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Synthesis, Structural Characterization, and Properties of Singly Bridged Double Cubanes Containing Two $[(Cl_4\text{-}cat)MoFe_3S_4Cl_3]^{2-}$ Subunits and Hydrazine or Pyrazine Bridges

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Nitrogenase, an enzyme that catalyzes the stepwise reduction of N_2 to NH_3 at ambient temperature and pressure, has been the subject of continuous research interest as a result of the extraordinary nature of the reaction it catalyzes and its fundamental importance to the earth's biosphere.[1] Recent crystallographic studies on the MoFe protein of nitrogenase, independently carried out by two different groups,[2,3] have resulted in structurally similar proposed models for the Fe/Mo/S active center. The latter is generally accepted as the site where the activation and reduction of substrate molecules takes place. The proposed structure for the Fe/Mo/S center is based on the interpretation of electron density maps and is consistent with EXAFS analyses results[4] as well as with other spectroscopic data.[5] The model contains Fe_4S_3 and $MoFe_3S_3$ cuboidal subunits triply bridged by either two S^{2-} and a light atom ligand[3] or by three S^{2-} ligands.[2] The cylindrically shaped Fe_7MoS_9 cluster is attached to the protein by a Fe-bound (at the Fe_4S_3 subunit) cysteinyl residue and also by a Mo-bound histidine residue.

In recent years our studies have been centered around a proposed nitrogenase active site model that consists of bridged cubane subunits with a $[Fe_4S_4](\mu\text{-}S)[MoFe_3S_4]$ core.[6] In a broad sense this proposed model is conceptually close to the suggested model for the center in nitrogenase[2,3] in that it contains a S^{2-} bridging ligand between redox active subunits. Efforts toward the synthesis of clusters with S^{2-}-bridged cubane cores in our laboratory have resulted in the synthesis of a series of doubly bridged double cubanes $\{[(Cl_4\text{-}cat)MoFe_3S_4Cl_2]_2(S)(\mu\text{-}L)\}^{n-}$, **I** ($L = S^{2-}$, $n = 6$;[6b] $L = CN^-$, N_3^-, OH^-, $n = 5$,[6b,c] $L = N_2H_4$, $n = 4$[6c]; **Ia-e**, respectively), and the $\{[Fe_4S_4Cl_3]_2(\mu\text{-}S)\}^{4-}$ singly bridged double cubane.[7] These new clusters are expected to be important in systematic studies that are designed to explore the redox properties of bridged, redox-active subunits and the role of the bridging units in affecting the storage and delivery of electrons.

Previously, various alkanethiolate- or arenethiolate-bridged double cubanes containing $MoFe_3S_4$ cubanes have been reported.[8] In addition a series of singly bridged double cubanes have been obtained by the coupling of site-differentiated Fe_4S_4 clusters.[9] The structures of these clusters have not been determined.

In this communication we report on the synthesis, structural characterization, and chemical and spectroscopic properties of the Et_4N^+ salt of the $\{[(Cl_4\text{-}cat)MoFe_3S_4Cl_3]_2(\mu\text{-}L)\}^{4-}$ singly bridged double cubanes and we report the structural characterization and spectroscopic properties of the Et_4N^+ salts of these clusters $L = N_2H_4$, **II**, and $L = C_4H_4N_2$, pyrazine, **III**.

The formation of **II** is accomplished readily by the reaction of $(Et_4N)_2[(Cl_4\text{-}cat)MoFe_3S_4Cl_3(CH_3CN)]$,[10] **IV**, with anhydrous hydrazine in a 2:1 molar ratio in CH_3CN solution and is obtained as black needlelike crystals upon addition of diethyl ether.[11,12] The pyrazine analog, **III**, also is obtained as black needlelike crystals by a similar procedure, but a longer reaction time is required as the formation of the bridged pyrazine complex[13] is slow with respect to the hydrazine complex (i.e. hours vs minutes). Single crystals of **II** and **III** suitable for X-ray diffraction were obtained from CH_3CN/diethyl ether mixtures, and their crystal and molecular structures were determined.[14,15] The synthesis of **II** can also be achieved by the chemical oxidation of **Ie** with 2 equiv of $(PF_6)Fe(Cp)_2$ in a reaction that oxidizes the bridging μ-S^{2-}-ligand in **Ie** to elemental sulfur. Conversely, the reaction of **II** with 1 equiv of Na_2S in CH_3CN leads cleanly to the formation of **Ie** in good yield. This reaction points the way to a convenient route for the synthesis of doubly bridged double cubanes with bridging ligands other than S^{2-}. Both of the above reactions demonstrate the relative robustness of the unsupported N_2H_4 bridge.

