Synthesis and Structural Characterization of the New $Mo_2Fe_6S_8(PR_3)_6(Cl_4\text{-cat})_2$ Clusters. Double Cubanes Containing Two Edge-Linked $[MoFe_3S_4]^{2+}$ Reduced Cores

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The recent structure determinations of the FeMo proteins from two nitrogenase enzymes (*Azotobacter vinelandii*[1a] and *Clostridium pasteurianum*[1a,b]) have revealed the identity of the common Fe/Mo/S cofactor. The latter can be extruded from the protein matrix and has been spectroscopically characterized.[2] This $MoFe_7S_9$ aggregate is composed of two cuboidal subunits (Fe_4S_3 and $MoFe_3S_3$) bridged by three μ-S ligands. The Mo atom is located *at one pole of the cluster* and is six-coordinate bound by three inorganic core S^{2-}, a bidentate homocitrate, and a histidine imidazole ligand in a distorted octahedral geometry.

In the last two decades, attempts to obtain analogs for the active site in nitrogenase have resulted in the syntheses and characterization of a plethora of Fe/Mo/S clusters.[3] Many of these molecules contain $MoFe_3S_4$ single cubanes[4] as subunits and have the Mo atoms directly involved in inter-subunit bridging.

In this communication we report on the synthesis, structural characterization, and reactivity of a new class of Mo/Fe/S clusters on the general type $Mo_2Fe_6S_8(PR_3)_6(Cl_4\text{-cat})_2$ (R = Et, **I**; *n*-Bu, **II**; Cl_4-cat = tetrachlorocatecholate dianion). These molecules represent the first examples of Fe-S edge-linked, reduced, $MoFe_3S_4$ cubanes with the Mo atoms at the periphery of the cluster. This new type of subcluster linkage, facilitated by two μ_4-S ligands, results in a smaller number of Fe-coordinated terminal ligands and for this reason may be relevant to the structures of the P-clusters and the nitrogenase cofactor.

The reaction of the $(Et_4N)_2[MoFe_3S_4Cl_3(Cl_4\text{-cat})(CH_3CN)]$ cluster,[5] **III**, (0.5 g, ~0.5 mmol) with 3 equiv of $NaBPh_4$ (or $NaPF_6$) in 40 mL of CH_3CN at ambient temperature, in the presence of 4 equiv of PEt_3, affords a black solid (**I**), which upon recrystallization from CH_2Cl_2/hexanes yields highly crystalline $Mo_2Fe_6S_8(PEt_3)_6(Cl_4\text{-cat})_2$, **I**, in 60−70% yields.[6,9] The ^1H NMR spectrum[6] clearly shows the presence of two sets of PEt_3 ligands. The Mössbauer spectrum (obtained at 125 K *vs* Fe metal) consists of a slightly asymmetric quadrupole doublet with values of isomer shift and quadrupole splitting of 0.47 and 0.98 mm/s, respectively. These values are close to those expected for a tetrahedrally coordinated Fe with an average oxidation state of +2.33.[11] In a CH_2Cl_2 glass, at 20 K, **I** is EPR silent. The $[MoFe_3S_4]$ subunits of **I** exist at the +2 oxidation level, and by comparison to **III** they are reduced by one electron. The reducing agent in the synthesis of **I** is the PEt_3 reagent that is involved in the reductive desulfurization of **III** thus generating reducing equivalents.[12] The byproduct of the above process, $Et_3P{=}S$, was identified from its characteristic infrared spectrum.[13] The reduced double cubane core in **I** is stabilized by the π-accepting PEt_3 ligands known to stabilize lower oxidation states of transition metals.[14] Previously, the reduction of *single* $MoFe_3S_4$ cubanes with "conventional" terminal ligands bound to the Fe atoms was found possible only with powerful reducing agents. From such studies clusters that contain the $[MoFe_3S_4]^{2+}$ cores have been isolated and spectroscopically characterized.[15]

