spectroscopy and thermochemistry of these species are underway.

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New Mo–Fe–S Clusters via Oxidative Decarbonylation Reactions: The $[MoFe_5S_6(CO)_6L_3]^{n-}$ (L = PEt_3, $n = 0$; L = I, $n = 2$) Capped Cubanes

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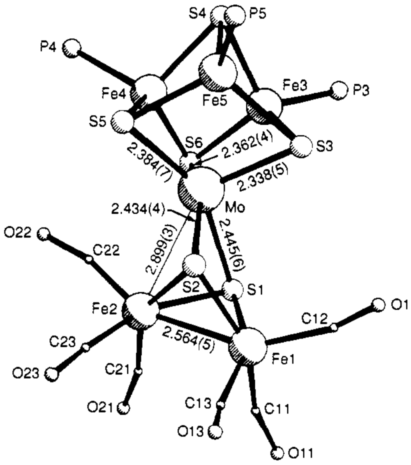
We have recently reported[2,3] a novel approach to the synthesis of Mo–Fe–S clusters as models for the iron-molybdenum cofactor (FeMo-co)[4] of nitrogenase, a small dissociable cluster of approximate stoichiometry[4,5] $MoFe_{6-7}S_{8-10}$ and as yet unknown structure that appears to constitute the site at which dinitrogen is reduced by the enzyme.[6] Our approach differs from other attempts to produce synthetic models[7,8] of FeMo-co in that the Mo–S–Fe unit(s) are formed by reaction of the $[Fe_2S_2(CO)_6]^{2-}$ ion[9] with various molybdenum sources; it has been the first to produce high-nuclearity clusters with >4Fe/Mo that approximate the core composition and Mo–Fe distance distribution of FeMo-co, e.g., the $[MoFe_6S_6(CO)_{16}]^{2-}$ ion (I).[2] Articulation of clusters such as I into more accurate structural models for FeMo-co requires the development of methodology for oxidative decarbonylation with preservation of the high-nuclearity nature of the cluster. We report herein initial results indicating that such reactions can be effected and that they produce Mo–Fe–S clusters with unusual and potentially relevant structures.



Mo-Fe3	2.655(3)	Fe3-Fe4	2.607(5)
Mo-Fe4	2.668(3)	Fe4-Fe5	2.605(4)
Mo-Fe5	2.677(3)	Fe3-Fe5	2.611(5)

Figure 1. PLUTO drawing of the $MoFe_5S_6(CO)_6(PEt_3)_3$ cluster, showing the atomic numbering scheme and selected interatomic distances. The ethyl groups on the PEt_3 ligands have been omitted for clarity.

Reaction of the Et_4N^+ salt of I[2] with 2 equiv of I_2 in THF at room temperature results in evolution of CO and formation of a dark brown solution. Removal of THF in vacuo, followed by dissolution in a minimal amount of MeCN, filtration, addition of Et_2O, and cooling to −20 °C overnight, produces $(Et_4N)_2[MoFe_5S_6(CO)_6I_3]$ (II) in virtually quantitative yield.[10] Although X-ray quality crystals of II have not yet been obtained, its identity is inferred by comparison to the phosphine derivative $MoFe_5S_6(CO)_6(PEt_3)_3$ (III), which precipitates as microcrystals in 50–60% yield upon addition of 3 equiv of PEt_3 to a solution of II in MeCN at room temperature.[11] The identity of III has been established by a single-crystal X-ray diffraction study,[12] which together with spectroscopic and magnetic studies demonstrates the existence of novel "capped-cubane" clusters containing the $[MoFe_5S_6(CO)_6]^{0,+}$ cores in III and II, respectively.

The structure of cluster III (Figure 1) consists of an $MoFe_3S_4$ cubane "capped" by an $Fe_2S_2(CO)_6$ unit to produce the $MoFe_5S_6(CO)_6$ core stoichiometry. Notable features of the structure include the following. (i) One Fe atom of I has been lost during the reaction, with retention of all six S atoms. (ii) An Fe–Mo bonding interaction is observed in the $MoS_2Fe_2(CO)_6$ unit: the Mo–Fe(2) distance is 2.899 (3) Å vs 3.614 (3) Å for Mo–Fe(1). This is compensated for by an increase of ca. 0.1 Å in the Fe(1)–Fe(2) distance vs the parent $Fe_2S_2(CO)_6$. Such a bonding interaction between the central metal and one of the Fe atoms of "a discrete $Fe_2S_2(CO)_6^{2-}$ unit" has not been previously ob-

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(10) Anal. Calcd for $(Et_4N)_2[MoFe_5S_6(CO)_6I_3]$, $C_{22}H_{40}Fe_5I_3MoN_2O_6S_6$: C, 19.18; H, 2.91; Fe, 20.28; I, 27.65; Mo, 6.97; N, 2.03; S, 13.97. Found: C, 19.03; H, 3.01; Fe, 19.74; I, 27.06; Mo, 6.76; N, 1.98; S, 13.89.