In the structure of **II** the anion (Figure 1A) is located on a crystallographic inversion center and shows the unsupported hydrazine molecule bridging two $[(Cl_4\text{-}cat)MoFe_3S_4Cl_3]^{2-}$ subunits. The torsion angle between the N–N bond of the hydrazine bridge and the Mo–Fe(2) vector is 79.02°. The $[(Cl_4\text{-}cat)MoFe_3S_4Cl_3]^{2-}$ subunits are unexceptional and similar to other such units structurally characterized previously.[8] The Mo–N distance is 2.291(14) Å, and the N–N bond in the μ-N_2H_4 ligand is 1.47(2) Å. The intramolecular Mo–Mo distance at 5.41 Å is

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(11) Besides the complexes characterized here, preliminary spectroscopic data have been collected for the singly bridged double cubane L = 4,4′-bipyridyl.

(12) Analysis for **II**, $Mo_2Fe_6S_8Cl_{14}C_{44}H_{84}N_6O_2$ (fw = 2041), is as follows. Found: C, 25.86; H, 4.15; N, 4.19. Calc: C, 25.89; H, 4.15, N, 4.12.

(13) Analysis for **III**, $Mo_2Fe_6S_8Cl_{14}C_{48}H_{84}N_6O_2$ (fw = 2089), is as follows. Found: C, 27.70; H, 4.17; and N, 4.14. Calcd: C, 27.60 H, 4.05, N, 4.00.

(14) Black crystals of **II** (MW = 2041) are monoclinic, space group $P2_1/c$ with $a = 15.057(5)$ Å, $b = 15.164(6)$ Å, $c = 18.557(6)$ Å, $\beta = 113.12(3)°$, and $Z = 2$. Single-crystal diffraction data were collected on a Siemens R3m diffractometer using Mo Kα radiation. The solution of the structure was carried out using direct methods and Fourier techniques. Anisotropic temperature factors were used for all atoms of the anion and the N atoms of the cations. The refinement of the structure was based on 2089 unique reflections ($2\theta_{max} = 40°$, $I > 3\sigma(I)$). Refinement of 299 parameters has coverged to R and R_w values of 0.047 and 0.046 respectively.

(15) Black crystals of **III** (MW = 2089) are triclinic, space group $P1$ with $a = 13.798(4)$ Å, $b = 17.201(6)$ Å, $c = 19.422(8)$ Å, $\alpha = 91.49(3)°$, $\beta = 94.45(3)°$, $\gamma = 111.35(2)°$, and $Z = 2$. The solution of the structure was carried out using a combination of Patterson, direct methods, and Fourier techniques. Anisotropic temperature factors were used only for the Mo, Fe, Cl, and S atoms. The refinement of the structure that was based on 3486 unique reflections ($I > 3\sigma(I)$; $2\theta_{max} = 40°$) and 532 parameters has converged to R and R_w values of 0.062 and 0.063, respectively.

