Structural Characterization and Reactivity Properties of a New Class of Mo/Fe/S Double Cubanes with Mo-Bound S-μ_2-η^1,O-η^1 Mercapto Carboxylate Ligands. New Catalysts for the Reduction of Hydrazine to Ammonia and Implications Regarding the Function of Nitrogenase

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The reaction of $(Et_4N)_2[MoFe_3S_4Cl_3(Cl_4\text{-cat})(CH_3CN)]$, **1**, with mercapto carboxylic acids of the general type HSCH(R)COOH affords in nearly quantitative yields the novel double cubanes of the formulation $[MoFe_3S_4Cl_3(SCH(R)COO)]_2^{4-}$ (R = H, mercaptoacetate, **2**; R = CH₃, thiolactate, **3**; R = CH₂COOH, thiomalate, **4**). Black crystals of (Et_4N)**2** are monoclinic, space group $C2/c$, with $a = 18.959(9)$ Å, $b = 12.657(7)$ Å, $c = 28.57(1)$ Å, $\beta = 98.03(4)°$, $V = 6790(5)$ Å³, and $Z = 4$. Black crystals of (Et_4N)**3** are monoclinic, space group $C2/c$, with $a = 16.281(5)$ Å, $b = 25.13(1)$ Å, $c = 19.019(7)$ Å, $\beta = 112.61(2)°$, $V = 7182(4)$ Å³, and $Z = 4$. The solutions of both structures were accomplished by direct methods. The refinement with full-matrix least-squares methods of 299 parameters based on 5942 unique reflections for (Et_4N)**2** ($2\theta_{max} = 45°$, $I > 3\sigma(I)$) and of 287 parameters based on 4728 unique reflections ($2\theta_{max} = 45°$, $I > 3\sigma(I)$) for (Et_4N)**3** resulted in final R (R_w) values of 6.09% (6.26%) and 7.00% (6.52%), respectively, for **2** and **3**. In both structures anisotropic temperature factors were assigned for all the non-hydrogen atoms in the cluster tetraanions. The tetraanions in **2** or **3** are composed of two $MoFe_3S_4$ subunits linked by the deprotonated thiol groups. In **2**, the mean intracubane Mo−S, Fe−S, and Fe−Cl bond distances are found at 2.356(3), 2.278(4), and 2.219(4) Å, respectively. The mean Mo···Fe and Fe···Fe distances are found at 2.727(2) and 2.728(3) Å, respectively. Similar metric features are found for **3**. Each of the two Mo atoms (separated by 3.916(3) Å in **2** and 3.899(3) Å in **3**) has a distorted octahedral coordination and in addition to three μ_3-S^{2-} ligands is coordinated to two μ_2-thiolato and a η^1-carboxylato ligands. The Mo−O(carboxylate) bond in **2** is 2.096(7) Å long (2.10(1) Å for **3**), and two types of Mo−S(bridging) bond lengths are present at 2.523(3) and 2.577(3) Å. The closest intercubane S···S distance is 3.266(6) Å. $(Et_4N)_2[MoFe_3S_4Cl_3(Cl_4\text{-cat})(CH_3CN)]$ also reacts with thiodiglycolic acid to form the $[MoFe_3S_4Cl_3(OOCCH_2SCH_2COO)]^{2-}$ cluster, **5**, in which the thioether dicarboxylate is coordinated to the Mo atom through its two carboxyl and thioether functionalities. Furthermore **1**, reacts with 3,4-dimercaptotoluene and thiosalicylic acid to form respectively compounds **6** and **7** with the bidentate ligands bridging the two $MoFe_3S_4$ subunits in a manner similar to that in **2** and **3**. EPR spectra are not observed for **2−4** in CH_3CN glasses at 5 K. The cyclic voltammetry of **2−4** shows multiple reductions and oxidation waves, and the two reduction waves are separated by 190−210 mV. The electrochemical data and the lack of the characteristic S = 3/2 EPR signal in solutions of **2−4** suggest that these molecules are electronically coupled and retain the double cubane structure in solution. Cluster **5** shows a characteristic $S = {}^3/_2$ EPR signal and displays a single reduction wave at −745 mV. The reduction of hydrazine to ammonia in the presence of cobaltocene and 2,6-lutidinium chloride was catalyzed by **3**. The core of the latter was found to be intact at the end of the catalytic reaction. It is proposed that in the presence of hydrazine, the dimeric structure of **3** collapses to generate single cubanes with Mo-coordinated, terminally bound hydrazine that undergoes subsequent protonation/reduction to ammonia.

Introduction

The synthetic Fe/Mo/S cubanes (single[1] or double[2]) show features associated with the metal−sulfido framework and the Mo atom coordination environment that structurally are quite similar to those of the nitrogenase Fe/Mo/S cofactor.[3] The structure of the latter was determined in recent crystallographic studies on the Mo−Fe protein.[4,5] In the synthetic cubane clusters, the $[MoFe_3S_4]^{3+}$ cores show EPR spectral characteristics of an $S = {}^3/_2$ ground state that electronically mimic the semireduced state of the Fe−Mo protein of nitrogenase and of

the extruded FeMo cofactor.[6] In the Fe/Mo/S cubanes, the six-coordinate Mo atom is located in a distorted octahedral environment bound by three core μ_3-S^{2-} ligands. In the vast majority of the Fe/Mo/S cubanes, the remaining set of ligands on the Mo atom are a bidentate ligand and either a neutral[7] or an anionic[8] ligand. Recently, $MoFe_3S_4$ cubane clusters were obtained that contain polycarboxylate ligands bound to the Mo site.[9] These clusters represent the first examples of models that

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may mimic the coordination of the homocitrate ligand to the Mo atom of the nitrogenase cofactor.[10,11]

In a previous communication, we reported the synthesis, structural characterization, and reactivity characteristics of a new class of Fe/Mo/S double cubanes that contain mercapto carboxylate ligands coordinated to the Mo atoms and also bridge the cubane subunits.[12] In this paper, we report in detail the synthetic and crystallographic studies briefly communicated previously.[12] Further, as a continuation of our studies of the catalytic reduction of nitrogenase substrates by the synthetic Fe/M/S (M = Mo,V) cubanes,[13,14] we report herein the catalytic reduction of hydrazine to ammonia by the mercapto carboxylate derivatives of these clusters.

Experimental Section

Synthesis. All experimental procedures were conducted under strictly anaerobic conditions using either a Vacuum Atmospheres Dri-Lab glovebox filled with prepurified nitrogen or standard Schlenk techniques. The chemicals in this research were used as purchased, except for solvents, which were purified as described elsewhere.[9b] All the carboxylic acids, hydrazine, lutidine, a 1.0 M standard solution of HCl/Et$_2$O, and cobaltocene were purchased from Aldrich Chemical Co. and used without further purification. Lutidine hydrochloride was synthesized by mixing 2,6-lutidine and HCl/Et$_2$O in Et$_2$O. Filtration of the milky white precipitate and drying *in vacuo* afforded an analytically pure material. Elemental analyses were performed by the Analytical Services Laboratory in the Department of Chemistry at the University of Michigan.

Physical Methods. Details on the instrumentation used for the spectroscopic and electrochemical studies can be found elsewhere.[9b]

Preparation of Compounds. (a). (Et$_4$N)$_2$[MoFe$_3$S$_4$Cl$_3$(Cl$_4$-cat)-(CH$_3$CN)] (1) was synthesized by a modified published procedure.[1d] Abbreviations used: Cl$_4$-cat = tetrachloro-catecholate, GA = glycolate, MAA = mercaptoacetate, TLA = thiolactate, TMA = thiomalate, TDGA = thiodiglycolate, DMT = 3,4-dimercaptotoluene, TSA = thiosalicylate, Lut·HCl = 2,6-lutidine hydrochloride.

