Use of Preassembled Fe/S and Fe/Mo/S Clusters in the Stepwise Synthesis of Potential Analogues for the Fe/Mo/S Site in Nitrogenase

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Received July 9, 1990 (Revised Manuscript Received September 24, 1990)

The extraordinary specificity and efficiency of metalloenzymes in catalysis are well recognized. Many reactions that are carried out in industrial processes catalytically, under severe conditions of temperature and pressure, occur in biological systems under ambient conditions. Understanding structure–function relationships for the catalytically active metal sites in metalloenzymes not only presents an intellectual challenge but also is expected to focus attention on hitherto unknown avenues leading to the design of new catalytic systems. Over the last two decades, a considerable amount of structural and spectroscopic information has been obtained for the metal centers in various metalloenzymes, and for many, a reasonable level of structural definition has become available. As a consequence of this progress in metalloenzymology, an intense interest in the synthesis of analogues for metalloenzyme active sites has emerged and has become a major area for research in the subdiscipline of bioinorganic chemistry.

Biological nitrogen fixation is a remarkable enzymatic process that facilitates the enzymatic reduction of dinitrogen to ammonia.[1] The importance of an Fe/Mo/S active center in the catalytic reduction of nitrogen to ammonia by nitrogenase has stimulated research in the

area of Fe/Mo/S cluster chemistry. Nearly 10 years ago, in an earlier Account we described[2] our initial attempts toward the synthesis of Fe/Mo/S complexes as possible precursors for nitrogenase active site analogues. Since then, work in this area by our group and others has continued, and significant contributions to the cluster chemistry of Fe/Mo/S systems have been made. Nevertheless, the synthesis of an acceptable analogue for the active site in nitrogenase still remains an unfulfilled goal. In this Account we present an update of our continuing work in this area.

Nitrogenase

The Fe/Mo/S aggregate present in the Fe–Mo component of nitrogenase[1] is recognized now as the site where elemental nitrogen is activated and reduced to ammonia, and it can be isolated as an extractable cofactor (FeMo-co).[3] Evidence for the intimate relation of this cofactor to the reduction of N_2 to ammonia is provided by the observation that extracts of nitrogenase from inactive mutant strains of microorganisms, that do not contain the Fe/Mo/S center, are activated upon addition of the FeMo-co.[3] The cofactor appears to be a small anionic cluster that does not contain amino acids[4] and, according to recent reports, may contain homocitrate.[5] The FeMo-co has been proven exceedingly difficult to crystallize, and its structure still re-

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mains to be determined. The elemental composition of the FeMo-co has been the subject of numerous elemental analyses,[3,6,7] and the latest of these[7] indicates an Fe:Mo:S ratio of $(7 \pm 1):1:(8 \pm 1)$.

A multitude of spectroscopic techniques have been employed in the study of the heteronuclear Fe/Mo/S site in nitrogenase and the nitrogenase cofactor. From a structural point of view the successful application of X-ray absorption spectroscopy (XAS) to the Fe/Mo/S site in nitrogenase has been an invaluable tool. The Mo extended X-ray absorption fine structure (EXAFS) analyses[8] indicate a Mo coordination sphere that contains as major features three to four sulfur atoms at 2.35 Å, two to three iron atoms at ~2.7 Å, and two to three light atoms (O, N) at 2.1 Å. The analyses of Fe EXAFS,[9,10] are consistent with an average Fe coordination environment of 3.4 ± 1.6 S(Cl) atoms at 2.25 (2) Å, 2.3 $\pm$ 0.9 Fe atoms at 2.66 (3) Å, 0.4 $\pm$ 0.1 Mo atom at 2.76 (3) Å, 1.2 $\pm$ 1.0 O(N) atoms at 1.81 (7) Å, and perhaps a second shell of Fe atoms[10] at a distance of 3.75 Å. Collectively the XAS data strongly suggest the possible presence of $Fe(\mu_2\text{-}S)_2Fe$ and $Mo(\mu_2\text{-}S)_2Fe$ units with Fe–Mo, Fe–S, Fe–Fe, and Mo–S distances of ~2.7, ~2.25, ~2.66, and ~2.35 Å, respectively. Spectroscopic results that further constrain the requirements imposed on the synthesis of active-site analogues have been obtained for nitrogenase by (a) Mossbauer studies that have shown an aggregate of six iron atoms each in a distinct magnetic environment coupled to an overall $S = ^3/_2$ spin system;[11,12] (b) [57]Fe electron nuclear double resonance (ENDOR) studies[13] that show a multitude of [57]Fe signals (five or six doublets) and indicate a rather asymmetric structure in which the iron atoms roughly can be grouped into two sets of trios, each set having very similar hyperfine parameters; and (c) [95]Mo ENDOR studies[13] that identify the presence of one molybdenum per spin system in a possible Mo oxidation state of +4.

In more recent developments, new nitrogenase systems that contain V in place of Mo have been isolated from *Azotobacter vinelandii* and *Azotobacter chroo-*
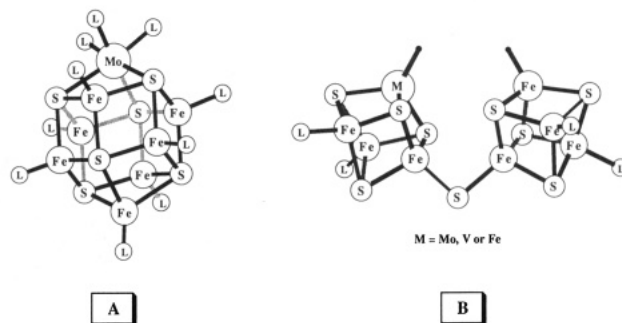
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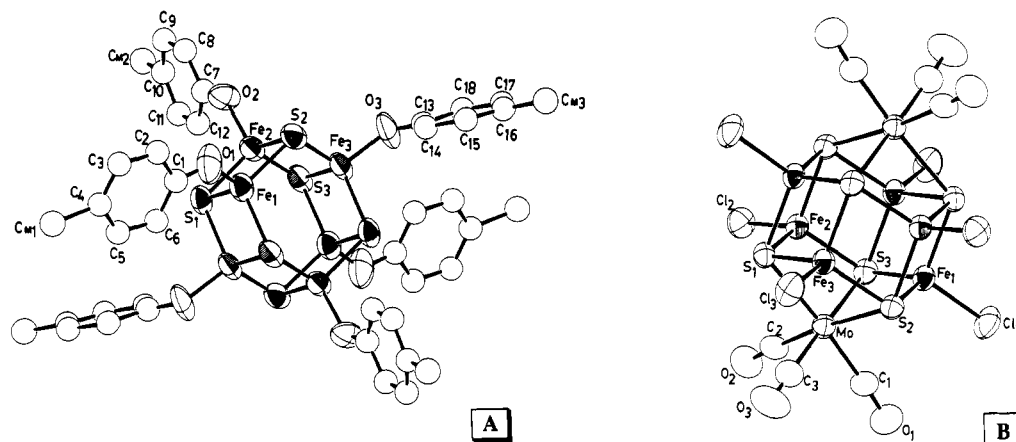
Figure 1. Proposed models for the Fe/Mo/S center in nitrogenase: A, the pentlandite model;[22] B, the double-cubane model.[24]