The cyclic voltammetry of **I** (on a glassy carbon electrode, in CH_2Cl_2 *vs* Ag/AgCl and Bu_4NClO_4 as supporting electrolyte) shows reductions at −890 (rev)[16] and −1450 (irr) mV and oxidations at +50 mV (qr) and +1550 mV (irr). These values are very different from the ones of the starting compound **III**, which exhibits a reversible reduction at −940 mV and an irreversible oxidation at +300 mV, under identical conditions.[36]

The crystal structure of **I**[17] shows the neutral cluster (Figure 1) to consist of two edge-linked, $MoFe_3S_4$ cubane subunits with a core μ_3-S ligand of one subunit coordinated to an Fe of the other. As a consequence of the bridging μ_4-S ligands and the lack of a full complement of terminal ligands, two of the Fe atoms in **I** and **II** are tetrahedrally coordinated only by S^{2-} ligands.

Core structural details[18] are available in the figure caption. The Mo−P bond in **I**, at 2.602(3) Å, is appreciably longer than the corresponding bond in the $MoFe_4S_6(PEt_3)_4Cl$ cluster,[3a] 2.488(4) Å. The mean Fe−P bond distance is 2.336(6) Å, comparable to the Fe−P bond in the $Fe_6S_6(P\text{-}n\text{-}Bu_3)_4Cl_2$ basket clusters, 2.31(1) Å.[10] Double cubane clusters with cores similar

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(6) Anal. Calcd for $Mo_2Fe_6Cl_8S_8P_6O_4C_{48}H_{90}$ (**I**, MW 1982.5): Mo, 9.68; Fe, 16.94; Cl, 14.29; S, 12.93; C, 29.05; H, 4.54. Found: Mo, 9.89; Fe, 16.71; Cl, 14.76; S, 11.57; C, 29.84; H, 4.32. Vibrations at 780 (m), 807 (m), 1096 (m), 1439 (vs), 1648 (w) and a set of four bands at 2880−2973 (w) cm^{-1} in the infrared spectrum suggest the presence of PEt_3.[7] In addition the Cl_4-cat ligand gives rise to stretches at 1430 (s), 1255 (m), 805 (m), and 525 (m) cm^{-1}.[8] Far-infrared spectrum of **I**: 375 (m), 420 (vs), 450 (s), 470 (m) cm^{-1}. The corresponding compound with P-*n*-Bu_3 also has been obtained, **II**. Anal. Calcd for $Mo_2Fe_6Cl_8S_8P_6O_4C_{84}H_{162}$ (**II**, MW 2488.3): Mo, 7.72; Fe, 13.50; C, 40.51; H, 6.51. Found: MO, 7.59; Fe, 13.77; C, 38.51; H, 6.27. **II** shows spectroscopic features similar to those of **I**. The electronic spectrum of **I** (in CH_2Cl_2) displays a broad absorption at 320 nm. The ^1H NMR spectrum of **I** ($CDCl_3$) shows broad signals at 1.89 (Mo−PCH_2CH_3), 1.20 (Fe−PCH_2CH_3), 0.07 (Fe−PCH2CH_3), and 0.01 (Mo−PCH_2CH_3) ppm, clearly indicating the presence of two sets of PEt_3 ligands in an approximate 2:1 intensity ratio. Magnetic susceptibility (solid): μ_{eff} (4 K) = 5.05 μ_B, μ_{eff} (300 K) = 7.42 μ_B.

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(9) Cluster **I** also forms in low yield (~25%), in the reaction of **III** with $FeCl_2(PEt_3)_2$[10] in CH_3CN in a 1:2 molar ratio.

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(13) The ν(P=S) vibration is found at 537 cm^{-1} (CsI disk). This spectrum completely agrees with a spectrum of an authentic sample of $Et_3P{=}S$.

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(16) Rev = reversible, qr = quasi-reversible, irr = irreversible.