(b) (Et$_4$N)$_4$[(MAA)MoFe$_3$S$_4$Cl$_3$]$_2$ (2). A sample of **1** (0.52 g, 0.50 mmol) was dissolved in 30 mL of CH$_3$CN. Mercaptoacetic acid (HSCH$_2$COOH, 5 mL of a 0.1 M stock solution in CH$_3$CN) was added

in a dropwise manner in the course of 5 min, causing a rapid color change to deeper brown with a greenish cast. The solution was stirred for a further 20 min and then filtered (no residue). Ether (100 mL) was layered on top of the filtrate, and after overnight standing at ambient temperature, a brown oily substance containing a microcrystalline material precipitated. The faintly colored supernatant liquid was decanted, and the oil was redissolved in CH$_3$CN and precipitated with ether. Isolation of the brown-black microcrystals and washing consecutively with EtOH, acetone, and ether gave 0.43 g of analytically pure material (quantitative yield). Anal. Calcd for Mo$_2$Fe$_6$-Cl$_6$S$_{10}$O$_4$N$_4$C$_{36}$H$_{84}$·CH$_3$CN (**2**, 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$_3$CN of solvation could be seen in the infrared spectrum, 2249 (w) cm^{-1} and was confirmed by X-ray crystallography.) Electronic spectrum (CH$_3$-CN): featureless. Far-infrared spectrum (cm^{-1}): 290 (m), 320 (w), 345 (vs), 356 (vs), 392 (m), 412 (m), 454 (w). Mid-infrared spectrum (cm^{-1}): ν_{asym}(C=O) 1600 (vs), 1650 (vs); ν_{sym}(C—O) 1305.

(c) (Et$_4$N)$_4$[(TLA)MoFe$_3$S$_4$Cl$_3$]$_2$ (3). A sample of **1** (1.00 g, 0.96 mmol) was dissolved in 40 mL of CH$_3$CN. A solution of thiolactic acid (HSCH(CH$_3$)COOH, 0.96 mL of a 0.1 M stock solution in CH$_3$-CN) was slowly dripped into the cluster solution, causing an instant color change from brown to darker brown with a greenish cast. Additional stirring (20 min), filtration, and dilution of the filtrate with ether caused an oily material to separate from the mixture after overnight standing. The supernatant liquid was decanted, ether (70 mL) was added to the flask, and the oil solidified to a black-brown powder after stirring vigorously for 1 h. This material is sufficiently pure for further reactions but can be recrystallized from CH$_3$CN/Et$_2$O (yield 0.80 g, 95%). Anal. Calcd for Mo$_2$Fe$_6$Cl$_6$S$_{10}$O$_4$N$_4$C$_{38}$H$_{88}$·CH$_3$CN (**3**, MW 1765.28): C, 27.19; H, 5.15; N, 3.97. Found: C, 26.51; H, 4.99; N, 3.51. Electronic spectrum (CH$_3$CN): featureless. Far-infrared spectrum: nearly identical to that of **2**. Mid-infrared spectrum (cm^{-1}): ν_{asym}-(C=O) 1629 (vs); ν_{sym}(C—O) 1301 (m).

(d) (Et$_4$N)$_4$[(TMA)MoFe$_3$S$_4$Cl$_3$]$_2$ (4). A sample of thiomalic acid (HSCH(CH$_2$COOH)COOH, 0.07 g, 0.48 mmol) was slowly added to a solution of **1** (0.50 g, 0.48 mmol) in 30 mL of CH$_3$CN. There was a gradual color change from brown-orange to darker brown. After being stirred for 1 h, the mixture was filtered (no residue) and ether (100 mL) was added to the filtrate. An oily material precipitated after standing for 5 h. This oil was redissolved in CH$_3$CN and precipitated with ether to yield a black microcrystalline substance, which was collected by filtration, washed with EtOH, acetone, and ether, and dried *in vacuo* (yield 0.41 g, 94%). Anal. Calcd for Mo$_2$Fe$_6$Cl$_6$S$_{10}$O$_8$N$_4$C$_{40}$H$_{88}$ (**4**, MW 1812.34): C, 23.84; H, 4.63; N, 3.09. Found: C, 24.02; H, 4.61; N, 2.68. Electronic spectrum (CH$_3$CN): featureless. Far-infrared spectrum: essentially identical to that of **2**. Mid-infrared spectrum

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(8) Ligand sets reported: substituted catecholate + anionic ligand L, where L = RS$^-$,[1b] RO$^-$,[1b] CN$^-$,[1b] N$_3^-$;[1d] oxalate + anionic ligand L, where L = Cl$^-$,[9] CN$^-$.[9b,14]

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(cm^{-1}): ν_{asym}(C=O) 1608 (vs), 1640 (vs), 1732 (s, due to free $-$COOH); ν_{sym}(C$-$O) 1305 (m).

(e) (Et$_4$N)$_2$[(TDGA)MoFe$_3$S$_4$Cl$_3$] (5). A sample of **1** (0.40 g, 0.38 mmol) was mixed with thiodiglycolic acid (HOOCCH$_2$SCH$_2$COOH, 0.06 g, 0.38 mmol) in 30 mL of CH$_3$CN. After 2 h of stirring, the solution was filtered, and upon addition of ether ($\sim$80 mL) to the dark brown filtrate and overnight standing, a brown-black powder and microcrystals precipitated. Isolation and recrystallization from CH$_3$-CN/Et$_2$O gave an analytically pure sample (yield 0.32 g, 93%). Anal. Calcd for MoFe$_3$Cl$_3$S$_5$O$_4$N$_2$C$_{20}$H$_{44}$ (**5**, MW 906.14): C, 26.49; H, 4.86; N, 3.09. Found: C, 26.37; H, 4.78; N, 3.08. Electronic spectrum (CH$_3$-CN, nm): 565 (br), 470 (br), 335. Far-infrared spectrum (cm^{-1}): 315 (m), 324 (m), 348 (s), 359 (vs), 383 (m), 397 (m), 414 (m). Mid-infrared spectrum (cm^{-1}): ν_{asym}(C=O) 1635 (vs), 1655 (vs); ν_{sym}(C$-$O) 1323 (s).

(f) (Et$_4$N)$_4$[(DMT)MoFe$_3$S$_4$Cl$_3$]$_2$ (6). A sample of **1** (0.10 g, 0.10 mmol) was dissolved in 20 mL of CH$_3$CN, and then 3,4-dimercapto-toluene (0.1 mL of a 0.1 M stock solution in CH$_3$CN) was added dropwise. There was a rapid color change from brown to brown-purple. After $\sim$3 h of stirring, the solution was filtered (no residue) and ether (100 mL) was added to the filtrate. After overnight standing at 5 °C a black, highly crystalline material precipitated, which was collected by filtration, washed thoroughly with ether, and dried *in vacuo* (yield 0.08 g, 88%). Anal. Calcd for Mo$_2$Fe$_6$Cl$_6$S$_{12}$N$_4$C$_{46}$H$_{94}$ (**6**, MW 1824.58): C, 30.25; H, 5.04; N, 3.07. Found: C, 31.07; H, 5.13; N, 3.11. Electronic spectrum (CH$_3$CN, nm): 520, 365, 310 (sh). Far-infrared spectrum (cm^{-1}): 283 (sh), 304 (m), 352 (s), 364 (vs), 395 (m), 413 (m). Mid-infrared spectrum (cm^{-1}): 804 (s), 869 (w), 1033 (m), 1067 (s), 1201 (m), 1393 (s), 1578 (m).