coccum and function under conditions of molybdenum deficiency.[14] In addition, a nitrogenase that does not contain either Mo or V has been isolated from a *nif*HDK deletion strain of *A. vinelandii* and may contain Fe in place of Mo.[15,16] The structural similarity of the "conventional" Fe/Mo/S centers to the Fe/V/S center in the V-nitrogenase stems from V EXAFS studies on the V–Fe protein from *A. chroococcum*.[17] These studies indicate a V coordination sphere very similar to that of the Mo coordination sphere in the Mo-nitrogenases.

The structural information available from the EXAFS analyses has been inspiring in the design of a plethora of proposed[18] structural models for the Fe/Mo/S site in nitrogenase. The latter include certain clusters that can be envisioned as derivatives of already known Fe/S compounds. Of the proposed models, many are based on an acceptable Fe:Mo:S stoichiometry but none has been obtained synthetically.

Approaches to the Synthesis of Fe/Mo/S Clusters

In recent years, synthetic Fe/Mo/S clusters have been obtained mostly either by the spontaneous self-assembly, SSA, of appropriate reagents[18] or by coordination of the MoS_4^{2-} ligand to certain $Fe(L)_2$ units.[2] The heterometallic complexes thus obtained display diverse structures and with no exception contain Fe-S_2Mo rhombic units. The principle and practice of SSA have been proven successful in the synthesis and isolation of analogue clusters that contain the Fe_2S_2 and Fe_4S_4 cores.[19] The SSA approach in the synthesis of Fe/Mo/S clusters[18] has made available various thermodynamically stable heteronuclear products that, as of now, do not include one with an Fe:Mo:S atom ratio similar to that in nitrogenase. Similarly, the smaller

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Figure 2. Representative structures of the $[Fe_6S_6(L)_6]^{n-}$ prismanes and their $Mo(CO)_3$ adducts: A, structure of the $[Fe_6S_6(p\text{-}CH_3C_6H_4O)_6]^{3-}$ cluster;[25e] B, structure of the $[Fe_6S_6(Cl)_6(Mo(CO)_3)_2]^{3-}$ cluster.[29e]

dinuclear or trinuclear MoS_4^{2-}-Fe complexes[2] have been found rather unreactive as "building blocks" toward the stepwise synthesis of larger clusters.

A third approach toward the synthesis of Fe/M/S aggregates consists of the use of preassembled Fe/S clusters in reactions with Mo reagents. In addition to the Fe_6S_6 "prismane"–Mo derivatives and the Fe/Mo/S doubly bridge double cubanes obtained in our laboratory (vide infra), the synthesis of the $[MoOFe_5S_6(CO)_{12}]^{2-}$,[20] $[MoFe_6S_6(CO)_{16}]^{2-}$,[21a] and $[MoFe_5S_6(CO)_6L_3]^{n-}$ clusters[21b] from $[Fe_2S_2(CO)_6]^{2-}$ also have been accomplished by this approach. The latter closely approach the nitrogenase cofactor stoichiometry and could be considered as acceptable models provided that they retain their integrity upon replacement of the carbonyl ligands with biologically relevant ligands.

Preassembled Fe/S and Fe/Mo/S Clusters as "Building Blocks"

Two structures proposed for the Fe/Mo/S center in nitrogenase that appear particularly appealing, at least from a structural point of view, are shown in Figure 1. One of these structures[22] (Figure 1A) contains the cubic $MoFe_7S_6$ core and structurally is related to the mineral pentlandites and the known $[Co_8S_6(SPh)_8]^{4-}$ clusters[22] and $[Fe_8S_6(I)_8]^{3-}$ clusters.[23] The other, Figure 1B, consists of two cubane units (Fe_4S_4 and $MoFe_3S_4$) singly bridged bu a μ_2-S^{2-} ligand.[24] A conceptually simple synthesis of the former of these structures became apparent upon discovery of the $[Fe_6S_6Cl_6]^{2-,3-}$ clusters and derivatives.[25] The bridged-cubane "model" (Figure 1B) was conceived as a realistic and experimentally attainable structure on the basis of its anticipated simple

synthesis by the assembly of known, preformed structural components.