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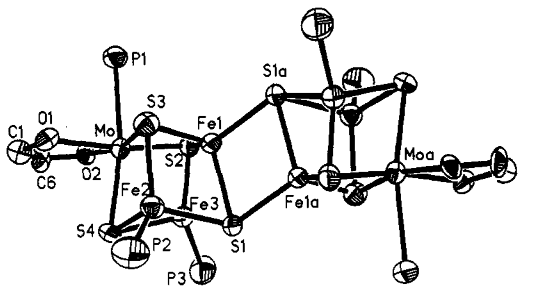

Figure 1. Structure of the $Mo_2Fe_6S_8(PEt_3)_6(Cl_4\text{-cat})_2$, **I**, double cubane (one of the two crystallographically independent molecules) showing the labeling scheme and 40% probability ellipsoids drawn by ORTEP. Mean values of selected interatomic distances (Å) and angles (deg) reported are from *both* crystallographically independent clusters. The first number in parentheses represents the calculated standard deviation of the mean, and the second is the number of *n* independent distances or angles: Mo···Mo 7.864(2), Mo···Fe 2.677(5,6) (range 2.658(2)–2.695(2)), Fe···Fe (intracubane) 2.639(2,6), Mo–S 2.387(12,6) (range 2.362(3)–2.434(3)), Fe–μ_3S (intracubane) 2.243(3,6), Fe–μ_4-S (intracubane) 2.339(13,6) (range 2.303(4)–2.383(4)), Fe···Fe (intercubane) 2.653(10,2) (range 2.673(3)–2.644(4)), Fe1–S1a (intercubane) 2.271(4,2), Mo–P 2.601(1,2), Fe–P 2.336(6,4), Mo–O (catecholate) 2.098(4,4), O1–Mo1–O2 77.5(3,2), S1–Fe1–S1a 110.3(2,2), Fe1–S1–Fe1a 69.7(2,2), P1–Mo1–S4 167.2(6,2). Ethyl groups on the phosphines and Cl_4-cat rings have been omitted for clarity.

to the one in **I** have been reported previously, and the $[(H_2O)_9Mo_3S_4MMS_4Mo_3(H_2O)_9]^{8+}$ clusters (M = Cu,[19a] Co[19b]) exhibits μ_4-S linkages between two subclusters and contain the $(M-\mu_4\text{-}S)_2$ structural units. The geometry of the μ_4-S ligands in **I** is very unusual and shows the fourth, extra-cube, lone pair (Fe–S bond) oriented ~70° from the expected location (for pyramidal geometry) on the normal to the plane defined by the "tips" of the three other lone pairs (Fe–S bonds). It is interesting to note that the longer Fe–S bonds in **I** (Figure 1) are not those externally linking the two subunits (Fe1–S1a) but rather those within the $MoFe_3S_4$ subunits (Fe1–S1).