(g) (Et$_4$N)$_4$[(TSA)MoFe$_3$S$_4$Cl$_3$]$_2$ (7). Solid thiosalicylic acid (HSC$_6$H$_4$-COOH, 0.08 g, 0.48 mmol) was added to a solution of **1** (0.50 g, 0.48 mmol) in 30 mL of CH$_3$CN under continuous stirring. The color became darker brown with a greenish cast. The solution was stirred for 30 in and then filtered (no residue). Upon addition of ether to the filtrate, a microcrystalline black solid precipitated. It was isolated by filtration, washed with EtOH, acetone, and ether, and finally recrystallized from CH$_3$CN/Et$_2$O (0.30 g, 69%). Elemental analyses have not been entirely satisfactory. Anal. Calcd for Mo$_2$Fe$_6$Cl$_6$S$_{10}$O$_4$N$_4$C$_{46}$H$_{88}$ (**7**, MW 1820.28): C, 30.33; H, 4.83; N, 3.08. Found: C, 26.93; H, 4.39; N, 3.23. Electronic spectrum (CH$_3$CN, nm): essentially feature-less. Far-infrared spectrum (cm^{-1}): 312 (m), 341 (s), 355 (vs), 384 (m), 394 (m), 411 (m). Mid-infrared spectrum (cm^{-1}): ν_{asym}(C=O) 1595 (vs), 1610 (vs), 1635 (sh); ν_{sym}(C$-$O) 1339 (s); ν(C$-$H, aromatic) 3053 (w).

Reaction of (Et$_4$N)$_4$[(TLA)MoFe$_3$S$_4$Cl$_3$]$_2$ (3) with N$_2$H$_4$ in a 1:2 Molar Ratio. A sample of **3** (0.5 g, 0.28 mmol) was dissolved in 50 mL of CH$_3$CN, and the solution was subsequently mixed with N$_2$H$_4$ (2.84 mL of a 0.2 M stock solution). The dark brown homogeneous solution was stirred for $\sim$8 h, and then Et$_2$O was layered onto it. After overnight standing, a microcrystalline material was isolated by filtration (yield 0.45 g, 90%). The elemental analyses have not been entirely satisfactory. Anal. Calcd for MoFe$_3$S$_5$Cl$_3$O$_2$N$_4$C$_{19}$H$_{48}$ (MW 8794.14; (Et$_4$N)$_2$[SCH(CH$_3$)COO)(N$_2$H$_4$)MoFe$_3$S$_4$Cl$_3$]): 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. Analysis for N$_2$H$_4$ by the *p*-(methylamino)benzaldehyde method showed 0.8 molecule of N$_2$H$_4$ per single cubane. Electronic spectrum (CH$_3$CN): featureless. Far-infrared spectrum: nearly identical to that of **3**. Middle-infrared spectrum (cm^{-1}): ν_{asym}(C=O) 1630(vs); ν_{sym}(C$-$O) 1300 (m); ν(N$-$H) 3292 (w), 3232(w), 3154(w); ν_{twist}(N$-$H) 1149-(m). Attempts to purify this material by recrystallization from CH$_3$-CN/Et$_2$O resulted in the formation of various amounts of starting material **3** with loss of N$_2$H$_4$.

Catalytic Reductions of Hydrazine. Reactions were performed anaerobically in CH$_3$CN. The final volume of the reaction mixture was 40 mL. The concentration of the catalyst was 2.0 × 10^{-4} M, and the concentrations of N$_2$H$_4$, Co(Cp)$_2$, and Lut·HCl were scaled accordingly. A typical protocol for a 10:1 substrate:catalyst ratio follows. The appropriate amount (0.50 mL) of a stock solution (5 mM) of the catalyst was added to CH$_3$CN (<40 mL). To this solution was injected *via* syringe 10 equiv of N$_2$H$_4$ (0.25 mL of a 0.20 M stock solution), and the volume was made up to 40 mL. Finally, cobaltocene (0.02 g) and Lut·HCl (0.03 g) were added to the mixture under rigorous

stirring. Aliquots of the solution (3 mL) were withdrawn by syringe and used for ammonia determination. The protocols and references for ammonia and hydrazine determinations are found in Table 5.

Experimental Procedure for the Recovery and Identification of the Cluster Catalyst 3. A sample of **3** (0.17 g, 0.1 mmol) was dissolved in 20 mL of CH$_3$CN. To this solution was added dropwise a 0.20 M stock solution of N$_2$H$_4$ in CH$_3$CN (0.96 mL, 0.2 mmol), and the volume was adjusted to 40 mL. Solid Co(Cp)$_2$ (0.07 g, 0.4 mmol) and LutHCl (0.11 g, 0.8 mmol) were added, and the mixture was stirred vigorously for 1.5 h. At this time, the precipitation of a black solid material was apparent. An aliquot of this mixture was tested for NH$_3$ by the indophenol method. The NH$_3$ found ($\sim$0.4 mmol) amounted to $\sim$100% conversion. A quantitative test for N$_2$H$_4$ by a literature method showed only a trace. This mixture was then filtered, and the black solid was isolated (0.08 g). The dark brown filtrate was collected and allowed to stand overnight at room temperature. At this stage, it was tested for NH$_3$ but none was detected. This implies that all the NH$_3$ had remained with the residue, very likely as NH$_4$$^+$ cations.

(a) Analysis of the Filtrate. The filtrate was evaporated to dryness, and the brown oil was washed thoroughly with EtOH until all of the Co(Cp)$_2$Cl was removed. The yellow washings were combined and found to contain only Co(Cp)$_2$Cl, by its characteristic electronic spectrum showing broad absorptions at 400, 300, and 260 nm. This spectrum is identical to the spectrum of a solution of "authentic" Co-(Cp)$_2$Cl in EtOH. The remaining brown solid ($\sim$0.07 g) was recrystallized from CH$_3$CN/Et$_2$O. The resulting material was characterized by electronic spectroscopy (the electronic spectrum of **3** is featureless, so only absorptions due to Co(Cp)$_2$$^+$ can be identified) mid-infrared spectroscopy (peaks assigned to Co(Cp)$_2$$^+$ 462 (m), 866 (m), 1414 (s), 3100 (m) cm^{-1}; peaks assigned to ν_{asym}(C=O) 1635 cm^{-1}, ν_{sym}(C$-$O) 1300 cm^{-1}; peaks assigned to Et$_4$N$^+$ 787 (w), 1008 (m), 1035 (w), 1184 (m), 1363 (m), 1393(m), 1458 (m), 1483 (m), 2948 (w), 2975 (m) cm^{-1}), and far-infrared spectroscopy (peaks at 290 (m), 315 (w), 342 (s), 353 (vs), 393 (m), 412 (m) cm^{-1}). The far-infrared spectrum agrees entirely with the spectrum of pure (Et$_4$N)$_4$ [MoFe$_3$S$_4$Cl$_3$(SCH-(CH$_3$)COO)]$_2$, **3**, and convincingly shows that the cluster core has remained intact. Mid-infrared spectroscopy indicates that the carboxy-late binding mode has not been altered. It also shows presence of two different cations, Et$_4$N$^+$ and Co(Cp)$_2$$^+$. Anal. Calcd for Mo$_2Fe_6CoS_{10}$-Cl$_6O_4N_3C_{40}H_{78}$ (MW 1783,14; [(Et$_4$N)$_3$(Co(Cp)$_2$)][MoFe$_3$S$_4$Cl$_3$(SCH-(CH$_3$)COO)]$_2$): C, 26.92; H, 4.37; N, 2.36. Found: C, 27.91; H, 3.89; N, 2.53. A sample of this "recycled" material was used to prepare a 0.05 M stock solution in CH$_3$CN. A 10:1 catalytic reaction was carried out (under conditions described above), and a 90% conversion to NH$_3$ was established after 0.5 h.