$[Fe_6S_6L_6]^{2-,3-}$ Clusters

The $[Fe_6S_6L_6]^{n-}$ clusters (Figure 2A) (L = Cl$^-$, Br$^-$, n = 3;[25a,b] L = Cl$^-$, Br$^-$, n = 2;[25c] L = p-RC$_6$H$_4$O$^-$, n = 3, 4[25d-f]) are characterized by paramagnetic, $S = \frac{1}{2}$ (n = 3), and diamagnetic, S = integer (n = 2), ground states. The $(Fe_6S_6X_6)^{3-}$ clusters (X = Cl, Br) are obtained by SSA reactions similar to those employed for the synthesis of the $(Fe_4S_4X_4)^{2-}$ cubanes. Unlike the $[Fe_4S_4]^{2+}$ and $[Fe_2S_2]^{2+}$ cores that are ubiquitous in biological systems and occur in various 4Fe and 2Fe ferredoxins,[19] the existence of $[Fe_6S_6]^{2+,3+}$ cores in Fe/S proteins has not been demonstrated unequivocally. The discovery of Fe_6S_6 centers in proteins, however, may be forthcoming, and a recent report suggests that an $[Fe_6S_6]^{3+}$ center indeed may be present in an Fe/S protein from *Desulfovibrio vulgaris*.[26]

$[Fe_6S_6L_6(M(CO)_3)_2]^{3-,4-}$ Octanuclear Clusters

The Fe_6S_6 core in the $[Fe_6S_6(L)_6]^{3-}$ prismanes (Figure 2A) is very nearly an exact fragment of the cubic metal sulfide cages found in the mineral pentlandites such as Co_9S_8[27] or $(Ni,Fe)_9S_8$.[28] In the latter, and also in the structure of the synthetic $[Co_8S_6(SPh)_8]^{4-}$ cluster,[22] recognizable M_8S_6 units consist of a cube of metal atoms inscribed into an octahedron of μ_4-S^{2-} ligands. The generation of a pentlandite type of $M_2Fe_6S_6$ cage from the prismane Fe_6S_6 core can be accomplished if one M atom is added to each of the two Fe_3S_3 faces of the Fe_6S_6 structural unit. The feasibility of effecting this addition has been explored by using the $[Fe_6S_6L_6]^{3-}$ prismanes as tridentate ligands in ligand substitution reactions with the $(CH_3CN)_3M(CO)_3$ complexes, M = Mo, W. The $[Fe_6S_6(L)_6(M(CO)_3)_2]^{n-}$ adducts (Figure 2B, n = 3, 4) are obtained in pure form[29] only when an approximate 2-fold molar excess of the $M(CO)_3$-

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Table I
Selected Structural and Spectroscopic Features of the $[Fe_6S_6(L)_6(Mo(CO)_3)_2]^{n-}$ Clusters

L	p-CH$_3$C(O)C$_6$H$_4$O$^-$	p-CH$_3$C$_6$H$_4$O$^-$	p-CH$_3$OC$_6$H$_4$O$^-$	p-(CH$_3$)$_2$NC$_6$H$_4$O$^-$	Cl$^-$	Br$^-$
n	4	3 [4][a]	3 [4][a]	3	3 [4][a]	3
Fe–Mo, Å	3.00 (2)	2.96 (1)	–	–	2.929 (3); [3.00 (1)]	2.95 (2)
Mo–S, Å	2.649 (6)	2.589 (3)			2.579 (3); [2.619 (3)]	2.572 (7)
L–M$_{CT}$,[b] nm	436	468; [426]	480; [420]	520	[370 (sh)]	314
$E_{1/2}$,[c] V						
3–/4–	–0.16	–0.29; [–0.29]	–0.31; [–0.31]	–0.40	+0.05; [+0.05]	+0.08
4–/5–	–0.67	–0.87; [–0.87]	–0.87; [–0.87]	–0.91	–0.54; [–0.54]	–0.50
Mossbauer[d]						
IS, mm/s	0.62	0.53; [0.60]	0.55; [0.62]	0.54	0.58; [0.63]	0.59
Δ_{eq}, mm/s	1.02	0.84; [1.04]	0.80; [0.87]	0.74	1.08; [1.00]	1.08
ν_{CO}, cm^{-1}	1897	1916; [1885]	1911; [1882]	1909	1945; [1912]	1948
	1832	1865; [1805]	1854; [1797]	1854	1918; [1852]	1912

[a] The values in brackets are for the 4– anions. [b] In CH$_3$CN solution. [c] Measurements in CH$_2$Cl$_2$; for all measurements, the scan rate was 200 mV/s; the potentials are reporteed vs SCE. [d] Isomer shifts (IS) and quadrupole splittings (Δ_{Eq}) at 125 K vs iron metal at room temperature.

(CH$_3$CN)$_3$ reagent is used. When stoichiometric amounts of M(CO)$_3$(CH$_3$CN)$_3$ are used, mixtures of the 1:1 and 2:1 adducts are obtained for L = halide[29e] or RO$^-$.[29f] The final oxidation level (n = 3 or 4) of the isolated adducts depends greatly on the potential of the 3–/4– redox couple for the $[Fe_6S_6(L)_6(M(CO)_3)_2]^{n-}$ clusters. The M(CO)$_3$(CH$_3$CN)$_3$ "reagent" complexes (that are used in excess) can serve as reducing agents for the $[Fe_6S_6(L)_6(M(CO)_3)_2]^{3-}$ clusters when the redox couples of the latter are more positive than –0.30 V. Such is the case when L = Cl, Br, or I, and as a result, only the tetraanionic adducts are obtained with halides as terminal ligands.[29e] The $[Fe_6S_6(L)_6(M(CO)_3)_2]^{4-}$ adducts (L = Cl, Br, I) also can be obtained in very good yields in reactions between M(CO)$_3$(CH$_3$CN)$_3$ and either the $[Fe_2S_2(X)_4]^{2-}$ or the $[Fe_4S_4(X)_4]^{2-}$ clusters.[29f] In these reactions, the M(CO)$_3$ units apparently serve as templates for the assembly of $[Fe_2S_2(X)_2(Sol)_2]^-$ fragments (Sol = CH$_3$CN) that very likely are present under the prevailing reducing synthetic conditions. The redox potentials of the $[Fe_6S_6(L)_6(M(CO)_3)_2]^{n-}$ clusters[29f] (L = p-RC$_6$H$_4$O$^-$, Table I), are affected by the nature of the para substituents in a manner similar to that observed for the parent prismane clusters. With electron-releasing R groups such as CH$_3$ or OCH$_3$, the 3–/4– redox couples are found at potentials more negative than –0.30 V, and as a result, the trianionic adducts that form initially do not undergo further reduction. With the electron-withdrawing C(O)CH$_3$ as a para substituent, the 3–/4– couple is found at –0.20 V, and in the presence of excess M(CO)$_3$(CH$_3$CN)$_3$, reduction of the trianion occurs and only the tetraanionic adduct is obtained.[29f] Chemical oxidation by Fe(Cp)$_2^+$ or reduction by BH$_4^-$ can be used for the synthesis of the trianionic and tetraanionic clusters from their one electron redox counterparts, respectively.

