J. Am. Chem. Soc. 1993, 115, 3344–3345

Single and Double MoFe$_3$S$_4$ Cubanes with Mo-Coordinated Polycarboxylate Ligands. Syntheses and Structural Characterization of (Et$_4$N)$_4${[MoFe$_3$S$_4$Cl$_4$]$_2$(μ-C$_2$O$_4$)} and (Et$_4$N)$_3$[MoFe$_3$S$_4$Cl$_4$(C$_2$O$_4$)] Clusters

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Received December 28, 1992

During the last two decades, a considerable amount of structural (EXAFS), spectroscopic, and other data have been obtained for the nitrogenase Fe/Mo/S active site, either within the MoFe protein,[1] or as an isolated FeMo cofactor.[2] The data have defined the Fe/Mo/S center in nitrogenase as an asymmetric polynuclear cluster containing Fe, Mo, and S in a $7\pm1:1:8\pm1$ ratio, and, in the semireduced state, displaying a characteristic EPR spectrum consistent with a $S = {}^3/_2$ magnetic ground state. Recently, a model for the Fe/Mo/S site has been deduced on the basis of single crystal X-ray studies[3] on the MoFe protein of *Azotobacter vinelandii* and the interpretation of electron density maps. This model is compatible with the stoichiometric and structural data and shows an elongated cluster with a Fe$_7$MoS$_8$ core. The six-coordinate Mo atom is located at one end of the cluster and, in addition to a protein-bound histidine, is coordinated to what has been proposed to be a bidentate homocitrate molecule. The latter was revealed earlier as an integral part of the FeMo cofactor as a result of extensive biochemical-genetic[4] and spectroscopic (^{95}Mo ENDOR) studies.[5] Among other polycarboxylic acids tested for their ability to replace homocitrate in the in vitro synthesis of the FeMo cofactor, only citrate showed some albeit limited activity.[6] The lack of synthetic Fe/Mo/S clusters with polycarboxylate anions coordinated to the Mo atom prompted us to explore the reactivity of the previously characterized [MoFe$_3$S$_4$Cl$_3$(Cl$_4$cat.)(L)]$^{2-}$ clusters **I** (L = CH$_3$CN, DMF, DMSO)[7] toward polycarboxylic acids such as oxalic, citric, and (*R*)-citramalic, or in some instances their salts ((Et$_4$N)H$_2$citrate). In this communication we report on the synthesis and crystal and molecular structure of (Et$_4$N)$_4${[MoFe$_3$S$_4$Cl$_4$]$_2$(μ-C$_2$O$_4$)} (**II**) and (Et$_4$N)$_3$[MoFe$_3$S$_4$Cl$_4$(C$_2$O$_4$)] (**III**), the first examples of MoFe$_3$S$_4$ cubane clusters with carboxylate ligands coordinated to the Mo atom, and on the general synthesis of other similar [MoFe$_3$S$_4$Cl$_3$(L′)]$^{n-}$ clusters **IV** (n = 3; L′ = citrate, (*R*)-citramalate).

The reaction of **I** with anhydrous oxalic acid in CH$_3$CN or DMF solution affords crystalline **II** in ~70% yield.[8] An intense $C{=}O$ vibration at 1630 cm^{-1} suggests a bridging tetradentate oxalate ligand.[9] The electronic spectrum of **II** (in CH$_3$CN) displays broad absorptions at 570 (ϵ = 3080) and 475 nm (ϵ = 5250). The Mossbauer spectrum (obtained at 125 K vs Fe) consists of a broad asymmetric quadrupole doublet with average values of isomer shift and quadrupole splitting of 0.49 and 0.94 mm/s, respectively.

Single crystals of **II** suitable for X-ray diffraction study were obtained by slow diffusion of Et$_2$O into a CH$_3$CN solution. The crystal structure determination[10] shows the tetraanion (Figure 1A) as a μ-oxalate-bridged double cubane. The anion is located on a crystallographic inversion center. The mean Fe-Fe, Fe–S, and Fe–Cl bond lengths at 2.723(3), 2.269(4), and 2.217(4) Å are unexceptional and similar to those reported for the MoFe$_3$S$_4$ single and double cubanes.[11] The Mo–Cl distance in **II**, 2.500(3) Å, is comparable with the Mo–Cl distance in the structure of the [MoFe$_3$S$_4$Cl$_4$(dmpe)]$^-$ cluster[11g] (2.490(2) Å).

