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Communications

Syntheses and Structural Characterization of a New Class of Double Cubanes That Contain $MoFe_3S_4$ Subunits and Molybdenum-Coordinated, Bridging Mercapto−Carboxylate Ligands. Effective Catalysts for the Reduction of Hydrazine to Ammonia

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The vast amounts of spectroscopic data[1] available for the remarkable Fe/Mo/S center in nitrogenase now can be discussed with reference to a specific structure. This structure has been revealed by recent crystallographic studies of the FeMo protein in nitrogenase[2,3] and can be described in terms of an elongated octanuclear assembly of seven Fe, one Mo and approximately nine S atoms. In this structure, the two $MoFe_3S_3$ and Fe_4S_3 cuboidal subunits are bridged by three S^{2-} ligands and the six-coordinate Mo atom is located at the periphery of the cluster, coordinated by a bidentate homocitrate molecule and an imidazole group from protein bound histidine. The presence of homocitrate as a component of the nitrogenase cofactor was deduced previously by a combination of analytical and spectroscopic techniques,[4] and the cuboidal MFe_3S_3 subunits (M = Mo, Fe) found in the nitrogenase center are structurally similar to the $MoFe_3S_4$ cores that are ubiquitous in many synthetic Fe/Mo/S clusters.[5]

Recently we explored the catalytic properties of the Fe/Mo/S cubanes that contain the $[MoFe_3S_4]^{3+}$ cores and tetrachlorocatecholate[6] (Cl_4-cat) or citrate[7] (citr) ligands bound to the molybdenum atom. These studies have shown that the Fe/Mo/S cubanes are able to catalytically reduce hydrazine to ammonia, in the presence of cobaltocene ($Co(Cp)_2$) and 2,6-lutidinium chloride (LutHCl) as sources for electrons and protons, respectively.[8] The comparatively superior catalytic effectiveness of the $[(citr)MoFe_3S_4Cl_3]^{3-}$ cluster, and the possible intimate importance of carboxylate ligands in the catalytic process prompted us to extend our synthetic and catalytic studies with various other carboxylate Fe/Mo/S cubane derivatives.

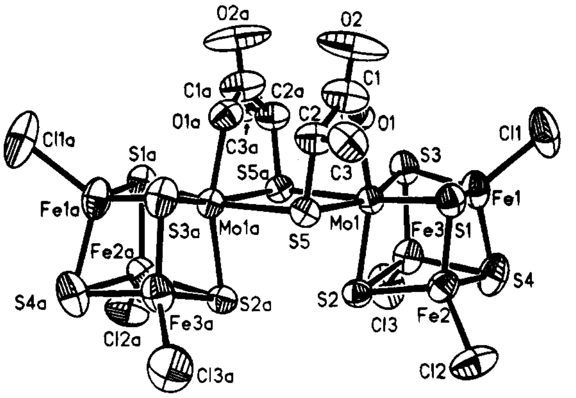

Figure 1. Structure and labeling scheme of $[MoFe_3S_4Cl_3(SCH(CH_3)COO)]_2{}^{4-}$ anion in **II**. Thermal elipsoids are drawn by ORTEP and represent 40% probability surfaces. Selected bond distances and angles: Mo1···Mo1a, 3.899(3) Å; S2···S2a, 3.370(9) Å; Mo1−S(cubane), 2.349(5) Å; S5···S5a, 3.300(7) Å; Mo−O(carboxyl), 2.10(1) Å; C=O(carboxyl), 1.18(2) Å, S5−Mo1−S5a, 80.3(1)°; O1−Mo1−S2, 162.3(3)°; Mo1−S5−Mo1a, 99.7(1)°.

In this communication we report the syntheses of the $(Et_4N)_4[(SCH(R)COO)MoFe_3S_4Cl_3]_2$ double cubanes (R = H, mercaptoacetate, **I**; R = CH_3, thiolactate, **II**; R = CH_2COOH, thiomalate; **III**) and the crystal and molecular structure and catalytic properties of **II**.

