Nitrogenase Substrates as Intercluster Bridging Units between the Mo Atoms in Doubly Bridged, Double Cubanes. The Synthesis and Characterization of the $[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}L)]^{n-}$ Anions (L = N_2H_4, n = 4; L = CN^-, n = 5)

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The enzymatic reduction of dinitrogen to ammonia is catalyzed by the nitrogenase enzymes[1] and is intimately associated with a multimetallic Fe/Mo/S site[1,2] of unknown structure. This site is characterized by an approximate Fe:Mo:S composition[3] of 7 ± 1:1:8 ± 2, and as indicated by Mo[4] and Fe[5] EXAFS analyses it may contain Fe-(μ_2-S)$_2$-Fe and Mo-(μ_2-S)$_2$-Fe rhombic structural subunits. In spite of extensive studies in recent years,[6,7] the synthesis of an acceptable structural analogue for the nitrogenase Fe/Mo/S site still remains an important unfulfilled goal. The recent discoveries of new nitrogenase systems that contain vanadium[8] and perhaps iron[9] in place of molybdenum prompted us to search for a synthetic analogue with a common Fe/S structural framework capable of accommodating different metals at one site and suitable in the bimetallic activation of nitrogenase substrates. A composite cluster that contains the known Fe_4S_4 and MFe_3S_4 subunits (M = Mo, V) coupled in a Fe-(μ_2-S)-Fe, singly bridged double cubane[10,11] would be in compliance with these proposed requirements. Preliminary results of our attempts to obtain such clusters were reported in recent communications where the synthesis and structural characterization of singly bridged[10] and doubly bridged[11] double cubanes have been described. These clusters have cores that consist of two $[MFe_3S_4]$ cubane units coupled by either one Fe-(μ_2-S)-Fe bridge (M = Fe) or doubly coupled by the Fe-(μ_2-S)-Fe and Mo-(μ_2-L)-Mo (L = S^{2-}, OH^-) bridges. In this communication we report on the synthesis and characterization of two new doubly bridged double cubanes that contain Mo-(μ_2-L)-Mo bridges with the biologically relevant N_2H_4 ligand and with CN^-. The synthesis (from $[Et_4N^+]_2[MoFe_3S_4(Cl)_3(Cl_4cat)CH_3CN]$[7]) and the structural characterization of $[Et_4N]_5\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}OH)\}$ (I) have been described previously.[11] The reaction of I with $N_2H_5^+Cl^-$ in CH_3CN in a 1:1 molar ratio affords in excellent yield the $[Et_4N]_4[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}N_2H_4)]$ salt,[12] II, where the N_2H_4 bridge has been introduced following protonation of the μ_2-OH ligand in I. The reactivity of the μ_2-OH^- ligand in I also is manifested in its reactions with $(R_3Si)X$ (X = CN, N_3). These stoichiometric reactions that are thermodynamically driven by the formation of the $(R_3Si)OH$ byproduct result in the introduction of X in place of OH^- and occur readily in CH_3CN solution at ambient temperature. The black, microcrystalline $[Et_4N]_5[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}CN)]$ (III)[13] also can be obtained in CH_3CN solution by the stoichiometric reaction of $[Et4N^+]_2[MoFe_3S_4(Cl)_3(Cl_4cat)CH_3CN]$ with $(Et_4N)CN$ followed by addition of Na_2S.

In the infrared spectrum of II, weak vibrations at 3226 and 3287 cm^{-1} are indicative of N_2H_4. The presence of N_2H_4 (97.6% of the expected amount) was further substantiated by spectrophotometric quantitative analysis with *p*-(dimethylamino)benzaldehyde as a reagent. This procedure[14a] has been employed previously[14b] for the detection of N_2H_4 as a bound intermediate during nitrogenase turnover. The C=N vibration in III at 2132 cm^{-1} is higher in energy than that in $[MoFe_3S_4(Cl)_3(Cl_4cat)CN]^{3-}$ (2112 cm^{-1}).[15] This hypsochromic shift is typical of end-to-end bridging cyanide.[16]