EPR spectra of frozen CH$_3$CN solutions of **II** are consistent with a $S = {}^3/_2$ spin system. The oxidation of **II** with tetrachloro-1,2-benzoquinone in the presence of an equimolar amount of tetrachlorocatecholate anion in CH$_3$CN or DMF solution affords **I** in ~60% purified yield. The oxidation of **II** by Cp$_2$FePF$_6$ results in cluster decomposition and formation of [Cl$_2$FeS$_2$MoS$_2$FeCl$_2$]$^{2-}$ linear trimer[12] that can be isolated in moderate yield. The reaction of **II** with 1 equiv of (Et$_4$N)$_2$(C$_2$O$_4$) in CH$_3$CN solution not unexpectedly affords the crystalline (Et$_4$N)$_3$[MoFe$_3$S$_4$Cl$_4$(C$_2$O$_4$)] single cubane **III**. This compound shows far-infrared and electronic spectra[13] different than those of **II** and the $C{=}O$ vibration at 1670 cm^{-1}. Single crystals of **III** were grown from CH$_3$CN/Et$_2$O mixtures.[14] The crystal structure of **III** (Figure 1B) shows the MoFe$_3$S$_4$Cl$_4$ unit similar to the corresponding subunits in **II** with a somewhat longer Mo–Cl bond of 2.525(3) Å.

The cyclic voltammetry of **II** (on a carbon glassy electrode in CH$_2$Cl$_2$ vs Ag/AgCl, Bu$_4$NClO$_4$ as supporting electrolyte) shows reductions (−40 mV, qr; −890 mV, qr; −1100 mV, irr; qr = quasireversible, irr = irreversible) and an oxidation (+500 mV, qr). These values are different from those obtained for **III** under the same conditions that consist of a single reduction (−1030 mV,

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[8] Anal. Calcd for Mo$_2$Fe$_6$Cl$_8$S$_8$O$_4$N$_4$C$_{34}$H$_{80}$ (**II**, MW 1676.11): C, 24.3; H, 4.8; N, 3.3. Found: C, 25.0; H, 4.8; N, 3.3. Far-infrared spectrum of **II**: 278 (w), 314 (m), 323 (m), 358 (s), 398 (sh), 413 (m), 465 (w) cm^{-1}.

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[10] Crystal and refinement data: black crystals (rectangular plates) of **II** are monoclinic, space group $C2/c$, with a = 29.70(1) Å, b = 12.462(3) Å, c = 19.477(4) Å, β = 155.76(2)°, Z = 4. Single crystal diffraction data for **II** were collected on a Syntex P2$_1$m/v diffractometer using Mo Kα radiation at ambient temperature. The solution of the structure was carried out by a combination of direct methods and Fourier techniques. The refinement of the structure by full-matrix least-squares methods was based on 3943 unique reflections ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$). Anisotropic temperature factors were used for all non-hydrogen atoms, and the H atoms were included in the structure factor calculation at their calculated positions (d_{C-H} = 0.96 Å) but were not refined. At the present state of refinement on 318 parameters, $R(R_w)$ = 0.0622(0.0568).

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[13] Anal. Calcd for MoFe$_3$Cl$_4$S$_4$O$_4$N$_3$C$_{26}$H$_{60}$ (**III**, MW 1011.53): C, 30.84; H, 5.93; N, 4.15. Found: C, 30.91; H, 5.97; N, 4.10. Far-infrared spectrum of **III**: 278 (w), 309 (w), 324 (m), 352 (s), 392 (w), 412 (m) cm^{-1}. Electronic spectrum of **III**: 450 (ϵ = 6420) and 310 nm (ϵ = 13 600).

