl_2 solution containing small amounts of DMF) can be envisioned as indicated in Scheme 1. The dissociation of the cubic subunits of **I** make available the solvated $[MoFeS_2]$ and $[Fe_2S_2]$ rhombic dimers. Association or reductive coupling of these dimers occurs to form the Fe_4S_4, $Mo_2Fe_2S_4$ as in **IV** and **V** and $MoFe_3S_4$ cores.[7]

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Supporting Information Available: The synthesis, structural determination summary, atomic coordinates, bond lengths and bond angles, and anisotropic thermal parameters for the Fe(DMF)Cl(Cl$_4$-cat)$_2$Mo$_2$Fe$_2$S$_4$(PEt$_3$)ClFe$_4$S$_4$(PEt$_3$)$_3$(CO)$_6$Cl (**III**) and Fe$_4$S$_4$(PEt$_3$)$_3$(CO)$_6$Cl (**IV**) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[18] Berg, J. M.; Holm, R. H. In *Iron−Sulfur Proteins*; Spiro, T. G., Ed.; Wiley: New York, 1982; Chapter 1.

[19] Holm, R. H. *Acc. Chem. Res.* **1977**, *10*, 427.

[20] Nelson, L. L.; Lo, F. Y.-K.; Rae, A. D.; Dahl, L. F. *J. Organomet. Chem.* **1982**, *225*, 309.

[21] Tyson, M. A.; Demadis, K. D.; Coucouvanis, D. *Inorg. Chem.* **1995**, *34*, 4519.

[22] It shows strong antiferromagnetic coupling at 4−10 K. $\mu_{eff} = 6.4\ \mu_B$ (10−300 K).