New Fe/Mo/S Clusters with $MoFe_3S_3$ Cuboidal Cores Similar to the One in the Fe/Mo Cofactor of Nitrogenase. Synthesis and Structural Characterization of the (C1$_4$-cat)$MoFe_3S_3(PEt_3)_2(CO)_6$ and (C1$_4$-cat)$Mo(O)Fe_3S_3(PEt_3)_3(CO)_5$ Clusters

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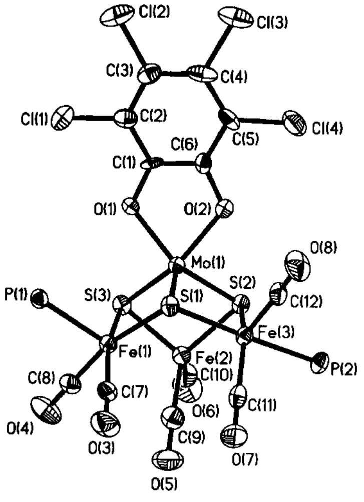
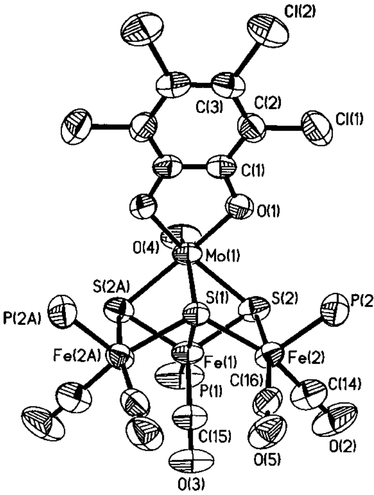
Recent X-ray crystal structure determinations of the FeMo protein of nitrogenase[1,2] have revealed in detail the structure of the Fe/Mo/S cofactor believed to be the site of substrate activation and reduction.[3] The $MoFe_7S_9$ core of the cofactor consists of two cuboidal subunits ($MoFe_3(\mu_3\text{-}S)_3$ and $Fe_4(\mu_3\text{-}S)_3$) bridged by three $\mu_2\text{-}S^{2-}$ ligands.

Partial structural analogs that contain $MoFe_3S_4$ units[4,5] have been found effective in the two electron and four electron reduction of substrates such as hydrazine,[6a−c] acetylene,[6d] and 1,2-dimethyldiazene.[6e] Within the MFe_3S_4 "cubanes" the heterometals (Mo or V), which are the sites of substrate reduction, do not interact with or reduce N_2. We have noted[7] that the sequence of steps in the stepwise reduction of the N_2 molecule generates intermediates with drastically different ligand characteristics such as N_2H_2 and N_2H_4. Further, in nitrogenase, the site within the Fe/Mo/S center that initially binds and activates N_2 (perhaps the $Fe_6(\mu_2\text{-}S)_3$ central unit[7]) may not be competent to bind and activate the reduction products or intermediates such as diazene or hydrazine. If this is indeed the case, steps subsequent to the first two electron reduction of N_2 may occur on other sites (Mo?) as the reduction proceeds to its conclusion.

Heteronuclear synthetic clusters that can be considered as structural analogs for the nitrogenase Fe/Mo/S center and contain sites of widely diverse coordination characteristics are not available. Such clusters are needed to evaluate the importance of multisite reactivity in the multielectron reduction of substrates. In this communication we present results of our synthetic studies in this area.



II



III

Figure 1. Structure and labeling of $(Cl_4\text{-cat})MoFe_3S_3(PEt_3)_2(CO)_6$, **II**, and $(Cl_4\text{-cat})Mo(O)Fe_3S_3(PEt_3)_3(CO)_5$, **III**. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Data for **II**: Fe−Mo = 2.680(1), 2.776(1), 2.849(1) Å; Fe−Fe = 2.625(1), 2.702(1), 3.636(1) Å; Mo−S(1) = 2.213(1) Å, Mo−S(2,3) = 2.305(1), 2.306(2) Å; Fe−S, 2.24(2) Å, (range: 2.174(2)−2.310(2) Å); Fe−P = 2.262(2), 2.258(2) Å; Fe−C = 1.778(9) Å (range: 1.754(7)−1.811(7) Å; Mo−O_{cat} = 2.009(3), 2.029(3) Å. Data for **III**: Fe(1)−Mo = 2.691(2) Å; Fe(2)−Mo = 3.726(2) Å; Fe(1)−Fe(2) = 2.572(2) Å; Fe(2)−Fe(2′) = 3.929(2) Å; Mo−(S(1) = 2.595(2) Å; Mo−S(2) = 2.428(2) Å; Fe−S (range: 2.220(3)−2.317(3) Å); Fe−P = 2.231(3), 2.198(3) Å; Fe−C = 1.77(1) Å; Mo−O_{cat} = 2.041(5) Å; Mo═O = 1.680(7) Å.

