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COMMUNICATION

THE SYNTHESIS, AND PROPERTIES OF Fe/Mo/S CLUSTERS WITH MoFe₃S₄ CUBANE SUBUNITS, Mo BOUND BIDENTATE OXALATE LIGANDS AND TERMINAL OR BRIDGING CYANIDE LIGANDS. STRUCTURAL CHARACTERIZATION OF (Et₄N)₃[(C₂O₄)(CN)MoFe₃S₄Cl₃] AND (Et₄N)₅{[(C₂O₄)MoFe₃S₄Cl₂]₂(μ-CN)(μ-S)}

KONSTANTINOS D. DEMADIS, SUE-JANE CHEN and DIMITRI COUCOUVANIS*

Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055, U.S.A.

Abstract—The reaction of $(Et_4N)_3[(C_2O_4)MoFe_3S_4Cl_4]$ (I) with $(Et_4N)CN$ affords $[(C_2O_4)(CN)MoFe_3S_4Cl_3]^{3-}$ (IV) in nearly quantitative yields. The reaction of I with 0.5 eq. of $(Et_4N)CN$ and 0.5 eq. of a source of S^{2-} affords the doubly-bridged double-cubane $\{[(C_2O_4)MoFe_3S_4Cl_2]_2(\mu_2\text{-}CN)(\mu_2\text{-}S)\}^{5-}$ (V) in ~30% yield. Single crystal X-ray structures were determined for IV and V. The mean Fe—Fe, Fe—S and Fe—Cl bond distances in IV at 2.713(3), 2.270(5) and 2.214(5) Å, are typical for MoFe₃S₄ cubane-like structures. The Mo—C(N) and C—N bond lengths are found at 2.19(2) and 1.04(2) Å, respectively. The pentaanion in V consists of two doubly-bridged cubane subunits bridged by a μ_2-CN⁻ ligand through the Mo atoms and a μ_2-S²⁻ through two Fe atoms. The Mo···Mo and Fe···Fe(intercube) distances and the Fe—μ_2-S—Fe angle are found at 5.267(4), 3.443(7) and 104.1(4)°. The spectroscopic and electrochemical features of IV and V are discussed.

Recent single crystal X-ray structure determinations of the Fe—Mo protein of nitrogenase from *A. vinelandii*[1(a),(b)] and *C. pasteurianum*[1(c),2] have revealed the structure of the catalytically active Fe/Mo/S center to near atomic resolution. The Fe/Mo/S cluster consists of two cuboidal subunits, Fe₄S₃ and MoFe₃S₃, bridged by two[1] or three[2] S²⁻ ions and anchored on the protein matrix by a Fe-coordinated cysteinyl residue and by a Mo-coordinated imidazole group from a histidine residue. Two of the coordination sites on the six-coordinate Mo atom were found occupied by a bidentate

homocitrate molecule. This observation verified previous chemical and spectroscopic studies that had identified a homocitrate molecule as an integral part of the Fe/Mo/S center.[3] Unusual structural features of the Fe/Mo/S center include the unprecedented trigonal planar coordination geometry for the six μ-S-bridged Fe atoms, and the unusually short Fe—Fe distances across the two subunits (2.5–2.6 Å).

The structure determinations of the Fe/Mo/S center in nitrogenase have put in perspective the relevance of numerous synthetic Fe/Mo/S clusters that have been proposed or synthesized as analogs for the enzyme active site.[4–6] It is now clear that the multitude of clusters that contain the MoFe₃S₄

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* Author to whom correspondence should be addressed.

Table 1. Comparison of selected distances (Å) and angles (°) in the singly- and doubly-bridged double-cubanes

Cluster	Mo···Mo	Fe···Fe (intercube)	Fe—μ_2-S—Fe	Ref.
$\{[(Cl_4cat)MoFe_3S_4Cl_2]_2(\mu_2\text{-OH})(\mu_2\text{-S})\}^{5-}$	4.248(5)	3.35(1)	97.8(8)	15
$\{[(Cl_4cat)MoFe_3S_4Cl_2]_2(\mu_2\text{-S})(\mu_2\text{-S})\}^{6-}$	4.926(8)	3.33(2)	98.7(8)	15
$\{[(Cl_4cat)MoFe_3S_4Cl_2]_2(\mu_2\text{-NH}_2NH_2)(\mu_2\text{-S})\}^{4-}$	5.22(1)	3.35	98.9	10
$[(Fe_4S_4Cl_3)_2(\mu_2\text{-S})]^{4-}$	—	3.433(4)	102.2(2)	14
$\{[(C_2O_4)MoFe_3S_4Cl_2]_2(\mu_2\text{-CN})(\mu_2\text{-S})\}^{5-}$	5.267(5)	3.443(7)	104.1(4)	a

^{a} This work.