The electronic spectra of II and III are nearly featureless and show a steadily increasing absorption from 750 nm to the UV region of the spectrum. The cyclic voltammetry of II and III (in CH_3CN solution vs Ag/AgCl) shows a quasireversible reduction ($E_{1/2}$ = 1.06 V, II; $E_{1/2}$ = −1.20 V, III) and two quasireversible oxidation waves ($E_{1/2}$ = +0.10, +0.32 V, II; $E_{1/2}$ = −0.03, +0.23 V, III). By comparison, the $[MoFe_3S_4(Cl)_3(Cl_4cat)CH_3CN]^{2-}$ single cube under the same conditions shows a quasireversible reduction at −0.8 V and an irreversible oxidation at +0.4 V. The ^{57}Fe Mossbauer spectra[17] of the EPR silent (20 K) II and III can be fitted satisfactorily by three quadrupole doublets in a 1:1:1 intensity ratio. Two of these doublets have similar isomer shift, IS, and quadrupole splitting, Δ_{Eq}, values (for II IS = 0.53, 0.51 mm/s and Δ_{Eq} = 1.17, 0.98 mm/s; for III IS = 0.51, 0.49 mm/s and Δ_{Eq} = 1.23, 0.98 mm/s). The third doublet has a considerably smaller IS value (for II IS = 0.33 and Δ_{Eq} 1.03 mm/s; for III IS = 0.30 and Δ_{Eq} = 1.05 mm/s) and probably is due to the Fe-(μ_2-S)-Fe sites where the Fe atoms contain no chloride in their coordination sphere. These data suggest that the two Fe atoms bound to the μ_2-S bridging ligands may be at a higher formal oxidation level (~+3) than the remaining four Fe atoms (~+2.7). The apparent insensitivity of the Mossbauer spectra to the nature of the bridging ligands in II and III suggests that any ligand-induced changes in the electronic structures of these dimers probably reside on the Mo atoms.

The structure of the anion in II has been determined[18] from

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(12) Analysis for II·CH_3CN. Calcd for $Mo_2Fe_6Cl_{12}S_9O_4N_7C_{46}H_{87}$ (MW 2042): Mo, 9.40; Fe, 16.45; S, 14.10; Cl, 20.83; N, 4.80; C, 27.03; H, 4.26. Found: Mo, 9.0; Fe, 15.9; S, 14.0; Cl, 20.3; N, 4.5; C, 26.9; H, 4.1. Evidence for the CH_3CN of solvation can be seen in the IR spectrum as a weak band at 2248 cm^{-1}.

(13) Analysis for III. Calcd for $Mo_2Fe_6Cl_{12}S_9O_4N_6C_{53}H_{100}$ (MW 2125): Mo, 9.04; Fe, 15.81; S, 13.55; Cl, 20.02; N, 3.95; C, 29.93; H, 4.71. Found: Mo, 8.7; Fe, 15.3; S, 13.9; Cl, 19.2; N, 3.8; C, 29.5; H, 4.7.

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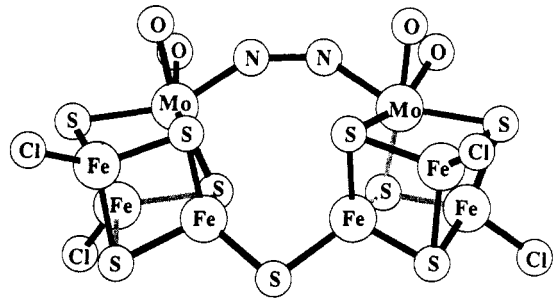

Figure 1. Preliminary structure[18] of the anion core in $[Et_4N]_4[[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}N_2H_4)]\cdot CH_3CN$. The structure has been drawn from crystallographically determined coordinates with use of the program Molecular Editor, and the catecholate phenyl rings have been omited for clarity.

data obtained from the best obtainable, albeit poor quality, crystals. The core structure in II (Figure 1) has been drawn on the basis of crystallographically determined coordinates and is presented with the intention of showing atomic connectivity. The anion has approximate C_{2v} symmetry and is located on a crystallographic mirror plane that contains the μ_2-S and the side-on, bridging N_2H_4 ligand and bisects the Mo-Mo and Fe-Fe intercube vectors. Most of the interatomic bond distances and angles in II and III are reasonable. Unfortunately the unacceptably high standard deviations of these values preclude a comparison of II or III to the structures of the μ_2-S or μ_2-OH analogues. A meaningful comparison can be made between the Mo-Mo distance in II (5.22 (1) Å) and that in I (4.248 (9) Å) and demonstrates the remarkable flexibility of the basic structure in accepting bridging ligands with differing steric demands.