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(9) Anal. Calcd for $Mo_2Fe_6Cl_6S_{10}O_4N_4C_{36}H_{84}\cdot CH_3CN$ (**I**; MW 1737.28): C, 26.24; H, 5.00; N, 4.03. Found: C, 25.93; H, 4.79; N, 3.90 (Evidence of CH_3CN of solvation can be seen in the mid-infrared spectrum, 2249 cm^{-1}). Anal. Calcd for $Mo_2Fe_6Cl_6S_{10}O_4C_{38}H_{88}\cdot CH_3CN$ (**II**; MW 1765.28): C, 27.19; H, 5.15; N, 3.97. Found: C, 26.51; H, 4.99; N, 3.51. Anal. Calcd for $Mo_2Fe_6Cl_6S_{10}O_8N_4C_{40}H_{88}$ (**III**; MW 1812.34): C, 23.84; H, 4.63; N, 3.09. Found: C, 24.02; H, 4.61; N, 2.68. Far-infrared spectra of **I**, **II** and **III** show very similar features: 290 (m), 320 (w), 345 (vs), 356 (vs), 392 (m), 412 (m), 454 (w) cm^{-1}.

(10) C=O vibrations, respectively: **I**, 1600, 1650 cm^{-1}; **II**, 1629 cm^{-1}; **III**, 1608, 1640, 1732 cm^{-1}. The 1732 cm^{-1} stretch in **III** is tentatively assigned to a noncoordinated −COOH group.

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Table 1. Catalytic Reduction of N_2H_4 to NH_4^+ by **II**, $[MoFe_3S_4Cl_3(SCH(CH_3)COO)]_2^{4-}$, in the Presence of $Co(Cp)_2$ as Reducing Agent and LutHCl as the Proton Source[a]

	NH_3 yield,[c] equiv[d] (% conversion)[e,f]						
$[N_2H_4]$/[catalyst][b]	5 min	10 min	15 min	30 min	1 h	1.5 h	12 h
1	0.90 (45)	1.16 (58)	1.28 (64)	1.52 (76)	1.66 (83)	1.90 (95)	1.98 (99)
10	12.0 (60)	15.0 (75)	16.0 (80)	18.0 (90)	19.6 (98)	20.0 (100)	20.0 (100)
20	18.8 (47)	20.8 (52)	21.2 (53)	24.0 (60)	25.6 (64)	29.6 (74)	35.6 (89)
40	19.2 (24)	19.2 (24)	20.0 (25)	22.4 (28)	24.0 (30)	27.2 (34)	48.8 (61)

[a] Reactions were carried out anaerobically in CH_3CN using the $(Et_4N)_4[MoFe_3S_4Cl_3(SCH(CH_3)COO)]_2$ double cubane as the catalyst and various amounts of N_2H_4 as shown. The concentration of the catalyst was 2.0×10^{-4} M, and the concentrations of N_2H_4, $Co(Cp)_2$, and LutHCl were scaled accordingly. [b] One molecule of N_2H_4 per single cubane unit was assumed. [c] Ammonia was quantified by the indophenol method (Chaney, A. L.; Marbach, E. P. *Clin. Chem.* (*Winston-Salem, N.C.*) **1962**, *8*, 130). Sporadically, N_2H_4 quantification with *p*-(dimethylamino)benzaldehyde (Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006) confirmed complete nitrogen balance. A modified literature protocol[21] for sampling and treatment of various samples was employed. [d] All numbers reported are mean values of triplicate determinations. [e] A catalytic disproportionation experiment, i.e. with N_2H_4 being both the substrate and the reducing agent ($3N_2H_4 \rightarrow 4NH_3 + N_2$) gave only 4% conversion after 12 h. [f] Reactions of catalyst with $Co(Cp)_2$ and LutHCl (absence of N_2H_4), or of N_2H_4 with $Co(Cp)_2$ and LutHCl (absence of catalyst) gave ammonia within background limits (<3%).