"cubane" cores can be considered in part as structural analogs for the center in nitrogenase.[4] Functional analogs of the nitrogenase Fe/Mo/S site are less common although electrochemically generated, reduced, derivatives of the $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ cluster have been found effective in the reduction of nitrogenase substrates in reactions that are mostly non-catalytic in nature.[7] Our interest in the chemistry of the MoFe$_3$S$_4$ cubanes has intensified following recent results that show these compounds catalytically active in the chemical reduction of hydrazine to ammonia.[8]

The first examples of MoFe$_3$S$_4$ cubanes, with polycarboxylate ligands coordinated to the Mo

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* Recent studies in our laboratory (see Ref. 11) indicate that the CN- ligands in either the single or the doubly-bridged double-cubanes undergo stoichiometric reduction in the presence of protons to CH$_4$ and NH$_3$.

† Analysis: Calc for MoFe$_3$Cl$_3$S$_4$C$_{27}$H$_{60}$N$_4$O$_4$ (IV) (MW-1002.08): C, 32.3; H, 6.0; N, 5.6%. Found: C, 32.4; H, 6.1; N, 5.5. Far IR spectrum of IV: 266(m), 318(m), 341(vs), 355(vs), 374(sh), 391(w), 414(m), 450(w) cm^{-1}. Electronic spectrum (nm in CH$_3$CN solution): 420 ($\varepsilon = 2300$), 320 ($\varepsilon = 5400$) and 240 ($\varepsilon = 14100$). The EPR spectrum of IV is similar to that of other MoFe$_3$S$_4$ single cubanes and characteristic of an S = 3/2 ground state.

‡ Crystal and refinement data: black needle crystals of IV are monoclinic, space group $P2_1/n$, with $a = 10.331(2)$, $b = 22.580(6)$, $c = 19.083(4)$ Å, $\beta = 91.973(17)°$ and $Z = 4$. Single crystal diffraction data for IV were collected on a Nicolet P3F four-circle automated diffractometer using Mo-$K\alpha$ radiation. The structure was solved by conventional methods. The refinement of the structure by full-matrix least-squares methods was based on 3303 unique reflections ($2\theta_{max} = 45°$, $I > 3\sigma(I)$). Anisotropic temperature factors were used for all non-hydrogen atoms and the hydrogen atoms were assigned idealized locations. Refinement on 415 parameters converged to a $R(Rw)$ value of 5.41(4.87).

atoms, were recently reported[9] and include the oxalato derivatives $(Et_4N)_3[(C_2O_4)MoFe_3S_4Cl_4]$ (I) $(Et_4N)_4\{[MoFe_3S_4Cl_4]_2(\mu_2\text{-}C_2O_4)\}$ (II) and the $(Et_4N)_3[(citr)MoFe_3S_4Cl_3]$, citrate cluster (III). Of these I and II have been characterized structurally and the identity of the microcrystalline III was based on total elemental analysis and detailed spectroscopic studies.[9] In the catalytic reduction of hydrazine to ammonia,[8] III was found a more efficient catalyst than the $(Et_4N)_2[(Cl_4cat)(CH_3CN)MoFe_3S_4Cl_3]$, catecholate analog[4] and prompted us to further study the chemistry of complexes such as I–III. In this communication we report on the syntheses and structural characterization of $(Et_4N)_3[(C_2O_4)(CN)MoFe_3S_4Cl_3]$ (IV) and the $(Et_4N)_5\{[(C_2O_4)MoFe_3S_4Cl_2]_2(\mu\text{-CN})(\mu\text{-}S)\}$, doubly-bridged, double-cubane (V). The synthesis of a doubly-bridged double-cubane, analogous to V but with tetrachlorocatecholate ligands in place of the oxalate ligands has been the subject of a previous report.[10] At that time, due to poor crystal quality and insufficient diffraction data, we were unable to determine an accurate structure and only atomic connectivity could be established for the $\{[(Cl_4cat)MoFe_3S_4Cl_2]_2(\mu\text{-CN})(\mu\text{-}S)\}^{5-}$ cluster.[10] The need for an acceptable structure of a doubly-bridged double-cubane, with a possibly activated* bridging cyanide ligand, is met in the structure of V and is the principal reason for this communication.