The infrared spectra of the pure 2:1 prismane adducts show two intense C=O bands (Table I). Differences in the frequencies of these bands, between clusters in two different oxidation levels, suggest that the reductions of the trianions affect mainly the M(CO)$_3$ units. In general, lower C=O stretching frequencies are observed in the $[Fe_6S_6(OR)_6(Mo(CO)_3)_2]^{n-}$ adducts.[29f]

The intense (($e \sim$ 1 × 10^4) L$_t$–Fe charge-transfer band in the electronic spectra of the $[Fe_6S_6(ArO)_6$(Mo(CO)$_3$)$_2]^{n-}$ adducts is bathochromically shifted (by ca. 30–50 nm) when compared to the same absorption in the "parent" prismanes. The shift to lower energies is expected for the adducts where the M(CO)$_3$ units

deplete electron density from the core sulfido ligands and indirectly from the iron atoms. The charge-transfer absorption is affected in a predictable manner by the oxidation level of the adducts and by the electronic characteristics of the terminal ligands L (Table I).

The Fe ions in the $[Fe_6S_6(p$-RC$_6$H$_4$O)$_6(M(CO)_3)_2]^{3-,4-}$ (M = Mo, W) clusters are antiferromagnetically coupled. The trianions are characterized by an $S = {}^1/_2$ spin ground state, and their EPR spectra (obtained only at temperatures <15 K) resemble those of the $[Fe_6S_6$-(ArO)$_6]^{3-}$ prismanes.[25] The corresponding tetraanions are EPR silent.
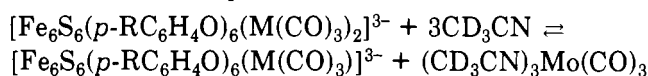
The ^{1}H NMR spectra of the aryloxy prismane adducts, in CD$_3$CN solution at ambient probe temperatures, show isotropically shifted resonances due to the phenoxide protons.[29f] The pattern of alternating signs of the isotropic shifts of the aryl proton resonances is similar to those observed for $[Fe_2S_2(ArO)_4]^{2-}$,[30] $[Fe_4S_4(ArO)_4]^{2-}$,[31] and $[Fe_6S_6(ArO)_6]^{3-}$,[25d,e] and it is typical for MXAr (X = S, O, Se) paramagnetic complexes. The pattern has been attributed previously to dominant Fermi contact interactions (a π delocalization mechanism) with negligible pseudocontact contributions.[32] The isotropic shifts observed for the aryloxy prismane adducts (Table I) are greater in magnitude than those of the $[Fe_6S_6(ArO)_6]^{3-}$ parent prismanes, the $[Fe_2S_2(ArO)_4]^{2-}$ dimers, and the $[Fe_4S_4(ArO)_4]^{2-}$ clusters. This observation suggests that there is more contact between the ring protons and the paramagnetic centers in the Fe$_6$S$_6$ cores of the adducts and, accordingly, may indicate that the Fe--O bond in the latter has more covalent character than that in the parent prismanes. By comparison to the trianionic adducts that have an $S = {}^1/_2$ ground state, the tetraanionic adducts (with an integer spin ground state) show even larger shifts than the trianionic adducts. For each resonance observed for the o-H, m-H, and p-R protons, an additional minor set of resonances (doublets) is present in the spectra of the 3– Mo(CO)$_3$ aryloxide adducts. The relative intensity of this set of doublets increases upon addition of $[Fe_6S_6(p$-RC$_6$H$_4$O)$_6]^{3-}$ and decreases upon addition of (CH$_3$CN)$_3$Mo(CO)$_3$. These observations are con-

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(31) Cleland, W. E.; Holtman, D. A.; Sabat, M.; Ibers, J. A.; Defotis, G. C.; Averill, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 6021.
(32) (a) Holm, R. H.; Phillips, W. D.; Averill, B. A.; Mayerle, J. J.; Herskovitz, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 2109. (b) Reynolds, J. G.; Laskowski, E. J.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5315.

sistent with the equilibrium

$$[Fe_6S_6(p\text{-}RC_6H_4O)_6(M(CO)_3)_2]^{3-} + 3CD_3CN \rightleftharpoons$$
$$[Fe_6S_6(p\text{-}RC_6H_4O)_6(M(CO)_3)]^{3-} + (CD_3CN)_3Mo(CO)_3$$

and suggest that the set of doublets in the spectra is due to the 3− 1:1 adduct. Upon prolonged standing, resonances that can be attributed to traces of free prismane also appear.

With strongly electron releasing para substituents, such as OMe and N(Me)$_2$, the intensity of the signals that arise from the 1:1 adducts is nearly twice that of the signals due to the 2:1 adducts. Indeed, with appropriate counterions, the isolation of pure 1:1 adducts may be possible in stoichiometric reactions between the $[Fe_6S_6(p\text{-}RC_6H_4O)_6]^{3-}$ prismanes (R = OMe and N(Me)$_2$ and (CH$_3$CN)$_3$Mo(CO)$_3$. The ^{1}H NMR spectra of the tetraanionic Mo(CO)$_3$ adducts or of the trianionic W(CO)$_3$ adduct[29] do not show dissociation of M(CO)$_3$.

Structures of the $[Fe_6S_6(L)_6(M(CO)_3)_2]^{n-}$ Clusters

The crystal structures of the centrosymmetric $[Fe_6S_6(L)_6(M(CO)_3)_2]^{n-}$ anions (L = Cl$^-$, Br$^-$, M = Mo, n = 3, 4;[29b,e] L = p-CH$_3$C(O)C$_6$H$_4$O$^-$, M = Mo, n = 4;[29f] L = PhO$^-$, M = W, n = 3[29c]) have been determined. All of these clusters show very similar $[Fe_6M_2S_6]^{2+,3+}$ cores (Figure 2B). These cores are best described as M$_2$Fe$_6$ rhombohedral units of nearly exact D_{3d} symmetry, with the two M atoms located in two opposite corners on the idealized 6̄-axis of the rhombohedron. A quadruply bridging S^{2-} ligand is located on each of the six faces of the rhombohedron (Figure 2B). By comparison to the structure of the $[Fe_6S_6Cl_6]^{n-}$ clusters (Figure 2A), the $[Fe_6S_6]$ subunits in the $[Fe_6M_2S_6]^{2+,3+}$ cores are slightly elongated along the idealized 6̄-axis and show slightly shorter Fe–Fe distances and Fe–S bond lengths.