Among the plethora of cubic or cuboidal metal sulfur clusters that have been reported,[4,5] the corner-sulfide voided M_4S_3 clusters are rather rare and include the $[Fe_4S_3(NO)_7]^-$ black Roussin anion,[8] the recently reported $[Fe_4S_3(NO)_4(PPh_3)_3]^-$

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variant,[9] and the $[(O)MCu_3S_3Cl_3]^{2-}$ heterometallic clusters.[10] Recently, we reported[11a] on the synthesis and structural determination of the $[(Cl_4\text{-cat})MoFe_3S_4(PEt_3)_3]_2$ fused-double cubane cluster,[11b] **I**, that contains $[MoFe_3S_4]^{2+}$ subunits reduced by $1e^-$ relative to the "conventional" $MoFe_3S_4$ cubanes.[3,4] This cluster is a convenient starting reagent for the synthesis of the hitherto unknown, mixed-metal, Roussin type complexes $(Cl_4\text{-cat})MoFe_3S_3(PEt_3)_2(CO)_6$, **II**, and $(Cl_4\text{-cat})Mo(O)Fe_3S_3(PEt_3)_3(CO)_5$, **III**. The reaction of **I** with CO under a pressure of 350 psi for 24 h affords **II** in 70% yield.[12] The same reaction under ambient pressure of CO and prolonged standing (10 d.) reproducibly affords crystals of **III** in rather poor yield (~1%).[12] The structures of **II** and **III** have been determined (Figure 1).[13] Both molecules are neutral and adopt a distorted Roussin-like cuboidal structure with $MoFe_3S_3$ cores. *These cores represent distorted versions of the $MoFe_3S_3$ unit in the cofactor of nitrogenase for which no synthetic analog is currently available.* In **II**, two of the Fe atoms are five coordinate (one square pyramidal and the other trigonal bipyramidal) at a distance of 3.636(1) Å from each other, and each is bound to two CO, two $\mu_3\text{-}S^{2-}$ and one Et_3P ligands. The third iron, bound to two CO and two $\mu_3\text{-}S^{2-}$ ligands, shows a distorted tetrahedral coordination and is found at 2.625(1), 2.701(1), and 2.680(1) Å from the other two irons and the Mo atom, respectively. The formally Mo^{IV} atom is square pyramidal with two catecholate oxygen donors and two $\mu_3\text{-}S^{2-}$ ligands in the equatorial plane ($Mo-S = 2.305(1)$ Å) and the other $\mu_3\text{-}S^{2-}$ ligand in the axial position. The "axial" Mo−S(1) bond at 2.213(1) Å is short but not quite as short as the Mo═S bonds in various thiomolybdates that usually are found[14] between 2.055 and 2.157 Å. A total electron count of $60e^-$ for this coordination/organometallic hybrid cluster would require each metal to bind to three of its neighboring atoms. This does not appear to be the case as five of the M−M distances are found within the range of 2.625(1)−2.902(1) Å and one is very long at 3.636(1) Å.