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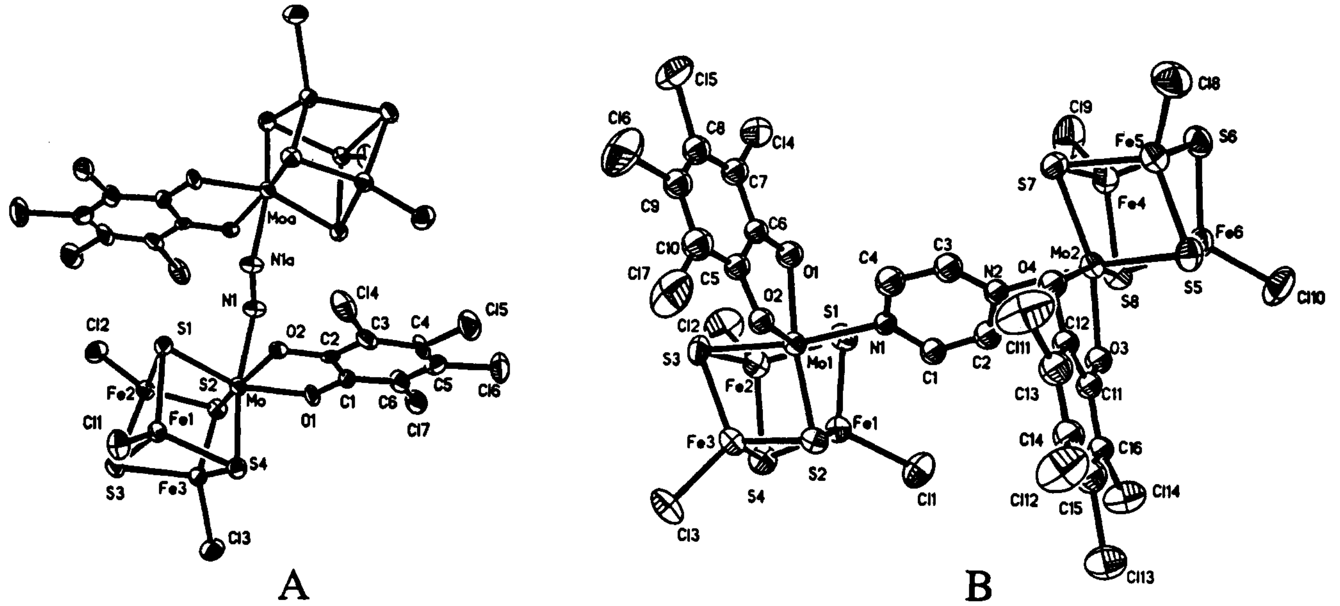

Figure 1. Structure and labeling of (A) the $(MoFe_3S_4Cl_3(Cl_4cat))_2(\mu\text{-}N_2H_4)^{4-}$ anion in II and (B) the $(MoFe_3S_4Cl_3(Cl_4cat))_2(\mu\text{-}C_4H_4N_2)^{4-}$ anion in III. Thermal ellipsoids as drawn by ORTEP represent 30% and 40% probability surfaces, respectively. Selected mean bond distances (Å) and angles (deg) not reported in the text include the following. Values for (A): Mo···Fe, 2.745(11); Mo–S, 2.353(4); Fe···Fe, 2.718(8); Fe–S, 2.277(3); Fe–Cl, 2.211(9); S1–Mo–N1, 84.3(4); S4–Mo–N1, 167.5(4); O1–Mo–N1, 78.3(5); S1–Mo–S2, 102.6(2). Values for (B): Mo···Fe, 2.735(4); Mo–S, 2.348(4); Fe···Fe, 2.724(8); Fe–S, 2.269(4); Fe–Cl, 2.212(8); S1–Mo1–N1, 84.6(6); S3–Mo1–N1, 168.7(6); O1–Mo1–N1, 81.8(6); S1–Mo1–S2, 103.1(3).

longer than the Mo–Mo distances in **Ia-e** that range from 4.24 to 5.22 Å (**Id,e**, respectively).

Unlike **II**, the asymmetric anion in **III** (Figure 1B) is located on a general position. The pyrazine ring is nearly orthogonal to the Mo(2)Fe(4)S(5)S(6) plane (dihedral angle, 89.56°) in one of the two subunits. The second cubane subunit is rotated nearly 90° with respect to the first one, around the Mo(1)–pyrazine–Mo(2) axis, with a pyrazine–[Mo(1)Fe(1)S(3)S(4)] dihedral angle of 5.16°. The Mo–N average distance is 2.328 Å, and the intramolecular Mo–Mo distance is 7.46 Å.

The infrared spectrum of **II** shows weak N–H vibrations at 3236 and 3272 cm^{-1} that are characteristic of end-on bound hydrazine.[16] The electronic spectra of **II** and **III** were obtained in CH_3CN and display the characteristic absorption profiles typical of the various $MoFe_3S_4Cl_3$ cubanes. There is a gradual increase in absorbance from 700 to 250 nm with an identifiable band at 460 nm (**II** ϵ = 10 800 cm^{-1} M^{-1}; **III**, ϵ = 11 200 cm^{-1} M^{-1}). Both compounds display linear Beer's law behavior thereby demonstrating that there is no solution equilibrium dissociation for either complex.