A structural comparison of the $[Fe_6M_2S_6]$ cores in the trianions and the tetraanions shows no significant differences within the Fe$_6$S$_6$ subunits. However, a significant shortening of the Mo–Fe and the Mo–S distances is found in the trianions. The crystallographic and Mossbauer data (vide infra) suggest that the highest occupied molecular orbital in the tetraanions consists mainly of Mo and S atomic functions and is antibonding in character.

The ^{57}Fe Mossbauer spectra of the $[Fe_6S_6(L)_6(Mo(CO)_3)_2]^{n-}$ clusters at two different oxidation levels (Table I) are similar, consistent with the structural data that also indicate that the Fe$_6$S$_6$ cores are not significantly perturbed as a result of a change in the oxidation level of the cluster. The ^{57}Fe isomer shifts in the $[Fe_6S_6(L)_6(Mo(CO)_3)_2]^{n-}$ clusters, significantly larger than those observed in the "parent" $[Fe_6S_6(L)_6]^{3-}$ clusters, suggest that in the former the Fe$_6$S$_6$ cores assume an oxidation level lower than the $[Fe_6S_6]^{3+}$ core in the $[Fe_6S_6(L)_6]^{3-}$ clusters. In a *formal* sense, both oxidation levels of the adducts can be described as containing the $[Fe_6S_6]^{2+}$ core. In the 3− adducts, this core is bound to Mo in a *formal* +0.5 oxidation state, while in the 4− adducts it is bound to Mo(0).

$[MoFe_3S_4(L)_3(R'_2cat)(L')]^{2-,3-}$ Single Cubanes

The chemistry of the $[MoFe_3S_4(L)_3(3,6\text{-}R'_2cat)(L')]^{2-,3-}$ single cubanes (L = RS$^-$, Cl$^-$; R′ = allyl, n-Pr; L′ = DMSO, DMF, CH$_3$CN, PR$_3$, RS$^-$, CN$^-$, RO$^-$) has been explored in great detail by R. H. Holm and coworkers and has been reviewed elsewhere.[18] The sol-

vated forms of these very important clusters (L = DMSO, DMF, CH$_3$CN) are obtained by solvolysis of the $[Mo_2Fe_6S_8(\mu\text{-}SR)_2(SR)_4(3,6\text{-}R'_2cat)_2]^{4-}$ weakly bridged cubane dimers.[33] The ligated single cubes are obtained readily by substitution of the solvent ligands by other ligands (L = PR$_3$, RS$^-$, CN$^-$, RO$^-$). The coordination environment around the Mo atom in these clusters closely resembles the one suggested by EXAFS analysis for the Mo center in nitrogenase.[18] The $[MoFe_3S_4(Cl)_3(Cl_4cat)(CH_3CN)]^{2-}$[34] (II) and $[Fe_4S_4Cl_4]^{2-}$[35] clusters were chosen as convenient reagents in the coupling reactions that led to the singly or doubly bridged double cubanes.

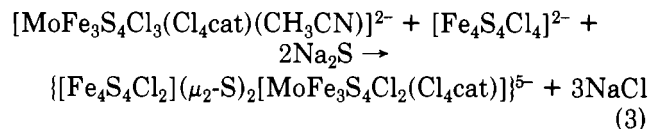### Singly Bridged and Doubly Bridged Double Cubanes

The synthesis of the homometallic singly bridged double cubane $[(Fe_4S_4Cl_3)_2S]^{4-}$ (I) is accomplished readily in CH$_3$CN solution[36] by the reaction
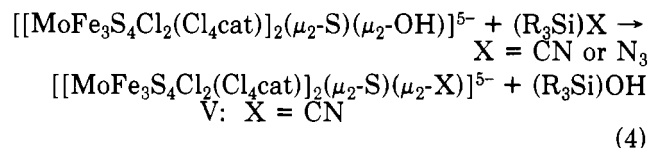
$$2[Fe_4S_4Cl_4]^{2-} + Na_2S \rightarrow [(Fe_4S_4Cl_3)_2S]^{4-} \quad (1)$$
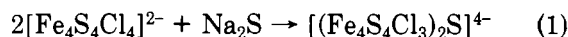
A similar coupling reaction (eq 2) gives in good yield the crystalline (Et$_4$N)$^+$ salt[24] of the heterometallic $[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)_2]^{6-}$ doubly bridged cluster (III) (Figure 3B). A variation of the same reaction in

$$2[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]^{2-} + 2(Et_4N)_2S \rightarrow$$
$$[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)_2]^{6-} \quad (2)$$
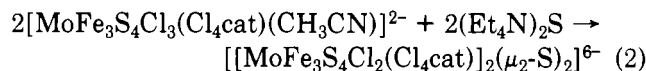
which the (Et$_4$N)$_2$[MoFe$_3$S$_4$Cl$_3$(Cl$_4$cat)(CH$_3$CN)] cluster first is reacted with 0.5 equiv of Et$_4$NOH followed by 0.5 equiv of Li$_2$S gives in good yield the crystalline μ-hydroxo (Et$_4$N$^+$)$_5$[[MoFe$_3$S$_4$Cl$_2$(Cl$_4$cat)]$_2$(μ_2-S)(μ_2-OH)] cluster[24] (IV). From the reaction of Na$_2$S, (Et$_4$N)$_2$[Fe$_4$S$_4$Cl$_4$], and II, in CH$_3$CN (eq 3), the Et$_4$N$^+$ salt of the "mixed cubane" is isolated with a solution EPR spectrum different from that of II but indicative of a $S = {}^3/_2$ ground state.[24] This cluster, which has not