The reaction of $(Et_4N)_2[(Cl_4\text{-cat})(CH_3CN)MoFe_3S_4Cl_3]$[6] with mercaptoacetic, thiolactic, and thiomalic acids in CH_3CN solution at ambient temperature cleanly affords microcrystalline **I**–**III**, respectively, in almost quantitative yields.[9] Intense C=O vibrations[10] in the infrared spectra are consistent with metal-bound monodentate carboxylate ligands.[11] The electronic spectra of **I**–**III** are nearly featureless and show a steadily increasing absorption from 750 nm to the UV region. Frozen CH_3CN solutions of **I**–**III** are EPR silent, implying strong electronic coupling between the two, thiolato-bridged, $MoFe_3S_4$ cubane subunits (*vide infra*).

Single crystals of $(Et_4N)_4[(SCH(CH_3)COO)MoFe_3S_4Cl_3]_2{\cdot}CH_3CN$, **II**, suitable for a X-ray diffraction study were obtained by vapor diffusion of Et_2O into a CH_3CN solution. The crystal structure determination[12] shows (Figure 1) the tetraanion (located on a crystallographic 2-fold axis) as a double cubane that contains the two $[(SCH(CH_3)COO)MoFe_3S_4Cl_3]^{2-}$ subunits bridged by the thiolate groups of the Mo-coordinated, bidentate, thiolactate ligands. Both of the Et_4N^+ cations in the asymmetric unit are disordered and the unit cell also contains four CH_3CN molecules of solvation. The mean Fe–Fe, Fe–S, and Fe–Cl bond lengths at 2.724(4), 2.274(7), and 2.218(7) Å are unremarkable and commonly found in a variety of other similar $MoFe_3S_4$ cores.[5] The Mo··Mo distance at 3.899(3) Å is comparable to the one found in the $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Br)_3(\mu\text{-}S_2)]_2^{4-}$ [13] at 3.97(7) Å. The latter represents the only other example of a double cubane bridged by two $\mu-\eta^1-\eta^1$ thiolate ligands. The Mo–O(carboxyl) bond length at 2.10(1) Å compares to corresponding metal–oxygen bonds found in a variety of metal–carboxylate complexes.[14] The interunit bridging is asymmetric and two Mo–S(bridge) bonds are found at 2.523(5) and 2.581(3) Å. The cyclic voltammetry of **I**–**III** shows[15] multiple reductions and oxidation waves and the two reduction waves are separated by ~200 mV. The electrochemical data also suggest that **I**–**III** are electronically coupled and retain the double cubane structure in coordinating solvents. Similar electronic perturbations between $MoFe_3S_4$ cubane subunits have been reported previously.[5,7,13]

The catalytic reduction of hydrazine by **II** (eq 1) in the presence of appropriate amounts of $Co(Cp)_2$ and LutHCl, in CH_3CN solution at ambient temperature, was

$$N_2H_4 + 2e\text{-} + 4H^+ \rightarrow 2NH_4^+ \tag{1}$$

investigated for various N_2H_4/cluster ratios. The results show (Table 1) that the catalytic reduction of N_2H_4 to NH_4^+ is nearly quantitative after ca. 1.5 h for the 1:1 and 10:1 ratios. Over the same time period, ammonia production yields drop gradually when the reaction is carried out with 20:1 or 40:1 N_2H_4:cluster ratios. This can be attributed to the rapid precipitation of the catalyst as its NH_4^+ salt or to the precipitation ("salting out") of $N_2H_4{\cdot}HCl$, which depletes the solution from substrate. Under the same conditions the $Fe_4S_4Cl_4^{2-}$ cluster[16] was tested as a potential catalyst, but was found to be inactive. The NH_4^+ salt of the cluster that precipitates out of solution redissolves upon addition of $(Et_4N)OH$, and the resulting solution continues to be active in the catalytic generation of NH_3 upon addition of N_2H_4, $Co(Cp)_2$, and LutHCl. Quantitative analytical studies of this system allowed for the recovery and characterization of the cluster at the end of the catalytic reaction.[17] The far-IR spectra of this material show the characteristic skeletal vibrations associated with the $MoFe_3S_4$ structural unit of the starting material.[17] The coordinatively saturated Mo atom in **II**, as well as the retention of the double cubane structure in solution, raise