(b) Analysis of the Residue. The black residue isolated at the end of the reaction described above ($\sim$0.08 g) was suspended in 20 mL of CH$_3$CN, and in order to solubilize it, Et$_4$NOH (0.2 M in EtOH) was added dropwise until a dark brown homogeneous solution resulted (vacuum was employed periodically, to remove the volatile products (NH$_3$ generated by deprotonation of NH$_4$$^+$). The solution was filtered (negligible amount of black residue), and Et$_2$O was added to the filtrate. A brown-black solid precipitated and was recrystallized from CH$_3$CN/Et$_2$O. The isolated brown-black solid was characterized by infrared spectroscopy and electronic spectroscopy and found to be essentially the same as the recovered catalyst from the "filtrate". The only difference between the two materials was the relative ratio of the Et$_4$N$^+$ and Co(Cp)$_2$$^+$ cations. Anal. Calcd for Mo$_2$Fe$_6$Co$_2$S$_{10}$Cl$_6$O$_4$N$_2$C$_{42}$H$_{68}$ (MW 1842.0; ((Et$_4$N)(Co(Cp)$_2$)$_3$[MoFe$_3$S$_4$Cl$_3$(SCH(CH$_3$)COO)]$_2$): C, 27.36; H, 3.69; N, 1.52. Found: C, 26.14; H, 2.93; N, 1.62. A sample of this material was used to prepare a 0.05 M stock solution in CH$_3$-CN. A 10:1 catalytic reaction was carried out (see protocol above), and an 87% conversion to NH$_3$ was established after 0.5 h.

X-ray Structural Determinations. Crystal data, intensity collection information, and structure refinement parameters for compounds **2** and **3** are provided in Table 1. Diffraction data were obtained at ambient temperature on a Nicolet P3F (Siemens) four-circle computer-driven diffractometer using graphite-monochromatized ($2\theta_{max}$ = 12.50°) Mo Kα radiation (λ = 0.710 73 Å). Intensity data were collected by using a $\theta-2\theta$ step scan technique. The computer programs were those of the SHELXTL structure determination package.

X-ray Measurements and Collection and Reduction of Data. (a)

Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for Compounds **2** and **3**

formula	$Mo_2Fe_6Cl_6S_{10}O_4$-$N_4C_{36}H_{84}$	$Mo_2Fe_6Cl_6S_{10}O_4N_4$-$C_{38}H_{88} \cdot CH_3CN$
MW	1696.28	1765.28
a (Å)	18.959(9)	16.281(5)
b (Å)	12.657(7)	25.13(1)
c (Å)	28.57(1)	19.019(7)
β (deg)	98.03(4)	112.61(2)
V (Å^3)	6790(5)	7182(4)
Z	4	4
crystal system	monoclinic	monoclinic
space group	$C2/c$	$C2/c$
crystal size (mm)	$0.35 \times 0.20 \times 0.05$	$0.32 \times 0.17 \times 0.10$
d_{calcd} (g/cm^3)^a	1.66	1.63
d_{obsd} (g/cm^3)^a	1.66	1.65
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
abs coeff μ (cm^{-1})	21.6	20.5
scan speed (deg/min)	1.50–15.00	1.50–15.00
scan range	$1.2 + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$	$1.2 + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$
data collected (octants)	$3–45°\ (+h,+k,\pm l)$	$3–45°\ (+h,+k,\pm l)$
no. of total reflns	9714	6682
no. of unique reflns	5942	4728
no. of refined reflns	2958	2774
no. of variables	299	287
data:param ratio	10.0	9.8
GOF	1.79	3.06
R (%)^b	6.09	7.00
R_w (%)^c	6.26^d	6.52^e

^{a} By flotation in dibromoethane/CCl$_4$ mixture. ^{b} $R = \sum(|F_o - F_c|)/\sum|F_o|$. ^{c} $R_w = [\sum(w|F_o - F_c|)^2/\sum w(F_o)^2]^{1/2}$. ^{d} $w^{-1} = \sigma^2(F_o) + 0.001(F_o)^2$. ^{e} $w^{-1} = \sigma^2(F_o) + 0.0001(F_o)^2$.

(Et$_4$N)$_4$[(MAA)MoFe$_3$S$_4$Cl$_3$]$_2$ (2). Suitable single crystals for a diffraction experiment were grown by vapor diffusion of Et$_2$O into a CH$_3$-CN solution of the compound. A black needle was cleaved to appropriate size, and a fragment ($0.35 \times 0.20 \times 0.05$ mm) was mounted in a sealed quartz capillary under Ar atmosphere.

(b) (Et$_4$N)$_4$[(TLA)MoFe$_3$S$_4$Cl$_3$]$_2$ (3). Appropriately sized single crystals suitable for an X-ray experiment were grown by vapor diffusion of Et$_2$O into a CH$_3$CN solution of the compound over a period of several days. A black needle ($0.32 \times 0.17 \times 0.10$ mm) was mounted in a quartz capillary as described previously. For both crystals, the determination of unit cell parameters and data collection and reduction routines were followed according to protocols described previously.[9b]

Solution and Refinement of the Structures. The direct methods routine SOLV of the SHELXTL 88 package of the crystallographic program was used to solve both structures. Trial positions of the Mo, Fe, and core S atoms were taken from the E map derived from the unique phase set with the next-to-highest combined figure of merit. The remaining non-hydrogen atoms were located by subsequent difference Fourier maps. The structures were refined by the block-cascade least-squares method. All Mo, Fe, S, Cl, O, and C atoms of the anions were refined anisotropically. The remaining atoms were assigned isotropic temperature coefficients.

(a) (Et$_4$N)$_4$[(MAA)MoFe$_3$S$_4$Cl$_3$]$_2$ (2). The two Et$_4$N$^+$ cations in the asymmetric unit are disordered. This disorder was modeled successfully by refining the methyl C at full occupancy, while the methylene C atoms were placed in two alternate positions at 40% and 60% occupancies, respectively. Fixed contributions for the H atoms (C—H bond length of 0.96 Å) with thermal parameters set to 1.2 times those of the bonded C atoms were included in the final stages of the refinement for all non-disordered C atoms. One CH$_3$CN solvent molecule is found per double cubane in the asymmetric unit.

(b) (Et$_4$N)$_4$[(TLA)MoFe$_3$S$_4$Cl$_3$]$_2$ (3). There are two Et$_4$N$^+$ cations in the asymmetric unit, both of which are disordered. The first cation exhibits the common disorder having its methylene carbons disordered and was modeled as described previously. The second cation appeared to have all of its carbon atoms disordered. Therefore, all of its methyl and methylene C atoms were placed at alternate positions and were assigned 50% occupancy. H atoms were treated as previously for the non-disordered C atoms.

Crystallographic Results. The final atomic positional and thermal parameters for the tetraanion **2** with standard deviations derived from

Table 2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters (Å$^2 \times 10^3$) for the Non-Hydrogen Atoms in [MoFe$_3$S$_4$Cl$_3$(SCH$_2$COO)]$_2^{4-}$, **2**

atom	x	y	z	$U_{eq}^{a,b}$
Mo(1)	5580(1)	926(1)	3123(1)	41(1)
Fe(1)	5475(1)	2436(1)	3793(1)	52(1)
Fe(2)	6402(1)	748(1)	3979(1)	56(1)
Fe(3)	6656(1)	2347(1)	3361(1)	49(1)
S(5)	5712(1)	878(2)	2238(1)	46(1)
S(1)	5535(1)	2769(2)	3022(1)	48(1)
S(2)	6809(1)	583(2)	3275(1)	54(1)
S(3)	5191(2)	702(2)	3870(1)	57(1)
S(4)	6631(2)	2539(2)	4152(1)	60(1)
Cl(1)	4739(2)	3524(3)	4101(1)	85(1)
Cl(2)	6900(2)	−345(3)	4524(2)	98(2)
Cl(3)	7477(2)	3330(2)	3096(1)	73(1)
O(1)	5421(4)	−704(5)	3032(3)	59(3)
O(2)	5263(5)	−2107(7)	1887(4)	96(5)
C(1)	5203(6)	−1169(10)	1981(5)	71(5)
C(2)	5884(6)	−496(9)	2098(5)	69(5)