$$[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]^{2-} + [Fe_4S_4Cl_4]^{2-} +$$
$$2Na_2S \rightarrow$$
$$\{[Fe_4S_4Cl_2](\mu_2\text{-}S)_2[MoFe_3S_4Cl_2(Cl_4cat)]\}^{5-} + 3NaCl \quad (3)$$

been fully characterized as yet, most likely has a core structure similar to the one proposed in Figure 1B and possesses an acceptable stoichiometry in reference to the nitrogenase cofactor. The reaction of IV with (R$_3$Si)$_2$S in CH$_3$CN solution gives III in excellent yield. Similar reactions (eq 4) with (R$_3$Si)X (X = CN or N$_3$) occur readily, and products analogous to III or IV can be isolated.[37] Very recently we have obtained[37] the

$$[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}OH)]^{5-} + (R_3Si)X \rightarrow$$
$$X = CN \text{ or } N_3$$
$$[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}X)]^{5-} + (R_3Si)OH$$
$$V: \ X = CN$$
$$(4)$$

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(34) Palermo, R. E.; Holm, R. H. *J. Am. Chem. Soc.* 1983, *105*, 4310.

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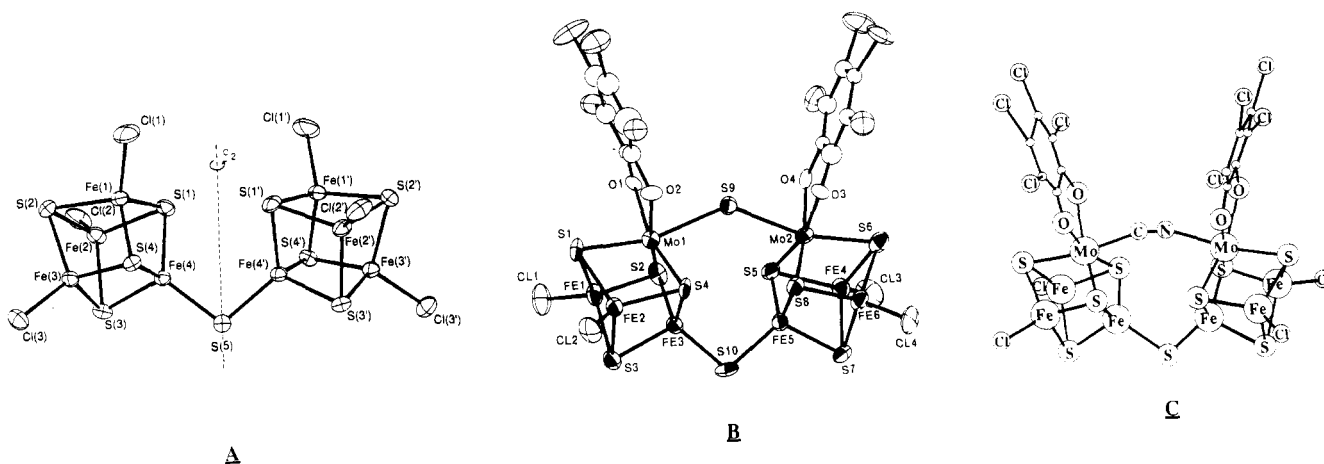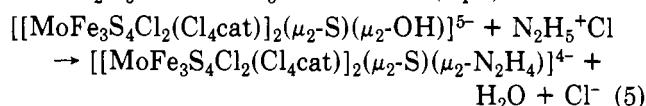(37) Coucouvanis, D.; Challen, P. R.; Koo, S.-M., manuscript in preparation.

Figure 3. Structures of the [(Fe$_4$S$_4$Cl$_3$)$_2$S]$^{4-}$ singly bridged double cubane[36] (I), A; the [[MoFe$_3$S$_4$Cl$_2$(Cl$_4$cat)]$_2$(μ_2-S)$_2$]$^{6-}$ doubly bridged double cubane[24] (III), B; schematic structure of the [[MoFe$_3$S$_4$Cl$_2$(Cl$_4$cat)]$_2$(μ_2-S)(μ_2-CN)]$^{5-}$ cluster[37] (V), C. The structure of the tetraanionic VI is very similar to V, with N$_2$H$_4$ in place of CN$^-$.

Et$_4$N$^+$ salt of the [[MoFe$_3$S$_4$Cl$_2$(Cl$_4$cat)]$_2$(μ_2-S)(μ_2-N$_2$H$_4$)]$^{4-}$ cluster (VI) (Figure 3B) in the reaction of IV with N$_2$H$_5$$^+Cl^-$ in CH$_3$CN solution (eq 5).

[[MoFe$_3$S$_4$Cl$_2$(Cl$_4$cat)]$_2$(μ_2-S)(μ_2-OH)]$^{5-}$ + N$_2$H$_5$$^+$Cl

$\rightarrow$ [[MoFe$_3$S$_4$Cl$_2$(Cl$_4$cat)]$_2$(μ_2-S)(μ_2-N$_2$H$_4$)]$^{4-}$ +

H$_2$O + Cl$^-$ (5)

The electronic spectrum of I is very similar to that of [Fe$_4$S$_4$Cl$_4$]$^{2-}$[35] and shows absorptions at 670 (e $\sim$ 10 700), $\sim$480 (sh, e $\sim$ 17 700), and 240 nm (e $\sim$ 57 500). The electronic spectra of III, IV, V and VI are nearly featureless and show a steadily increasing absorption from 750 nm to the UV region of the spectrum. The cyclic voltammetry of I, in CH$_3$CN solution vs SCE, shows two quasireversible waves at −0.80 and −1.10 V. The two waves presumably arise as a result of the 1e$^-$ reduction of each of the two subclusters. The 300-mV separation between these waves indicates that intercluster interactions in I are substantial. The cyclic voltammetry of the doubly bridged double cubanes (in CH$_3$CN solution vs Ag/AgCl) shows a quasireversible reduction wave between −1.0 and −1.3 V and two quasireversible oxidation waves between −0.10 and +0.04 V. By comparison, the single cube, II, shows a quasireversible reduction at −0.8 V and irreversible oxidation at $\sim$+0.4 V.