[14] Crystal and refinement data: black crystals of **III** are monoclinic, space group $P2_1/n$, with a = 10.379(3) Å, b = 22.682(8) Å, c = 18.735(7) Å, β = 92.21(1)°, Z = 4. Single crystal diffraction data for **III** were collected on a Nicolet P3F automated diffractometer using Mo Kα radiation. The structure solution was performed by using direct methods and Fourier techniques. 3617 unique reflections were used for the refinement of the structure by the full-matrix least-squares method ($2\theta_{max}$ = 45°, $I > 3\sigma(I)$), leading to $R(R_w)$ = 0.0435(0.0439).

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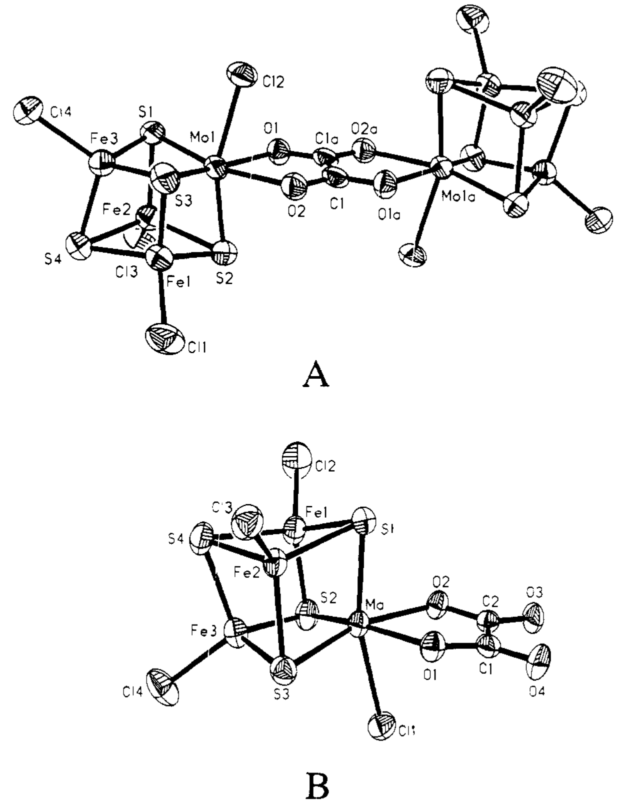

Figure 1. Structure and labeling of **A**, the $[(MoFe_3S_4Cl_4)_2(\mu\text{-}C_2O_4)]^{4-}$ anion in **II**, and **B**, the $[(MoFe_3S_4Cl_4)(C_2O_4)]^{3-}$ anion in **III**. Thermal ellipsoids as drawn by ORTEP represent the 40% probability surfaces. Selected bond distances and angles not reported in the text include for **A**, Mo–O, 2.207(7) Å; C–O, 1.26(2) Å; C1a–C1, 1.526(9) Å; Mo···Mo, 5.72 Å; O–Mo–O, 75.4(2)°; Cl2–Mo1–S2, 160.5(1)°; and for **B**, Mo–O, 2.130(6) Å; C–O(bound), 1.28(1) Å; C–O(unbound), 1.22(1) Å; C1–C2, 1.56(1) Å; O–Mo–O, 75.1(2)°; Cl1–Mo–S1, 165.5(1)°.

irr) and two oxidations at +250 mV, irr; +500 mV, qr. The presence of multiple reduction waves in **II** suggests that the dimeric structure is retained in solution and the two subunits influence each other electronically. The fact that **II** is not EPR silent also indicates that the $C_2O_4^{2-}$ bridge does not permit strong electronic coupling of the two cubane subunits. Similar electronic perturbations have been reported previously between $MoFe_3S_4$ cluster subunits bridged by thiolato or persulfido ligands.[11]