^{a} Equivalent isotropic U is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor ($U_{eq} = {}^1\!/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$). ^{b} Estimated standard deviations are given in parentheses.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [MoFe$_3$S$_4$Cl$_3$(MAA)]$_2^{4-}$, **2**, and [MoFe$_3$S$_4$Cl$_3$(TLA)$_2^{4-}$, **3**

Bond Distances

	2	**3**
Mo···Mo	3.916(3)	3.899(3)
Mo···Fe (mean)	2.727(2)	2.727(3)
Fe···Fe (mean)	2.728(3)	2.724(3)
Fe···S (mean)	2.278(4)	2.275(7)
Fe···Cl (mean)	2.219(4)	2.218(7)
S(5)···S(5a)	3.266(6)	3.300(7)
S(1)···S(1a)	3.364(6)	3.370(9)
Mo(1)—S(1)	2.350(3)	2.330(4)
C(1)—O(1)	1.318(14)	1.298(23)
Mo(1)—S(2)	2.351(3)	2.366(4)
Mo(1)—S(3)	2.368(4)	2.352(5)
Mo(1)—S(5a)	2.577(3)	2.581(3)
Mo(1)—S(5)	2.523(3)	2.523(5)
Mo(1)—O(1)	2.096(7)	2.098(10)
S(5)—C(2)	1.824(12)	1.813(15)
C(1)—C(2)	1.545(17)	1.512(28)
C(1)—O(2)	1.226(15)	1.181(22)

Angles

	2	**3**
S(1)—Mo(1)—S(2)	102.9(1)	102.5(1)
S(5a)—Mo(1)—S(3)	165.0(1)	160.6(1)
S(2)—Mo(1)—S(3)	103.7(1)	103.1(2)
S(5a)—Mo(1)—O(1)	83.5(2)	77.2(3)
S(2)—Mo(1)—O(1)	87.8(2)	86.5(2)
S(5)—Mo(1)—S(5a)	79.6(1)	80.3(1)
S(2)—Mo(1)—S(5a)	162.1(1)	167.7(2)
O(1)—Mo(1)—S(5a)	79.1(2)	77.2(3)
S(5)—Mo(1)—S(1)	84.8(1)	87.5(2)
S(5)—Mo(1)—S(2)	86.9(1)	89.7(1)
S(1)—Mo(1)—S(3)	102.7(1)	103.5(2)
S(1)—Mo(1)—O(1)	163.6(2)	162.3(3)
S(3)—Mo(1)—O(1)	86.4(2)	89.0(3)
S(1)—Mo(1)—S(5)	87.6(1)	87.5(2)
Mo(1)—S(5)—Mo(1a)	100.3(1)	99.7(1)

the inverse matrices of the least-squares refinements are compiled in Table 2. Similar parameters for the cations and the H atoms have been deposited as supporting information. Selected intramolecular distances and angles for the anions in **2** and **3** are included in Table 3 with labeling schemes as shown in Figures 1 and 2, respectively, for **2** and **3**. Due to the similarity of the structures of **2** and **3**, the crystallographic coordinates for **3** will not be reported herein but have been previously deposited.[12]
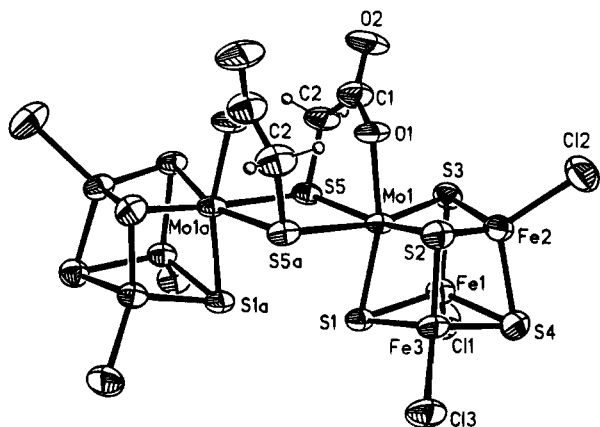
Figure 1. Structure of the [MoFe₃S₄Cl₃(SCH₂COO)]₂⁴⁻ (2) double cubane showing the 40% probability ellipsoids (drawn by ORTEP) and the atom-labeling scheme.
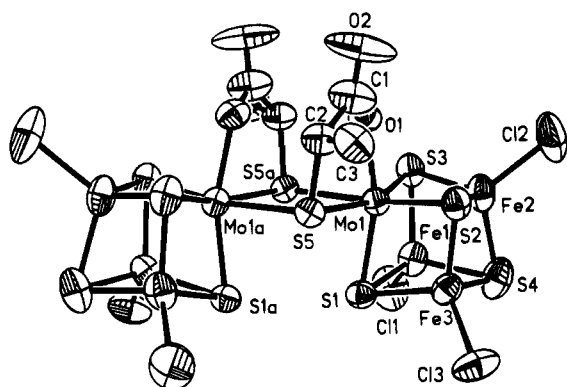

Figure 2. ORTEP plot of the [MoFe₃S₄Cl₃(SCH(CH₃)COO)]₂⁴⁻ (3) anion with atom-labeling scheme. Thermal ellipsoids represent 40% probability.

Results and Discussion

Synthesis. The CH₃CN solvent molecule in the [(Cl₄-cat)MoFe₃S₄Cl₃(CH₃CN)]²⁻ cluster, 1, can be replaced with a variety of neutral or anionic ligands such as RS⁻,[1b] RO⁻,[1b] CN⁻,[1b,d] N₃⁻,[1d] PEt₃,[1b] hydrazines,[1d,2h] and pyrazine.[2h] These facile substitution reactions are of paramount importance in the catalytic reductions by 1 of nitrogenase substrates. The latter (hydrazine, acetylene) are thought to replace CH₃CN in 1 and undergo activation and subsequent reduction.[13,15] The Mo-bound bidentate tetrachlorocatecholate, Cl₄-cat, ligand in 1 can be easily protonated with appropriate carboxylic acids to yield cubanes with Mo-bound polycarboxylate ligands including oxalate,[9,14b] methylimino diacetate,[9b] citrate,[9] malate,[9] citramalate,[9] diglycolate,[16] and nitrilotriacetate.[16] The reaction of 1 with glycolic acid (HOCH₂COOH), GA, did not take place to any appreciable extent (even after prolonged reaction time, ~3 d, at 50 °C) presumably due to the low acidity of the −OH group,[17] which renders the acid incapable of protonating the Cl₄-cat ligand. On the contrary, reaction of 1 with mercaptoacetic acid, MAA, the thio analog of glycolic acid, occurs readily (within 10 min) with a nearly quantitative protonation and substitution of the Cl₄-cat ligand. This reaction apparently takes place due to the higher acidity of the −SH group vs the −OH group. This phenomenon has been studied thoroughly

and generalized to a variety of mercapto carboxylic acids.[18] In the case of MAA, pK_a(SH) = 10.40 whereas, for GA, pK_a(OH) > 15. The formation of the MAA derivative, 2, is manifested by dramatic changes in the infrared spectrum (see section on vibrational spectroscopy). The isolated product is a double cubane with MoFe₃S₄ subunits bridged by the deprotonated thiolate functionalities of the Mo-bound MAA ligands. A reasonable assumption would be that the first product that forms during the course of the reaction is the [MoFe₃S₄Cl₃(SCH₂-COO)(CH₃CN)]²⁻ cubane. This cluster subsequently loses the labile solvent ligand to allow coordination of the already Mo-bound thiolate moiety of a neighboring cubane, thus forming a dimer of cubanes. An alternative course of events in the early stages of the formation of 2 could be substitution of the CH₃-CN ligand in 1 to give a [MoFe₃S₄Cl₃(Cl₄-cat)(HSCH₂-COOH)]²⁻ intermediate with a monodentate MAA ligand. Formation of 2 eventually follows protonation of the Cl₄-cat ligand. Dimeric complexes with the bridging mode of MAA found in 2 (vide infra) are ubiquitous in the literature.[19] The dimerization occasionally is prevented by bulky substituents on the −CH₂− group of the acid.[20] A typical example is thiobenzilic acid, which has been used in the synthesis of monomeric Mo complexes as models for the enzyme xanthine oxidase.[20c,d,f] The reaction of 1 with mercaptopropionic acid (HSCH₂CH₂COOH), an acid similar in acidity to MAA,[18] did not occur at all, even after a prolonged period of reaction time (4 d) and elevated temperatures. This lack of reactivity may be explained in terms of the lower thermodynamic stability of an expected six-membered ring compared to that of a five-membered ring. It appears that the thermodynamic driving force for the Cl₄-cat ligand substitution in 1 is determined by both the acidity of the −SH group and ring size effects.