The Mossbauer spectrum of I consists of a broad asymmetric quadrupole doublet with average IS (isomer shift) and Δ_{Eq} (quadrupole splitting) values of 0.48 and 0.98 mm/s, respectively. Each of the Mossbauer spectra for III, IV, and VI can be fitted by assuming two doublets in a 2:1 intensity ratio. The major components show IS values that range from 0.50 to 0.53 mm/s and Δ_{Eq} values that range from 1.10 to 1.19 mm/s. The minor components have IS values in the range from 0.30 to 0.34 mm/s and Δ_{Eq} values between 1.05 and 1.13 mm/s. The spectra are consistent with the structures of these clusters that, to a first approximation, show two distinct Fe sites. Furthermore it appears that the two Fe atoms bound to the μ_2-S bridging ligands are at a higher formal oxidation level ($\sim$+3) than the remaining four Fe atoms.

A crystal structure of I shows[36] the tetraanion (Figure 3A) as a μ_2-S^{2-} singly bridged double cubane. The anion is located on a crystallographic 2-fold axis that passes through the μ_2-S^{2-} ligand. The structural details of the

Fe$_4$S$_4$Cl$_3$ subclusters are very similar to those reported[35] for the [Fe$_4$S$_4$Cl$_4$]$^{2-}$ cluster, and the Fe–S bridge bonds at 2.206 (4) Å are similar to those found[35] in [Fe$_2$S$_2$Cl$_4$]$^{2-}$ (2.200 (1) Å). The long Fe–Fe distance across the Fe–μ_2-S–Fe bridge in I, at 3.433 (4) Å, is a direct consequence of intercube S–S repulsions that also result in an oblique Fe–μ_2-S–Fe angle of 102.2°. The structure of III shows the hexaanion (Figure 3B) as a di-μ_2-sulfido doubly bridged double cubane with two homometallic M–μ_2-S–M bridges[24] (M = Mo, Fe). The anion in IV has a similar structure with a μ_2-OH ligand bridging the two Mo atoms.[24] The gross structures of the anions in V and VI (Figure 3C) have been determined from data obtained from the best obtainable, albeit poor quality, crystals. In both of these structures the anions have nearly exact C$_{2v}$ symmetry and are located on crystallographic mirror planes that contain the two, side-on, bridging ligands and bisect the Mo–Mo and Fe–Fe vectors. Among the outstanding structural features in III, IV, V, and VI are short Fe–S bonds in the Fe–μ_2-S–Fe bridge and oblique Mo–μ_2-E–Mo angles of 137.2 (7)° (E = S^{2-}), 158(2)° (E = OH$^-$), 161° (Mo–C–N, E = CN$^-$), and 162° (Mo–N–N, E = N$_2$H$_4$). A decrease in the Mo–Mo distance is observed from 5.221 (8) Å in V and 5.22 (1) Å in VI to 4.296 (8) Å in III, to 4.248 (9) Å in IV, and demonstrates the remarkable flexibility of these molecules, in accepting bridging ligands with differing steric demands. The Fe–μ_2-S–Fe angles and the Fe–Fe distances within the intercube bridges do not show as pronounced a variation and are found at 101.1 (9)° and 3.47 (1) Å in V, 98.7 (8)° and 3.33 (1) Å in III, and 97.8 (8)° and 3.35 (2) Å in IV.

Conclusions and Directions for Future Research

The [Fe$_6$S$_6$(L)$_6$(Mo(CO)$_3$)$_2$]$^{n-}$ adducts possess a Mo:Fe stoichiometry of 1:3, magnetic ground states $S = 1/2$ and $S = 0$ for $n = 3$ and 4, respectively, and structural features that only qualitatively resemble those of the Fe/Mo/S site in nitrogenase. Furthermore, the large size of the highly reduced Mo atoms in these compounds results in Fe–Mo and Mo–S distances considerably longer than those revealed by EXAFS analyses in nitrogenase and the nitrogenase cofactor. Clearly, derivatives of the [Fe$_6$S$_6$(L)$_6$(Mo(CO)$_3$)$_2$] clusters are needed that possess a more acceptable Mo:Fe ratio and
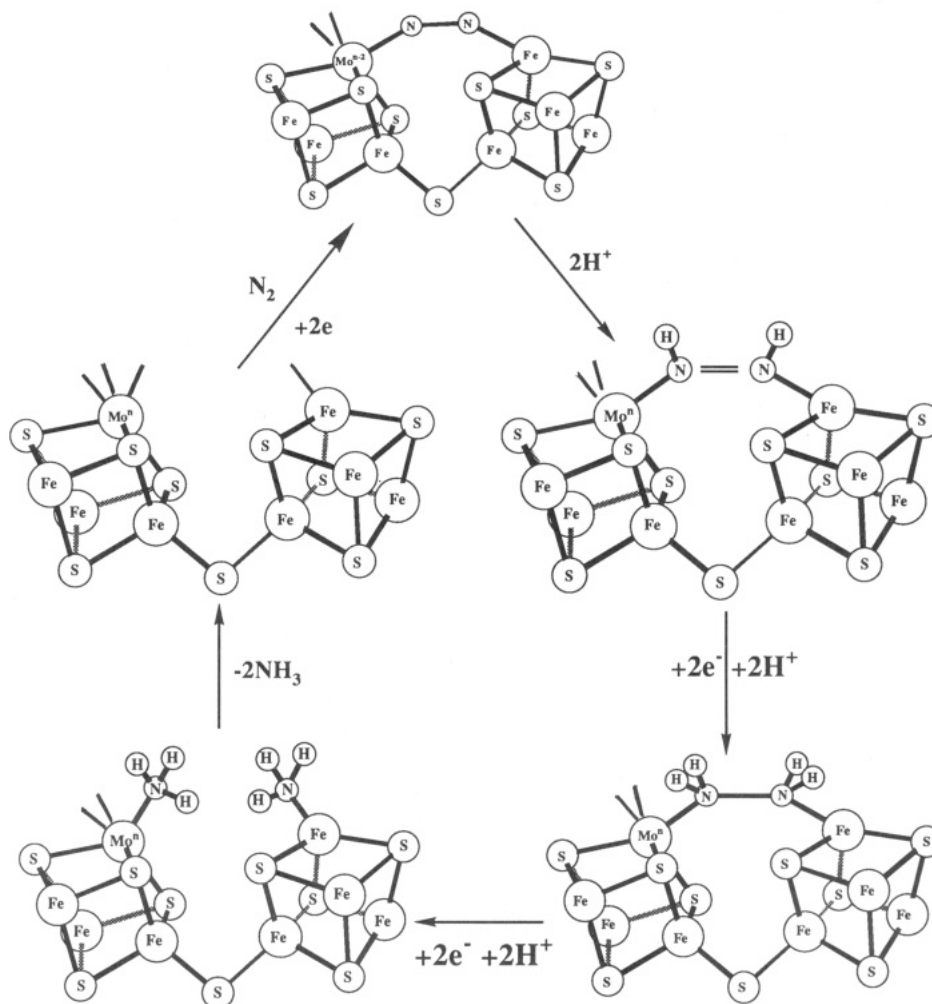
Figure 4. A feasible mechanism for the catalytic reduction of N_2 to NH_3 employing the model shown in Figure 1B.