The reaction of I with 1 eq. of $(Et_4N)CN$ in CH$_3$CN solution, cleanly affords black, highly crystalline, IV in nearly quantitative yield.† In IV the C≡O vibration is found at 1670 cm^{-1} and a weak vibration at 2123 cm^{-1} is assigned to terminally bound CN$^-$. Single crystals of IV suitable for diffraction studies were grown from CH$_3$CN/ether mixtures. The crystal structure‡ shows the trianion as a single cubane possessing crystallographically required C_s symmetry. Three of the coordination

sites on the Mo atom are occupied by the terminal oxalate and cyanide ligands (Fig. 1(A)). The mean Fe—Fe, Fe—S and Fe—Cl bond lengths at 2.713(3), 2.270(5) and 2.214(5) Å are unexceptional and similar to those reported for several single and double cubanes.[4,5] The Mo—C bond, 2.192(15) Å (typical for Mo(III, IV)–cyanide complexes[12]) and the almost linear Mo—C—N angle, 178.61(13)°, are comparable to values reported for [(Cl₄cat)MoFe₃S₄(SEt)₃(CN)]³⁻ at 2.194(25) Å and 178.1(22)°, respectively.[13]

The reaction of I with 0.5 eq. Of (Et₄N)(CN), followed by the addition of 0.5 eq. of (Et₄N)₂S— in CH₃CN solution follows the protocol described previously in the synthesis of other doubly-bridged and singly-bridged double-cubanes[14,15] and gives black crystalline V in moderate purified yields (30%).* The C—N vibration in V is found at 2136 cm⁻¹, and is hypsochromically shifted relative to IV. Such shifts are typical for end-on bridging CN.[12] Unequivocal evidence for the bridging nature of the CN ligand was obtained from a X-ray structure determination. Single crystals of V were grown by slow diffusion of ether into a CH₃CN solution of the compound.† The pentaanion in V (Fig. 1(B)) is a doubly-bridged double-cubane, with a CN-bridging the two Mo atoms and a S²⁻ bridging two Fe atoms. The C and N atoms of the cyanide bridge are nearly impossible to differentiate and very likely are positionally disordered. Among the outstanding structural features in V, are included long

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*Analysis: Calc for $Mo_2Fe_6Cl_4S_9C_{45}H_{100}N_6O_8$ (V) (MW-1809.06): C, 29.8; H, 5.5; N, 4.6%. Found: C, 29.5; H, 5.4; N, 4.5. Far IR spectrum of V: 328(sh), 336(vs), 346(vs), 360(sh), 395(m), 409(s) and 470(w) cm⁻¹. Electronic spectrum (nm in CH₃CN solution): 525 (ε = 9600), 440 (ε = 9800) and 240 (ε = 45,000). Solutions of V in CH₃CN were found EPR silent.

† Crystal and refinement data: black crystals (blocks) of V are monoclinic, space group $P2_1/n$, with $a = 15.125(4)$, $b = 21.254(7)$, $c = 23.399(10)$ Å, $\beta = 94.62(3)°$ and $Z = 4$. Single crystal diffraction data were collected on a Nicolet P3F four-circle diffractometer using Mo-K_α radiation. The structure solution was carried out by direct methods and the core structure was confirmed independently by a heavy-atom Patterson map. The refinement of the structure using full-matrix least-squares methods was based on 3557 unique reflections ($2\theta_{max} = 40°$, $I > 5\sigma(I)$). The atoms of the pentaanion, except the C of the cyanide and one C of the oxalate, were refined anisotropically, as well as the N atoms of the cations. The H atoms were included in the structure factor calculation at idealized locations, but were not refined. Refinement on 511 parameters has led to a conventional R (R_w) value of 8.73(9.42).

‡ qr = quasireversible, irr = irreversible.

Mo···Mo and Fe···Fe(intercube) distances of 5.267(5) and 3.443(7) Å, respectively, and a Fe—μ_2-S—Fe angle of 104.1(4)°. The Mo—C, Mo—N and C—N bond lengths are found at 2.25(3), 2.30(3) and 1.02(4) Å, respectively, and the Mo—C(N)—N(C) angles are 157(3) and 160(3)°. A comparison of the C—N bond length in V with the one in IV shows no significant difference as expected by the similarity in the frequencies of the C—N vibrations in the two clusters. The Fe—μ_2-S—Fe angle and the intercube Fe···Fe distance in V are similar to those reported for the [(Fe₄S₄Cl₃)₂(μ_2-S)]⁴⁻ singly-bridged double-cubane,[14] at 102.2(2)° and 3.433(4) Å, respectively. In the {[(Cl₄cat)MoFe₃S₄Cl₂]₂(μ_2-X)(μ_2-S)}ⁿ⁻ doubly-bridged double-cubanes[15] with monatomic bridges the Fe—μ_2-S—Fe angles are more acute and the Mo···Mo and Fe···Fe(intercube) distances (Table 1) are shorter than those in V. Thus, for X = OH⁻, $n = 5$ the corresponding values are 97.8(8)°, 4.248(5) Å, and 3.35(1) Å and for X = S²⁻, $n = 6$, values of 98.7(8)°, 4.926(8) Å and 3.33(2) Å have been reported.[15] The structure of the anion in V is quite similar to the isostructural {[(Cl₄cat)MoFe₃S₄Cl₂]₂(μ_2-X)(μ_2-S)}ⁿ⁻ anions[9] (X = CN⁻, $n = 5$ and X = N₂H₄, $n = 4$).