The reaction of 1 with thiomalic acid, TMA, yields a product with the same core as the one in 2 above but with an additional, noncoordinated, −CH₂COOH group. This is somewhat surprising, since thiomalate is known to be a good metal chelator[20e] and was perhaps expected to bind to the Mo in a tridentate fashion.

Cluster 1 also reacts readily with thiodiglycolic acid, TDGA. This ligand coordinates to the Mo in a tridentate mode through its two −COO⁻ groups and its thioether functionality. The gross structure of this cluster and atomic connectivity has been established on the basis of the best available, albeit low- quality, crystallographic diffraction data.[21] To our knowledge, this is the first example of complexation of a thioether group to the

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(21) The gross structure of the (Et₄N)₂[(thiodiglycolate)MoFe₃S₄Cl₃] (5) cluster was determined. Unfortunately, poor crystal quality together with severe cation disorder did not allow for a successful refinement of the structure, so presentation of metric features is not warranted at this time. Nevertheless, the connectivity of the cluster was established and shows the dianion as a MoFe₃S₄Cl₃ single cubane core with the TDGA coordinated to the Mo atom through its two carboxyl and thioether functionalities. A schematic diagram of 5 is represented in Figure 3. Crystallographic data: monoclinic, space group P2₁/n, a = 11.325(5) Å, b = 20.690(6) Å, c = 15.716(8) Å, β = 98.00(4)°, V = 3637(3) Å³, Z = 4, d$_{calcd}$ = 1.63 g/cm³, T = ambient, μ = 20.3 cm⁻¹.
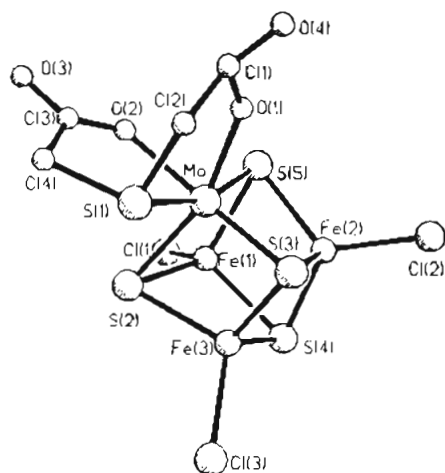
Figure 3. Core structure of the $[MoFe_3S_4Cl_3(OOCH_2SCH_2COO)]^{2-}$ (5) from crystallographically determined coordinates.[21]

Scheme 1
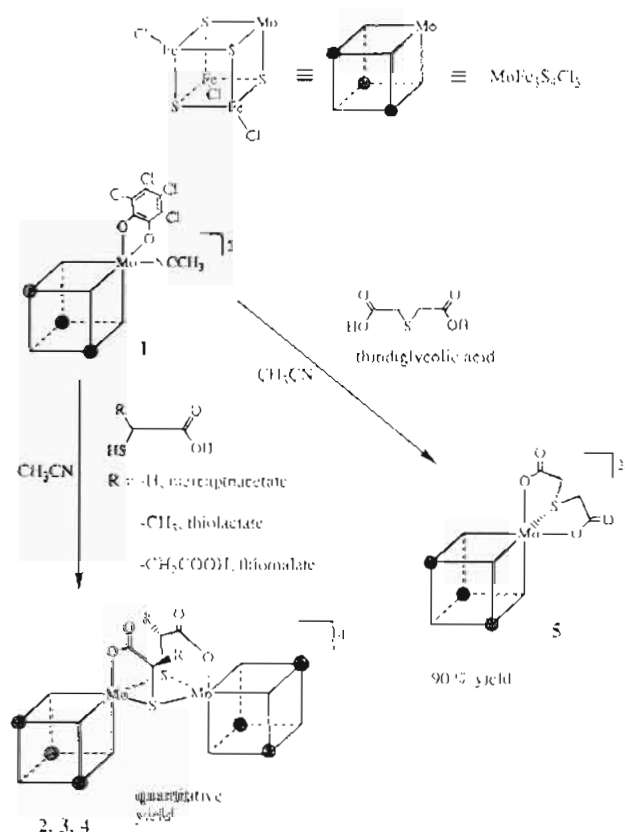
MoFe$_3$S$_4$ cubanes. Metal–thiodiglycolate coordination compounds have been synthesized and structurally characterized.[19d,22] The syntheses of the mercapto carboxylate cubanes are shown in Scheme 1. Finally, It should be noted that the reaction of $[MoFe_3S_4(SPh)_3(al_2\text{-}cat)(CH_3CN)]^{2-}$ [1d] (al = allyl) with an excess of PhSH affords the double cubane $[Mo_2Fe_6S_8\text{-}(SPh)_9]^{3-}$.[23,24] In this instance, protonation of the Mo-bound al$_2$-cat induces dimerization and yields exclusively the μ-SPh double cubane.

Vibrational Spectroscopy. (a) Far-Infrared Region. All the mercapto carboxylate cubanes show intense absorptions in the 300–360 cm^{-1} region. More specifically, a set of two peaks at 345 and 355 cm^{-1} can be assigned to Mo–μ_3-S, Fe–μ_3-S, and Fe–Cl skeletal vibrations or a combination of them.[25,26] Such absorptions are characteristic of the $[MoFe_3S_3Cl_3]^0$ structural core.[9,26] For comparison, **1** exhibits the above set of vibrations at 346 and 361 cm^{-1}.[9b] In addition to these vibrations, a vibration around 320 cm^{-1} can be tentatively assigned to the Mo–S (thiolate) bond. Such vibrations have been previously detected in the $Mo^V_2(MAA)_5(H_2O)_2$ complex[27] and a variety of Mo complexes with cysteine or related ligands such as cysteine esters[28a] or cysteamine chelates.[28b]

(b) Mid-Infrared Region. The vibrational spectroscopic features of the starting compound **1** have been discussed to some extent elsewhere.[9] Peaks assigned to Mo-bound Cl$_4$-cat (1255, 1430, 542 cm^{-1}) and Mo-bound CH$_3$CN (2284, 3212 cm^{-1}) vanish upon reaction of **1** with mercapto carboxylic acids. At the same time intense C=O absorptions in the 1600–1750 cm^{-1} region appear due to the metal–carboxylate moiety. More specifically, **2** and **3** give rise to $\nu_{asym}(C=O)$ at 1600, 1650, and 1629 cm^{-1}, respectively, while the corresponding $\nu_{sym}(C-O)$ values are found at 1305 and 1301 cm^{-1}. Consequently, the Δ values ($\Delta = \nu_{asym}(C=O) - \nu_{sym}(C-O)$) are 345 and 328 cm^{-1}, respectively, typical for terminally coordinated metal–carboxylate complexes.[29] Compound **4** shows a medium-intensity peak at 1732 cm^{-1} due to a noncoordinated, protonated carboxylate moiety. Such a vibration is absent from spectra of **2, 3,** and **5,** which evidently lack such a group. Free –COOH vibrations have been detected for MoFe$_3$S$_4$ cores with Mo-bound citrate[9] or nitrilotriacetate,[16] which also possess a free –COOH group. Also, vibrations in the same region have been seen for diorganotin(IV) mercaptosuccinate complexes.[22d,30]