The electrochemistry of **II** and **III** was investigated in both coordinating (CH_3CN) and noncoordinating (1,2-dichloroethane) solvents. Cyclic voltammetric measurements in 1,2-dichloroethane on a Pt electrode (vs a standard Ag/AgCl electrode) show quasi-reversible (q-r) reduction and oxidation waves at –900 mV (ΔE = 125 mV) and +320 mV (ΔE = 123 mV) for **II** and at –915 mV (ΔE = 100 mV) and +370 mV (ΔE = 100 mV) for **III**. For both clusters the voltammetric waves appear as single sharp peaks in differential pulse voltammetry and are distinctly different than the q-r reduction and oxidation waves displayed by the $[(Cl_4\text{-cat})MoFe_3S_4Cl_3(CH_3CN)]^{2-}$ cluster, **IV**. The latter cluster shows waves at –860 and +400 mV under identical experimental conditions.[17] The voltammetric traces of **II** and **III** are quite similar in both CH_3CN and 1,2-dichloroethane solution. The absence of waves attributable to **IV** in CH_3CN solutions indicates that the bridged clusters retain their integrity and do not dissociate in solution. To further verify this conclusion the $[(Cl_4cat)MoFe_3S_4Cl_3(pyz)]^{2-}$ single cubane, **V**, with a terminal pyrazine ligand was independently synthesized.[18] This compound displays a q-r reduction at –890 mV (ΔE = 125 mV) and an irreversible oxidation at +350 mV. Again, this is readily distinguishable from **III**, and there is no voltammetric evidence for the formation of **V** when **III** is dissolved in CH_3CN.

In contrast to the single oxidation and reduction waves of **II** and **III** the cyclic voltammetric data of the doubly bridged, double cubane **I** (L = N_2H_4, n = 4) show two q-r reduction waves at –1300 and –1060 mV and two q-r oxidation waves at +100 and +320 mV. The 220 mV–240 mV "split" of the voltammetric waves in **I** reflects the extent of mutual electronic communication. This communication, between the two identical $S = {}^3/_2$ subunits in **I**, causes electron delocalization that results in a coupling of spins to an overall zero or integer spin ground state and accounts for the absence of EPR signals in **I**.

The lack of doubling of the voltammetric waves shows that the two cluster subunits in **II** and **III** are not perturbing each other to a significant extent via the hydrazine and pyrazine bridges, respectively. Further evidence of this is provided by the EPR spectra of **II** and **III** that show signals characteristic of $S = {}^3/_2$ ground states and no indications of magnetic coupling. The differences in the redox and EPR spectroscopic behavior, between the singly bridged double cubanes and the doubly bridged double cubanes at similar Mo–Mo distances (Mo–Mo: in **Ie**, 5.22 Å; in **II**, 5.41 Å), demonstrate the critical role that the number and type of bridging ligands play in the intercluster exchange process. The role of the bridging ligands in various singly and doubly bridging double cubanes is presently under investigation in our laboratory.

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Supplementary Material Available: Tables S1 and S2, containing listings of positional parameters, thermal parameters, and selected distances and angles of **II** and **III** (18 pages). Ordering information is given on any current masthead page.

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(17) In CH_3CN solution the waves become more irreversible but the basic pattern remains the same. The complexes **II** and **III** display reduction and oxidation waves at –922 and +364 mV and at –905 and +330 mV, respectively. The complex $[(Cl_4\text{-cat})MoFe_3S_4Cl_3(CH_3CN)]^{2-}$ in contrast shows reduction and oxidation waves at –903 and +306 mV, respectively.

(18) Reaction of $[(Cl_5cat)MoFe_3S_4Cl_3(CH_3CN)]^{2-}$ with excess pyrazine in CH_3CN followed by addition of diethyl ether afforded black needlelike crystals. Anal. Calcd for $MoFe_3S_4Cl_7C_{26}H_{44}N_4O_2$ (fw = 1084.6): C, 28.79; H, 4.09; N, 5.16. Found: C, 28.93; H, 3.98; N, 5.27. An X-ray structure determination revealed the connectivity of the anion, but disorder in the cations resulted in an R = 0.14 with unit cell $P2_1/n$, a = 14.643(7) Å, b = 11.263(6) Å, c = 27.53(1) Å, β = 95.91°, and Z = 4.