In the structure of **III** a crystallographic mirror plane bisects the cluster and contains the Mo, O, Fe, and S atoms. The molecule could be described as a derivative of **II** with a $(O)Mo^{VI}$ in place of the Mo^{IV} ion. The structural details of **III** however suggest that the molecule contains a $Mo^{IV}{=}O$ group and therefore the two electron oxidation may involve the $[Fe_3S_3]$ core.[15] The Mo═O (1.672(1) Å) group *trans* to one of the $\mu_3\text{-}S^{2-}$ ligands results in a distorted $MoFe_3S_3$ core by comparison to the one in **II**. The S^{2-} ligand *trans* to the Mo-bound oxo group, in addition to the weak bond it forms with the Mo atom (2.597(1) Å), is bound to all three of the iron atoms and can be described as a $\mu_4\text{-}S^{2-}$ ligand. The 66 valence electrons of **III** would require six electrons for M−M bond formation to satisfy the effective atomic number of $18e^-$ per M. This appears to be the case as three short M−M bonds from the central Fe atom to the other metal atoms in the cluster are found in the range 2.570(1)−2.691(1) Å. The $\mu_4\text{-}S^{2-}$ ligand interaction with the Fe atom on the mirror plane occupies a coordination site that could be freed for an additional ligand for the Fe atom, if the $\mu_4\text{-}S^{2-}$ ligand was converted to an $\mu_3\text{-}S^{2-}$ ligand. *The possibility of $\mu_4\text{-}S^{2-}$ ligands serving as sites of nascent coordination unsaturation is intriguing, particularly with reference to $[M(\mu_3\text{-}S)]_n$ clusters that at first sight appear coordinatively saturated.* The cyclic voltammetry of **II** on a glassy carbon electrode, in CH_2Cl_2 solution, shows two quasireversible reduction waves at −0.756 and −0.888 V and an irreversible oxidation at 0.846 V.[16] In a formal sense the oxidized $[(cat)Mo^{IV}]^{2+}$ and $[(cat)(O)Mo^{IV}]$ subunits in **II** and **III** are bridged to reduced $[Fe_3S_3]^{2-}$ and $[Fe_3S_3]$ subunits, respectively, in a description that emphasizes the multisite character of these clusters. Currently, the ability of **II** and **III** and their reduced forms to serve as catalysts in the reduction of nitrogenase substrates is the focus of our attention.

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Supporting Information Available: Tables S1 and S2, containing listings of data collection parameters, positional parameters, thermal parameters, and selected distances and angles of **II** and **III** (16 pages). Ordering information is given on any current masthead page

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(12) Data for **II**: Anal. Calcd for $MoFe_3S_3P_2Cl_4O_8C_{24}H_{30}$: C, 28.54; H, 2.99. Found: C, 28.33; H, 2.87. IR Spectrum: ν(C−O), 1900 (m), 1937 (vs), 1961 (vs), 1977 (s), 2003 (vs), 2026 cm^{-1} (s). Data for **III**: Anal. Calcd for $Mo(O)Fe_3S_3P_3Cl_4O_7C_{29}H_{45}$: C, 31.21; H, 4.06. Found: C, 31.43; H, 4.11. IR spectrum: ν(C−O), 1893 (m), 1959 (vs), 1974 (vs), 1989 (s), 2021(vs), ν(Mo═O), 928 cm^{-1}.

(13) Black crystals of **II** are monoclinic space group $P2_1/c$ with $Z = 4$. The cell dimensions (Å, deg) are $a = 14.962(3)$, $b = 15.571(3)$, $c = 16.047(3)$, and $\beta = 103.7(3)$, Black crystals for **III** are orthorhombic, space group *Pnma* with $Z = 4$, $a = 24.966(5)$ Å, $b = 14.783(3)$ Å and $c = 11.875(2)$ Å. Single-crystal X-ray diffraction data for both **II** and **III** were collected on a Nicolet P3m diffractometer using Mo Kα radiation. The solutions of all structures were carried out by a combination of heavy-atom Patterson techniques, direct methods, and Fourier methods. Full-matrix refinement of 346 parameters on 3392 data ($2\theta = 40°$, $I > 2\sigma(I)$) for **II** and 254 parameters on 2984 data ($2\theta = 45°$, $I > 2\sigma(I)$) for **III** converged to final R (wR_2) values of 0.030 (0.094) and 0.054 (0.164), respectively.

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(15) The oxidation state of the Fe atoms in **III** can be evaluated by comparative Mossbauer spectroscopic studies currently under way.

(16) The potentials are reported vs Ag/AgCl as a reference electrode using tetrabutylammonium hexafluorophosphate as supporting electrolyte. In the same cell, under identical conditions, ferrocene undergoes oxidation at 0.409 V.