Electronic and EPR Spectra. The electronic spectra of all the compounds reported herein are featureless and show a steadily increasing absorption from 750 nm to the UV region. Therefore, electronic spectroscopy is not a useful diagnostic tool for the characterization of these compounds. No EPR spectra are detected in CH$_3$CN solutions of **2–4** at temperatures as low as 4 K. The lack of the $S = {}^3/_2$ EPR signal, typically observed with the $[MoFe_3S_4]^{3+}$ cores,[9,31] indicates strong electronic coupling between the $[MoFe_3S_4]^{3+}$ subunits, resulting in the absence of a signal. A number of precedents of such coupling are available. The doubly-bridged double cubane clusters (DBDC's) of the general type $\{[(L\text{-}L)MoFe_3S_4Cl_2]_2(\mu_2\text{-}X)(\mu_2\text{-}S)\}^{n-}$ (L-L = Cl$_4$-cat or oxalate; X = S^{2-}, $n = 6^{2f}$; X = OH$^-$,[2f]

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Table 4. Cyclic Voltammetric Data for the Clusters **1**–**6**[a,b]

compd	solvent	redns (mv)	oxidns (mV)
1	CH₃CN	−920, qr	+300, irr
1	ClCH₂CH₂Cl	−940, qr	+350, irr
2	CH₃CN	−970, qr; −1170, irr	+350, irr; +500, irr
3	CH₃CN	−900, qr; −1110, irr	+150, irr; +500, irr
4	CH₃CN	−860, qr; −1050, irr	+200, irr; +500, irr
5	CH₃CN	−745, rev	+150, irr; +500, irr
6	CH₃CN	−956, qr	+195, irr; +600, irr

[a] Electrochemical studies were performed with a BAS electroanalyzer. The electrochemical cell used had a platinum disc as the working electrode, a Pt wire auxiliary electrode, and an Ag/AgCl reference electrode. Tetrabutylammonium perchlorate (Bu₄NClO₄) was utilized as the supporting electrolyte. Typical concentrations used were ∼10⁻³ M in electroanalyte and 10⁻² M in supporting electrolyte. [b] qr = quasireversible, irr = irreversible, rev = reversible.

CN⁻,[2g,14b] or N₃⁻,[26] $n = 5$; X = NH₂NH₂, $n = 4$[2g]) are "EPR-silent" due to coupling through the μ_2-S bridge. In the case of the mercapto carboxylate clusters under consideration, electronic coupling occurs through the thiolate groups of the bridging ligands. In contrast, the single cubane **5** exhibits a clean EPR signal consistent with a $S = {}^3/_2$ ground state ($g_{max} = 4.990$, $g_x = 2.461$, $g_{min} = 1.837$) as expected for an isolated [MoFe₃S₄]³⁺ core. Very similar spectra have been reported for other single MoFe₃S₄−hydroxy−polycarboxylate cubane clusters.[9]

Electron Transfer Properties. Cyclic voltammetric results for the clusters under discussion are presented in Table 4, and representative cyclic voltammograms are given in Figure 4. Clusters **2**–**4** show two quasi-reversible reduction processes, separated by 190−210 mV. Such separations are typical for similar electronically perturbed subunits, and this behavior has been analyzed in detail in a number of cases.[9,23,24,32,33] The electrochemical behavior of the clusters under discussion shows that these compounds retain integrity in coordinating solvents (CH₃CN) and the entire cluster behaves as an entity with strongly interacting subunits. The above results are in full agreement with, and indirectly verify, the EPR observations. Cluster **5** has a single reduction at −745 mV. This value can be compared with that of the corresponding reduction of [MoFe₃S₄Cl₃(methylimimodiacetate)]²⁻ [9b] at −830 mV (in CH₃-CN). All the mercapto carboxylate cubanes show irreversible oxidation waves. This is not unexpected, considering the presence of the redox-active thiolate ligands. Similar irreversible redox behavior has been observed with the thiolato triply bridged [Mo₂Fe₆S₈(SR)₉]³⁻ double cubanes.[2b] A *single* reduction wave is found with cluster **6** at −955 mV, which is considered an indication that its dimeric structure collapses in CH₃CN solution to generate single [MoFe₃S₄Cl₃(DMT)-(CH₃CN)]²⁻ cubanes. EPR results show this compound to have an $S = {}^3/_2$ ground state and verify the above hypothesis.

Description of the Structures. The tetraanion in **2** is located on a crystallographically imposed C_2 axis passing through the center of the rhomb defined by the two Mo atoms and the two bridging S atoms. Mean values of intracubane Mo−S, Fe−S, and Fe−Cl distances are found at 2.356(3), 2.278(4), and 2.219-(4) Å, respectively. The Mo···Fe and Fe···Fe distances are 2.727(2) and 2.728(3) Å, respectively. The above metric features are commonly found in similar metal−sulfur cores and will not be considered in any further detail. For more information on this topic, we refer to a plethora of other publications.[1,2i,23] The Mo atom is found in a distorted
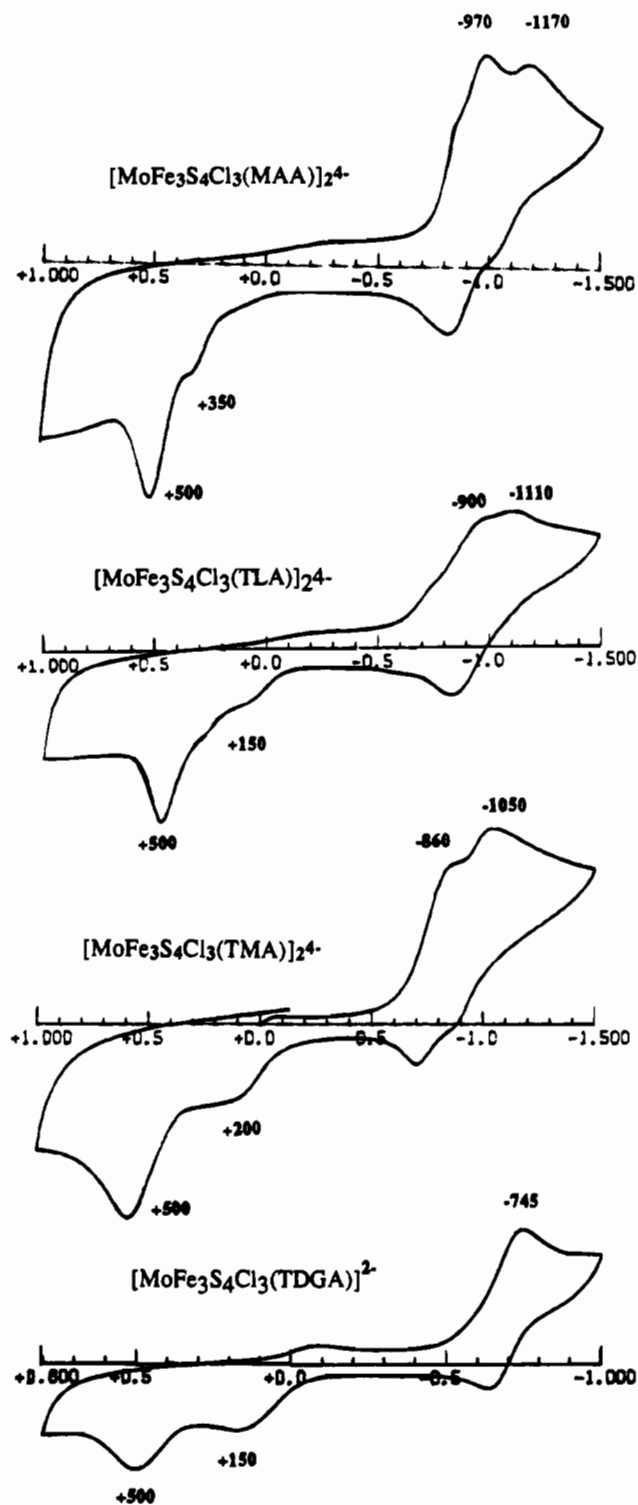