a Mo atom in a +3 or +4 oxidation state. The former of these requirements is met with the $[Fe_6S_6(p-RC_6H_4O)_6(M(CO)_3]^{3-}$ 1:1 adducts that exist in solution in equilibrium with the 2:1 adducts. Thus far it has not been possible to isolate the 1:1 adducts in pure form. Isolation of pure 1:1 adducts should be possible either by the serendipitous choice of the correct counterion, and favorable lattice stabilization energy, or by blocking one of the Fe_3S_3 faces of the parent prismanes with appropriate tridentate ligands. The second requirement, of higher oxidation state for the Mo atoms, could be realized by oxidative decarbonylation of the $Mo(CO)_3$ subunits with appropriate reagents. Recently we demonstrated[38] that decarbonylation of the $Mo(CO)_3$ units in the $[Fe_6S_6(Cl)_6(M(CO)_3)_2]^{3-}$ adduct occurs with tetrachloro-1,2-benzoquinone. However, the adduct does not retain the Fe_6S_6 core structure and instead rearranges to the tetrachlorocatecholate single cubane $[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]^{2-}$. Decarbonylation reactions with various other oxidizing reagents are under investigation in attempts to isolate derivative clusters with pentlandite type Mo^{IV}-Fe_6S_6 cores. The latter are expected to possess many of the characteristic features of the Fe/Mo/S center in nitrogenase.

The recent discoveries of nitrogenases that contain vanadium and perhaps iron in place of molybdenum and the structural similarity of the V cofactor to the FeMo–co underscore the need for a synthetic analogue

with a common Fe/S framework capable of accommodating different metals at one site. Composite clusters that contain the known Fe_4S_4,[19] $MoFe_3S_4$,[18] or VFe_3S_4[39] structural units in Fe–μ_2-S–Fe bridged double cubanes (Figure 1B) may represent such a synthetic analogue. The attractive features of a model such as the one shown in Figure 1B include (a) an acceptable Fe/M/S stoichiometry of 7:1:9; (b) a site for the bimetallic activation of molecular nitrogen as proposed previously;[40] (c) the presence of at least four distinct iron sites as indicated by ENDOR studies for the Fe/Mo/S site in nitrogenase; (d) a flexible (M) site capable of accommodating Mo,V (or Fe); and (e) the presence of redox-active subunits for the storage and delivery of electrons. Our studies thus far indicate that the Fe–μ_2-S–Fe bridged double cubanes III, IV, V, and VI are flexible enough to bind not only OH⁻ and S^{2-} but also N_2H_4 (a nitrogenase substrate) and CN⁻. The singly bridged double cubane I (Figure 3A) and the $\{[Fe_4S_4Cl_2](\mu_2-S)_2[MoFe_3S_4Cl_2(Cl_4cat)]\}^{5-}$ mixed-cubane, $S = {}^3/_2$, cluster arguably have a certain value as synthetic analogues. Further exploration of the reactivities of the doubly bridged double cubanes are expected to provide insights regarding nitrogenase chemistry. The remarkable ability of the $[Fe_3S_4(L)_3]^{3-}$ "ligand" to coor-

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(41) Coucouvanis, D.; Al-Ahmad, S.; Salifoglou, A.; Dunham, R. W.; Sands, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1353.

dinate to either Mo(III), as in $[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]^{2-}$, or Mo^0, as in $[Mo(CO)_3Fe_3S_4(L)_3]^{3-}$ (L = Cl, EtS, PhS),[41] is now well documented. The stabilization of low oxidation states, in $[Fe_3S_4(L)_3]^{3-}$ complexes of Mo with the $[Fe_3S_4(L)_3]^{3-}$ "ligand", is possible with π acceptor ligands such as CO. In contrast, higher oxidation states of Mo with the same "ligand" are stabilized with π donor ligands. This is aptly illustrated in the synthesis of the $[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]^{2-}$ cluster by the oxidative decarbonylation of $[Mo(CO)_3Fe_3S_4(L)_3]^{3-}$ with tetrachloro-1,2-benzoquinone. The question remains as to whether, under strongly reducing conditions, a cluster such as $[MoFe_3S_4Cl_3(Cl_4cat)(CH_3CN)]^{2-}$ or another member in this class of clusters (perhaps with homocitrate in place of the catechol ligands) can bind to N_2. If such a reaction is feasible, it is possible to envision a catalytic cycle for the reduction of N_2 by a cluster such as the one shown in Figure 1B. The reduction of N_2 to ammonia (Figure 4) could occur, in the presence of a source of protons, as the $MoFe_3S_4$ unit mediates successive electron transfer, in two-electron steps, to a bridging, activated N_2 molecule. The bimetallic activation and reduction of N_2 on a $Fe-\mu_2-S-Mo$ site, of unspecified origin, has been suggested previously[40] as a possible pathway toward N_2 fixation. A search for N_2 and $HN=NH$ derivatives and studies of the reactivities of the doubly bridged double cubanes currently are under way.