The syntheses of II and III demonstrate the feasibility of introducing nitrogenase substrates in an "end-to-end" bridging mode within two μ_2-S-bridged cubane subunits and establish a methodology for the rational synthesis of analogous mixed-cubane clusters. Whereas II and III posess Mo-L-Mo bridges (L = CN^-, N_2H_4) and a stoichiometry of no direct consequence to the nitrogenase active site problem, mixed clusters analogous to II and III that contain $MoFe_3S_4$ and Fe_4S_4 as subunits could be biologically relevant. The latter will provide the first examples of molecules with Mo-L-Fe bridges, will have a biologically relevant Fe:Mo:S ratio, and will be potentially capable in the heterobimetallic coordination of nitrogenase substrates. A Mo-μ_2-S-Fe unit has been suggested previously[19] as a possible site for the activation and reduction of N_2 in nitrogenase.

An intriguing question arises as to whether, under strongly reducing conditions, clusters similar to I, II, and III or derivatives (perhaps with homocitrate[20] in place of the catechol ligands) can be obtained with N_2 as an intercube bridging ligand. Toward this goal the reactivity of I, II, and III, and of analogous "mixed" clusters[11] that contain Fe_4S_4 and $MoFe_3S_4$ subunits, currently is under investigation.

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(18) Black crystals of II·CH_3CN (MW 2042) are orthorhombic with space group *Pmcn* and a = 15.502 (6) Å, b = 19.661 (4) Å, c = 27.024 (6) Å, and Z = 4; d_{calc} = 1.64 g/cm^3; d_{obs} = 1.63 g/cm^3; MW_{calc} = 2020 ± 20. Single-crystal X-ray diffractometer data were collected for II and the structure was solved by a combination of heavy-atom Patterson techniques, direct methods, and Fourier techniques. All atoms in the anion were located, however, due to the poor quality of the crystal and limited data (II: Mo Kα, $2\theta_{max}$ = 35°, 1317 data with $I > 3\sigma I$); a satisfactory model for the disordered Et_4N^+ cations in the structure has not yet been found. At present with a complete anion refined but only parts of the Et_4N^+ cations included in structure factor calculations R = 0.16. All attempts to obtain better crystalline derivatives of II have failed. With the expectation that it will be possible to obtain high-quality data from better crystals, perhaps with different counterions, deposition of crystallographic data is not warranted at this time.

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Nucleophilic Activation of Triruthenium Carbonyl Complexes by Semilabile Ancillary Ligands. Cluster-Assisted Codimerization of Alkynes and Ethylene To Give 1,2-Disubstituted 1,3-Butadienes

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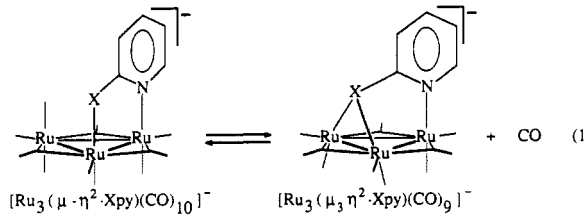
In connection with earlier observations that the variable hapticity of halides plays a "lightly stabilizing" role for coordination sites in some anion-promoted systems based on the complexes $[PPN][Ru_3(X)(CO)_n]$, (X = Cl, Br, I; n = 11, 10, 9),[1-4] we report that amido, mercapto, and alkoxy groups modified by a pyridyl substituent[5] give related activated species $[PPN][Ru_3(X\text{-}(C_5H_4N))(CO)_n]$ ([PPN][**1a-c**], n = 10; [PPN][**2a-c**], n = 9; $PPN^+ = (C_6H_5)_3PNP(C_6H_5)_3^+$; **a**, X = N($C_6H_5$); **b**, X = S; **c**, X = O) that are involved in the equilibrium shown in eq 1.[6,7]



Furthermore, the corresponding hydrido amido complex $Ru_3(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}N(C_6H_5)(C_5H_4N)(CO)_9$ (**3a**) is seen to activate alkynes selectively via the alkenyl complex **5a** and to promote an alkyne-ethylene codimerization[8] under mild conditions (Scheme I).

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