The cyclic voltammetry of IV (on a Pt working electrode, in CH₂Cl₂, vs Ag/AgCl, Bu₄NClO₄ as supporting electrolyte) shows a single reduction (−1090 mV, qr‡) and an oxidation (+330 mV, irr‡). In contrast, V shows multiple reductions (−1110 mV, irr; −1500 mV, irr) and oxidations (+50 mV, qr; +300 mV, qr), under the same conditions. The doubling of the voltammetric waves in V with appreciable differences in redox potentials suggests that the double-cubane structure is retained in solution and indicates significant electronic communication between the two cuboidal subunits. The lack of an EPR signal in solutions of V also indicates electronic communication and effective spin coupling between the S = 3/2 subunits. The reactivity properties of IV and V presently are under investigation.[11]

Supplementary material available—Tables S1 and S2 containing listings of positional parameters, thermal parameters and selected distances and angles of IV, and V (ORTEP diagrams included) (24 pages), Tables S3 and S4 listing calculated and observed structure factors for IV and V (40 pages) can be obtained from the author on request.
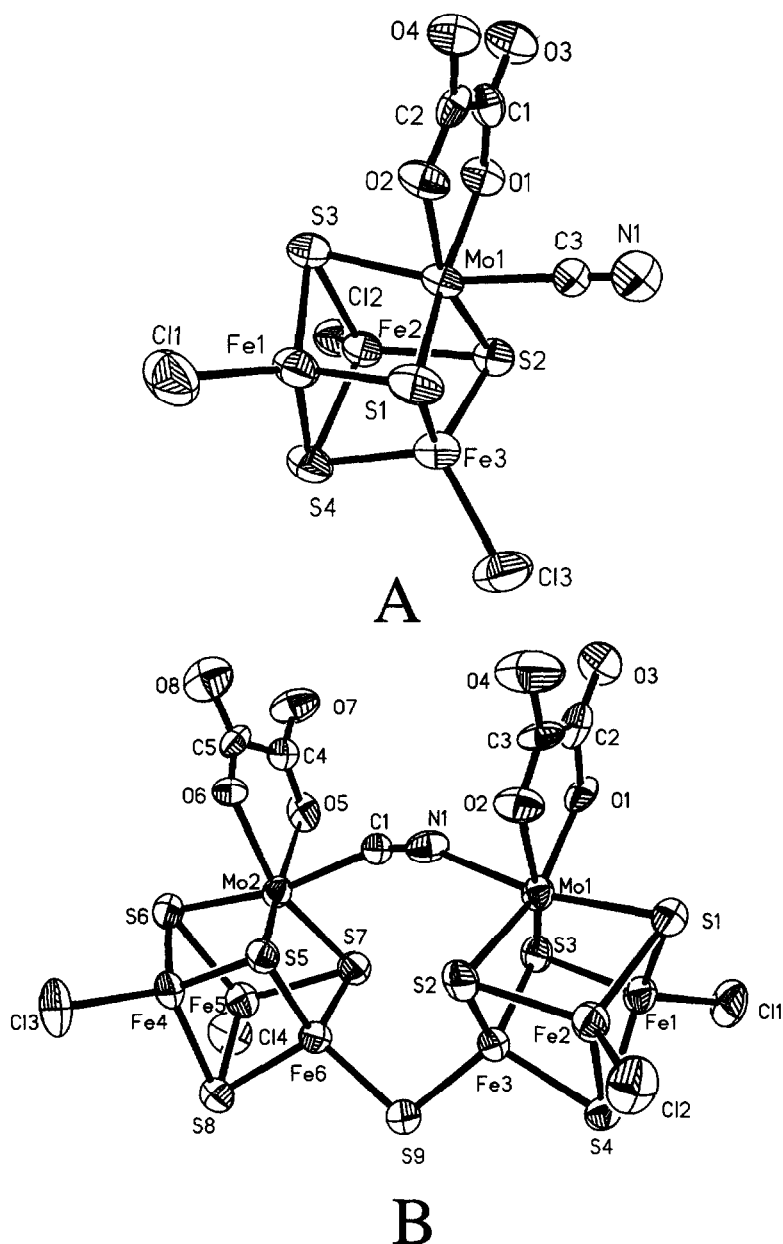
Fig. 1. The structures of (A) the $[(C_2O_4)MoFe_3S_4Cl_3(CN)]^{3-}$ and (B) the $\{[(C_2O_4)MoFe_3S_4Cl_2]_2(\mu_2\text{-}CN)(\mu_2\text{-}S)\}^{5-}$ clusters showing atoms as 40% probability ellipsoids drawn by ORTEP.

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