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(12) Crystal and refinement data: black crystals (rectangular plates obtained from CH_3CN/Et_2O) of (Et_4N)**II** are monoclinic, space group *C*2/*c*, with $a = 16.281(5)$ Å, $b = 25.13(1)$ Å, $c = 19.019(7)$ Å, $\beta = 112.61(2)°$, and $Z = 4$. Single-crystal diffraction data for **II** (4728 reflections) were collected on a Nicolet P3F automated diffractometer ($\theta - 2\theta$ technique, $3° < 2\theta < 45°$) using Mo Kα radiation. The solution of the structure was carried out by direct methods. The refinement by full-matrix least-squares methods was based on 2774 unique reflections ($2\theta_{max} = 45°$, $I > 3\sigma(I)$). Anisotropic temperature factors were used for all non-hydrogen atoms in the anion. Refinement on 287 parameters converged to R (R_w) = 7.00% (6.52%).

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(15) Cyclic voltametry of **I**–**III** was carried out on a Pt disk electrode, in CH_3CN vs Ag/AgCl, with Bu_4NClO_4 as supporting electrolyte. The following results were obtained. For **I**: reductions at −970 mV, qr; −1170 mV, irr; (qr = quasireversible, irr = irreversible) oxidations at +350 mV, irr; +500 mV, irr. For **II**: reductions at −900 mV, qr; −1110 mV, irr; oxidations at +150 mV, irr, +500 mV, irr. For **III**: reductions at −860 mV, qr; −1050 mV, irr; oxidations at +200 mV, irr; +500 mV, irr.

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(17) See supplementery material.

(18) Cyclic voltametric measurements on IV in CH_3CN solution show quasireversible reduction waves at −0.970 and −1.200V cathodically shifted relative to **II**. Analysis for N_2N_4 in **IV** by the *p*-(dimethylamino)benzaldehyde method, showed 0.8 molecule of NH_2NH_2 per single cubane. The elemental analyses on **IV** have not been entirely satisfactory. Anal. Calcd for $MoFe_3S_5Cl_3O_2N_4C_{19}H_{48}$ (**IV**; MW 894.14); $(Et_4N)_2[(SCH(CH_3)COO)(N_2H_4)MoFe_3S_4Cl_3])$: C, 25.50; H, 5.36; N. 6.26. Found: C, 22.67, 23.27; H, 4.76, 4.98; N, 6.55, 6.55. Attempts to purify **IV** by recrystallization resulted in the formation of various amounts of the starting material **II** with loss of N_2H_4.

a question concerning the possible binding site of N_2H_4 prior to its activation. To address this question, **II** was allowed to react with 2 equiv of N_2H_4 in CH_3CN. The isolated product,[18] **IV**,was different than **II** and displayed N—H vibrations at 3292, 3232, and 3154 $cm^{-1}$and the ν(N—H) twist at 1149 cm^{-1}. These are characteristic vibrations for end-on, Mo-bound, hydrazine[19] in the $MoFe_3S_4$ cubanes.[20] It appears likely that, in a catalytic cycle, hydrazine coordination to the Mo atoms breaks down the dimeric structure of **II** and the subsequent reduction to NH_3 proceeds in a manner analogous to that reported for the $[MoFe_3S_4Cl_3(Cl_4\text{-cat})(CH_3CN)]^{2-}$ cluster.[8] The generation of single $MoFe_3S_4$ cubanes in this reaction also is suggested by the appearance of the characteristic $S = {}^3/_2$ EPR signal following the addition of N_2H_4 to solutions of **II**. A thorough study of the role of Mo-bound carboxylate ligands in the activation of N_2H_4 by $MoFe_3S_4$ cubanes is currently under way in our laboratory.

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Supplementary Material Available: Text giving experimental procedures, and details on analytical studies, figures giving far-infrared spectra an ORTEP diagram of **II**, and tables giving crystal data, positional parameters, thermal parameters, and selected bond distances and angles of **II** (15 pages). Ordering information is given on any current masthead page.

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