(11) The extreme oxygen sensitivity of III made obtaining reproducible elemental analysis data extremely difficult; the following values are typical of the ≥4 analyses obtained. Anal. Calcd for $MoFe_5S_6(CO)_6(PEt_3)_3$, $C_{24}H_{45}Fe_5MoO_6P_3S_6$: C, 26.44; H, 4.16; Fe, 25.62; Mo, 8.80; P, 8.52; S, 17.65. Found: C, 26.91; H, 4.25; Fe, 23.49; Mo, 8.50; P, 7.24; S, 18.28.

(12) Crystals of III were obtained by addition of excess Et_3P to a filtered reaction mixture containing $(Et_4N)_2[MoFe_6S_6(CO)_{16}]$ (1 equiv), I_2 (2 equiv) and ca. 20 equiv of LiCl in MeCN, followed by cooling to −20 °C overnight. The compound is virtually insoluble in MeCN and was obtained in very low yields by this method. X-ray diffraction measurements were performed on an Enraf-Nonius CAD4 four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Data were collected by the θ–2θ technique over the range $1.0° \geq 2\theta \geq 50°$. A total of 2857 reflections with $I \geq 3\sigma(I)$ were used in the refinement. III crystallizes in the triclinic space group $P\bar{1}$, with $a = 10.760$ (3) Å, $\beta = 11.726$ (4) Å, $c = 18.558$ (5) Å, $\alpha = 80.80$ (4)°, $\beta = 85.42$ (3)°, $\gamma = 70.30$ (4)°, $V = 2175$ (3) Å^3, and $Z = 2$. The structure was solved by using the direct-methods program MULTAN; least-squares refinement gave $R = 4.7\%$ and $R_w = 6.2\%$ with anisotropic thermal parameters for all non-hydrogen atoms.

served.[3,13-16] As a result of this interaction, cluster III has only C_1 symmetry, with four Fe atoms at bonded distances to Mo. This may be relevant to the structure of FeMo-co, as the most recent EXAFS results on nitrogenase[17] suggest the presence of four Fe atoms as neighbors to Mo, and recent ENDOR studies[18] have been interpreted as favoring a low-symmetry structure for FeMo-co. (iii) The dimensions of the $MoFe_3S_4^{2+}$ cubane unit in III are anomalous compared to those of other clusters containing such units.[7a,19] The mean Mo–Fe and Fe–Fe distance are only 2.67 and 2.61 Å, respectively, which are 0.05 and 0.1 Å *shorter* than those observed in other single- and double-cubane clusters,[7a,19] while the mean Mo–S and Fe–S distances of 2.36 and 2.25 Å, respectively, are not unusual.[7a,19] (iv) The mean Mo–S distance in III (2.39 Å) is 0.06 Å shorter than that in I, consistent with a formal Mo oxidation state of ca. +3 and comparable to the value of 2.37 Å observed by EXAFS for FeMo-co.[17] This indicates that reaction of I with I_2 proceeds by oxidation of both the Fe and Mo sites. (v) The Fe atoms of the $MoFe_3S_4$ cubane are ligated by PEt_3 groups, with a mean Fe–P distance of 2.33 Å. This result is somewhat surprising, since no $MoFe_3S_4$ cubanes with phosphine ligands to Fe have been reported, although phosphines do bind at the Mo site.[19,20] High-nuclearity Fe–S–PR_3 clusters such as $[Fe_6S_8(PEt_3)_6]^{2+}$,[21a] $Fe_7S_6(PEt_3)_4Cl_3$,[21b] and $Fe_6S_6(PBu_3)_4Cl_2$[21c] have been reported, but there appears to be little correlation of Fe–P bond distances with formal Fe oxidation state.[21c]