The protonation of the $Cl_4cat.^{2-}$ ligand in **I** by oxalic acid has been extended to other polycarboxylic acids, such as citric or (*R*)-citramalic. After unexceptional workup and recrystallization from CH_3CN/ether, the reaction of **I** with citric acid (H_3cit) gives crystalline $[MoFe_3S_4Cl_3(L')]^{n-}$ **IVa** ($L' = citr^{3-}$, $n = 3$) in ~60% yield. A similar reaction with (*R*)-citramalic acid affords microcrystalline **IVb** ($L' = citrm^{3-}$, $n = 3$). The reaction of **I** with $(Et_4N)H_2$(citrate) gives crystalline **IVc** ($L' = citr^{3-}$, $n = 3$). Thus far, we have been unable to obtain crystallographic quality crystals for any of these complexes; however, analytical and spectroscopic data leave little doubt that these clusters are analogous to the catecholate $MoFe_3S_4$ cubanes with tridentate carboxylate ligands coordinated to the Mo atom.[15,16] The spectroscopic and electrochemical properties of **IVc** are representative of this class of clusters. The cyclic voltammogram of **IVc** (in dichloroethane vs Ag/AgCl) shows well-defined reduction (−1050 mV, qr) and oxidation (+260 mV, qr) waves.[17] The infrared spectrum shows three very strong C═O vibrations[15] and a weak band at 3543 cm^{-1} assigned to an O–H stretch. The 1720- and 3543-cm^{-1} bands are tentatively assigned to ν_{asym}(C═O) and ν_{asym}(O–H) vibrations of a noncoordinated -COOH group.[18] The presence of a "free" -COOH moiety was further substantiated by the reaction of **IVc** with 1 equiv of $(Et_4N)OH$, which affords a material displaying essentially the same infrared spectroscopic characteristics as **IVc** but lacking the absorption at 1720 cm^{-1}. Reaction of **I** with (*R*)-citramalic acid, which lacks a third -COOH group, affords a material that does not exhibit such a vibration.

It is well established that the p*K* of the citrate hydroxyl group is substantially lowered when the citrate ion is coordinated to a transition-metal ion.[18,19] As a result, it is reasonable to assume that the citrate ligand binds to the Mo atom through two of its carboxyl (possibly one terminal and the central ones) and its deprotonated hydroxyl groups. This renders the cluster with a 3− overall charge and an uncoordinated -COOH "arm". Evidence from vibrational spectroscopy,[15] together with chemical analysis,[16] is in accord with the above hypothesis. This coordination mode is similar to the one proposed for the homocitrate molecule in the Fe-Mo cofactor of nitrogenase.[6] At present, the general scope of the reaction of **I** with carboxylic acids (including the biologically important (*R*)-homocitric acid) is under investigation in our laboratory.

Acknowledgment. The support of this work by a grant from the National Institutes of Health (GM-33080) is gratefully acknowledged.

Supplementary Material Available: Tables S1, S2 containing listings of positional parameters, thermal parameters and selected distances and angles for **II** and **III** (17 pages); Tables S3, S4 listing calculated and observed structure factors for **II** and **III** (31 pages). Ordering information is given on any current masthead page.

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[15] EPR spectra are consistent with a $S = {}^3/_2$ system. C═O vibrations respectively: **IVa**, 1576, 1667, 1723 cm^{-1}; **IVb**, 1580, 1650 cm^{-1}; **IVc**, 1604, 1650, 1720 cm^{-1}.

[16] Anal. Calcd for $MoFe_3Cl_3S_4O_7N_2C_{22}H_{40}\cdot{}^1/_2CH_3CN$ (**IVa**, MW 968.13): C, 28.48; H, 4.90; N, 3.61. Found: C, 28.66; H, 5.32; N, 3.92. (Evidence of CH_3CN of solvation can be seen in the mid-infrared spectrum, 2249 cm^{-1}.) Anal. Calcd for $MoFe_3Cl_3S_4O_5N_2C_{21}H_{40}\cdot{}^1/_2CH_3CN$ (**IVb**, MW 924.13): C, 28.56; H, 5.14; N, 3.79. Found: C, 28.18; H, 5.27; N, 3.86. Anal. Calcd for $MoFe_3Cl_3S_4O_7N_3C_{30}H_{65}$ (**IVc**, MW 1077.08): C, 33.42; H, 6.03; N, 3.90. Found: C, 33.31; H, 6.00; N, 3.96.

[17] Cyclic voltammetry of **I** under identical conditions in 1,2-dichloroethane vs Ag/AgCl: −870 mV (reduction), +102 mV (oxidation).

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