In dimethylformamide, DMF, solution the double cubane structure of **I** appears to undergo solvolytic cleavage. The cyclic voltammetry of **I** in DMF displays a set of three reductions at −1180, −1404, and −1700, suggestive of an equilibrium process. The double cubane structure of **I** is readily ruptured in the presence of ligands such as Cl^- or PEt_3. The reaction of **I** with Et_4NCl in CH_3CN in a 1:2 ratio rather than forming the anticipated $[(Cl_4\text{-cat})(PEt_3)MoFe_3S_4(PEt_3)_2Cl]^-$ cluster leads to the displacement of all the Fe-bound PEt_3 ligands and formation of the $[MoFe_3S_4Cl_3(Cl_4\text{-cat})(PEt_3)]^{2-}$ cluster[20] in what appears to be an "all or nothing" reaction. Reactions of **I** with alkyl or aryl thiolates appear to be taking the same route. **I** also reacts with PEt_3 in CH_2Cl_2 and gives the $MoFe_3S_4(Cl_4\text{-cat})(PEt_3)_4$ neutral single cubane cluster,[21] **IV**. The $[Fe_4S_4Cl_4]^{2-}$ cluster[22] was allowed to react with $NaBPh_4$ in the presence of PEt_3. The only isolable product was the $Fe_6S_6(PEt_3)_4Cl_2$ basket cluster,[10] in good yields. Compound **I** readily reacts with π-acids such as CO, Bu^{t}NC, and NO^+.[23] On the contrary, **I** does not react with σ-bases such as CH_3CN, NH_2NH_2, or the tridentate chelate tris-pyrazolyl borate. These results can be expected in light of the fact that the $[MoFe_3S_4]^{2+}$ subunit is reduced and should not show pronounced affinity for anionic ligands or σ-bases. The general scope of the reactivity of cluster **I** towards small molecules relevant to nitrogenase chemistry is under way in this laboratory.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for **I** (12 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(17) Crystal and refinement data: Black crystals (rectangular plates) of **I** are monoclinic, space group $P2_1/c$, with $a = 25.554(4)$ Å, $b = 12.740(2)$ Å, $c = 26.634(5)$ Å, $\beta = 112.405(4)°$, $V = 8016(2)$ Å^3, and $Z = 4$. Single-crystal diffraction data for **I** were collected initially on a Nicolet P3F diffractometer. A low yield of reflection data could be obtained (~15%) and was used to solve the structure and reveal the atomic connectivity using Mo Kα radiation. Subsequently, and using the same crystal, data were collected at Siemens Analytical and X-Ray Instruments Inc., Madison, WI, employing a CCD detector (at ~80% yield). The refinement of the structure by full-matrix least-squares methods was based on these data: 15 390 reflections ($2\theta_{max} = 40°$, $I > 4\sigma(I)$). Refinement on 712 parameters converged to a conventional $R = 9.33\%$. The reaction pathway described in ref 9 gave single crystals of **I** in a triclinic form, space group $P\bar{1}$ with $a = 12.1377(6)$ Å, $b = 13.6889(6)$ Å, $c = 13.7462(2)$ Å, $\alpha = 64.053(3)°$, $\beta = 78.972(3)°$, $\gamma = 86.153(3)°$, $V = 2015.45(6)$ Å^3, and $Z = 2$. The structure of this form also was determined, and the cluster was found to be identical to the one in the monoclinic cell.

(18) The core is located on a crystallographically imposed inversion center. There are two pairs of crystallographically independent clusters in the unit cell.

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(20) Anal. Calcd for $MoFe_3S_4Cl_7O_2PC_{28}H_{55}N_2$ (MW 1163): C, 28.89; H, 4.73; N, 2.41. Found: C, 28.21; H, 4.66; N, 2.31.

(21) Anal. Calcd for $MoFe_3S_4Cl_4O_2PC_{30}H_{60}$ (**IV**, MW 1109.24): C, 32.46; H, 5.41; N, 0.0. Found: C, 32.19; H, 4.57; N, 0.0. This compound displays two reversible reduction waves at −287 and −1345 mV and multiple oxidation waves at +804, +1194, and +1800 mV. Its electronic spectrum displays absorptions at 480 and 310 nm.

(22) Wong, G. B.; Bobrik, M. A.; Holm, R. H. *Inorg. Chem.* **1978**, *17*, 578.

(23) Reactions of **I** with CO, Bu^{t}NC, and $(NO)(BF_4)$ were performed anaeroically in CH_2Cl_2, and products were isolated in each case and presently are under investigation. Among these compounds the better characterized $MoFe_3S_4(Cl_4\text{-cat})(PEt_3)_3(^tBuNC)_3$, **V**, exhibits featureless electronic spectra and a ν(N–C) stretching vibration at 2155 cm^{-1}. Anal. Calcd for $MoFe_3Cl_4S_4P_3O_2C_{39}H_{72}N_3$ (**V**, MW 1240.39): C, 37.73; H, 5.81; N, 3.39. Found: C, 37.14; H, 4.71; N, 3.65.