Elemental analyses and IR spectra (CH_2Cl_2; ν(CO): (III) 2051 (s), 2012 (s), 1983 (m), 1967 (sh), 1946 (sh); (II) 2058 (s), 2020 (s), 1993 (m), 1976 (sh), 1963 (sh) are consistent with the presence of a similar "capped-cubane" structure in the iodide complex, II, as well. The stoichiometry, the blue shift of ca. 10 cm^{-1} in all CO stretching modes, and the comparative electronic properties of II vs III, however, make it clear that the $MoFe_5S_6(CO)_6$ core of II is one electron more oxidized than that in III and that the oxidation is centered on the $MoFe_3S_4$ cubane, which thus has a net 3+ charge (corresponding to the $MoFe_3S_4^{3+}$ or α core observed by Holm et al. in the single cubane clusters[7a,22]). Thus, variable temperature magnetic susceptibility measurements from 4 to 300 K are consistent with the presence of an $S = {}^3/_2$ ground state for II ($\mu_{eff} = 4.20 \pm 0.05\ \mu_B$ over the range 20–100 K), but with appreciable population of higher spin levels at $T > 100$ K (μ_{eff}, μ_B (T, K) = 4.43 (156), 4.67 (235), 4.93 (298)). The $MoFe_3S_4^{3+}$ core of the single cubane clusters exhibits room temperature magnetic properties due to an $S = {}^3/_2$ state,[7a,22] suggesting that the Mo–Fe interaction in the $MoS_2Fe_2(CO)_6$ unit results in the presence of low-lying excited states that are partially populated at room temperature. The EPR spectrum of II (ca. 1 mM in MeCN) at ca. 15 K exhibits g values of 4.34, 2.95, and 2.01, consistent with a rhombically distorted $S = {}^3/_2$ ground state. Similarly, magnetic data for III are consistent with an $S = 2$ ground state (as reported for the $MoFe_3S_4^{2+}$ or β core[22,23]) ($\mu_{eff} = 5.10 \pm 0.10\ \mu_B$ over the range 4–35 K, increasing to a value of 6.43 μ_B at room temperature), but as with III, population of higher spin excited states is appreciable at higher temperatures. The chemical shifts of the Et_3P ligands decrease with increasing temperature, consistent with the observed magnetic behavior (CD_3CN; isotropic shifts in ppm vs Et_3P diamagnetic reference (T, °C): (PCH_2CH_3) 16.69 (−30), 12.86 (45); (PCH_2CH_3) 2.66 (−30), 2.16 (45)). Electrochemical measurements show the expected[7a,24,25] one-electron-transfer process for the $[MoFe_5S_6(CO)_6]^{+/0}$ redox couples (cyclic voltammetry at Pt; 200 mV/s; potentials vs SSCE): (II) −0.77 V, reversible (50 mM $Et_4N^+I^-$/40 mM $Bu_4N^+PF_6^-$ in CH_3CN); (III) −1.09 V, quasi-reversible (50 mM $Bu_4N^+PF_6^-$ in THF)). In addition, III shows a quasi-reversible oxidation at +0.13 V. These values are in the range observed for the single cubane clusters[7a] and are consistent with localization of the reduction/oxidation on the $MoFe_3S_4$ subunit of the clusters.

Clusters II and III thus constitute members of a novel class of high-nuclearity Mo–Fe–S cluster. Their stoichiometry, their low symmetry, and the presence of an additional Mo–Fe bonding interaction external to the $MoFe_3S_4$ cubane unit immediately suggest that elaboration to more realistic FeMo-co models may be possible by further oxidative decarbonylation. Variations of the chemistry described above have been found to effect total decarbonylation of I–III and will be the subject of future communications.

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Supplementary Material Available: Tables of positional and thermal parameters and bond lengths and angles for III (10 pages); table of observed and calculated structure factors for III (17 pages). Ordering information is given on any current masthead page.

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Studies on Tumor Promoters. 7. The Synthesis of a Potentially General Precursor of the Tiglianes, Daphnanes, and Ingenanes[1]

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The phorbol esters (e.g., **1a**, Scheme I) have been vigorously studied over the past half-century since the discovery that these *noncarcinogenic* compounds amplify the effect of certain carcinogens in animals.[2] Recent epidemiological studies[2a,3] and the

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(1) (a) Presented in part at the 194th National Meeting of the American Chemical Society, New Orleans, LA, 1987; paper CHED 49. (b) Taken in part from the Ph.D. Dissertation of H.Y.L., Stanford University, 1988.

(2) For a recent comprehensive treatment of this subject and lead references, see: (a) *Naturally Occurring Phorbol Esters*; Evans, F. J., Ed.; CRC: Boca Raton, FL, 1986. (b) *Mechanism of Tumor Promotion*; Slaga, T. J., Ed.; CRC: Boca Raton, FL, 1984; Vols. I–IV. (c) Hecker, E.; Adolf, W.; Hergenhahn, M.; Schmidt, R.; Sorg, B. In *Cellular Interactions by Environmental Promoters*; Fujiki, H., et al, Eds.; Japan Science Society: Tokyo/VNU Science, Utrecht, 1984; pp 3–36. (d) Weinstein, I. B.; Galtoni-Celli, S.; Kirschmeier, P.; Lambert, M.; Hsiao, W. In *Biochem. Basis Chem. Carcinogenesis*; Greim, H. et al., Eds.; Raven: New York, 1984; p 193. (e) Hecker, E. *Arzneim.-Forsch.* **1985**, *35*(II), 12a, 1890. (f) Blumberg, P. M. *Cancer Res.* **1988**, *48*, 1. (g) A common but nonsystematic numbering system is used herein; for the Chemical Abstractions numbering, see: Tseng, S. S.; Van Duuren, B. L.; Solomon, J. J. *J. Org. Chem.* **1977**, *42*, 3645.

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