Figure 4. Representative cyclic voltammograms of clusters **2**–**5**. Peak potentials are indicated. Experimental conditions are as described in Table 4.
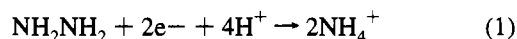
octahedral environment. Apart from the three μ_3-S ligands, one carboxylate and two thiolate functionalities complete the coordination sphere of each Mo atom. Two different Mo−S$_{bridging}$ bond distances are observed: a short one at 2.523(5) Å and a longer one at 2.581(3) Å. Mo/Fe/S clusters having alkanethiolates as bridging ligands between two Mo atoms have been reported in the literature and structurally characterized.[23] More specifically, the Mo−S$_{bridging}$ bond length in the [Mo₂Fe₆S₈(SEt)₉]³⁻ cluster[2a,24] is 2.567(4) Å, similar to the one found for the double cubane **2**. The short−long pattern in the Mo−S$_b$ bond distances is also found in the [Mo₂O₂-

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(SCH$_2$COO)$_4$]$^{2-}$ compound,[19c] which contains the same "Mo$_2$-(MAA)$_2$" core. In the latter, the Mo−S$_b$ bond lengths are seen at 2.490(1) and 2.471(1) Å, slightly shorter than those in cluster **2**, due to the Mo(VI) oxidation state. The Mo•••Mo separation in MAA is 3.916(3) Å, a value that compares well with the corresponding Mo•••Mo distance in [MoFe$_3$S$_4$(S-*p*-C$_6$H$_4$Br)$_3$-(μ-S$_2$)]$_2$$^{4-}$,[34] at 3.97(7) Å. The latter is the only other MoFe$_3$S$_4$ double cubane cluster known which is *doubly*-bridged through the Mo atoms. The long Mo•••Mo distance in **2** or **3** precludes direct metal−metal interaction and suggests that the lack of an EPR spectrum is a consequence of effective antiferromagnetic coupling through the bis(thiolate) bridge. The Mo−O(carboxyl) bond at 2.10(1) Å is within the expected range of similar bonds.[29a,35] Both mercaptoacetate chelate ligands are *cis* with respect to each other. This is somewhat intriguing, considering that a hypothetical *trans* configuration would be sterically more favorable, while the cubane-to-cubane distance wouldn't be altered. At this time, we are unable to assign this phenomenon to stereochemical reasons. The closest core S•••S intercubane contact in **3** is found at 3.370(9) Å and is too long to be considered even as a weak disulfide bond.[36] Similar, but longer S•••S contacts have been observed for the [(Fe$_4$S$_4$Cl$_3$)$_2$(μ-S)]$^{4-}$ cluster[37] at 3.67 Å. The S•••S contacts in the doubly-bridged, double cubanes [(cat-Cl$_4$)(CH$_3$CN)MoFe$_3$S$_4$Cl$_3$)$_2$(μ-S)(μ-X)]$^{n-}$, for different intercluster bridges X are of similar magnitude: X = S^{2-}, 3.61 Å; X = OH$^-$, 3.20 Å; X = NH$_2$NH$_2$, 3.55 Å; X = CN$^-$, 3.81 Å. The S•••S distance in **2** between the bridging S(thiolate) atoms is 3.300(7) Å and also cannot be considered as a bonding interaction.[38]

Catalytic Reactivity. Reductions of Hydrazine to Ammonia. The ability of **3** to act as a catalyst in the reduction of hydrazine to ammonia (eq 1) in the presence of Co(Cp)$_2$ and

$$NH_2NH_2 + 2e- + 4H^+ \rightarrow 2NH_4^+ \qquad (1)$$

Lut·HCl as reducing agent and source of protons, respectively, was investigated for various N$_2$H$_4$:cluster ratios. The results (Table 5) show that the catalytic conversion of N$_2$H$_4$ to NH$_4^+$ is nearly quantitative after ca. 1.0 h for the 1:1 and 10:1 ratios. For the higher N$_2$H$_4$:cluster ratios (20:1 or 40:1) ammonia production levels drop gradually. This observation has been attributed to the precipitation ("salting out") of N$_2$H$_4$ as N$_2$H$_4$·HCl, which depletes the reaction medium from substrate, and/or the precipitation of the catalyst combined with the NH$_4^+$, N$_2$H$_5^+$, or Co(Cp)$_2^+$ cations. Analytical and spectroscopic results verify the above statement (see Experimental Section). Ammonia production yields increase when a more dilute reaction mixture is used to avoid or delay precipitation. For

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Table 5. Catalytic Reduction of N$_2$H$_4$ to NH$_4^+$ by the [MoFe$_3$S$_4$Cl$_3$(SCH(CH$_3$)COO)]$_2$$^{4-}$ Cluster, **2**, in the Presence of Co(Cp)$_2$ as Reducing Agent and Lut·HCl as Proton Source[a]

N$_2$H$_4$[b]: catalyst	NH$_3$ yield,[c] equiv[d] (% conversion)[e]				
	5 min	15 min	30 min	1 h	12 h
1	0.90 (45)	1.28 (64)	1.52 (76)	1.66 (83)	1.98 (99)
10	12.0 (60)	16.0 (80)	18.0 (90)	19.6 (98)	20.0 (100)
20	18.8 (47)	21.2 (53)	24.0 (60)	25.6 (64)	35.6 (89)
40	19.2 (24)	20.0 (25)	22.4 (28)	24.0 (30)	48.8 (61)

[a] Reactions were carried out anaerobically in CH$_3$CN using the (Et$_4$N)$_4$[MoFe$_3$S$_4$Cl$_3$(SCH(CH$_3$)COO)]$_2$ double cubane (**3**) as the catalyst and various amounts of N$_2$H$_4$ as shown. The concentration of the catalyst was 2.0×10^{-4} M, and the concentrations of N$_2$H$_4$, Co(Cp)$_2$, and LutHCl were scaled accordingly. [b] One molecule of N$_2$H$_4$ 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$_2$H$_4$ quantification with *p*-(dimethylamino)benzaldehyde (Watt, G. W.; Chrisp, J. D. *Anal. Chem.* **1952**, *24*, 2006) confirmed complete nitrogen balance. A modified literature protocol for sampling and treatment of various samples was employed: Schrock, R. R.; Glassman, T. E.; Vale, M. G.; Kol, M. *J. Am. Chem. Soc.* **1993**, *115*, 1760. [d] All numbers reported are mean values of triplicate determinations. [e] Reactions of catalyst with Co(Cp)$_2$ and LutHCl (absence of N$_2$H$_4$) or of N$_2$H$_4$ with Co(Cp)$_2$ and LutHCl (absence of catalyst) gave ammonia within background limits (<3%).

example, for a 100:1 substrate:catalyst ratio ([catalyst, **3**] = 1.26 $\times 10^{-5}$ M), the following results were obtained, time (percent conversion): 5 min (58), 30 min (58), 1 h (66), 12 h (71). These results suggest enhanced conversion rates by comparison to those obtained using cluster **1** as the catalyst under identical conditions, time (percent conversion): 5 min (30), 30 min (34), 1 h (38), 12 h (61). *This may implicate the carboxylate ligand and/or the mercapto group in the catalytic process, possibly as a proton transfer device that assists in substrate reduction.*[39] The core of the catalyst **3** is found intact at the end of the reaction, and the "recycled" material continues to be catalytically active in additional N$_2$H$_4$ reduction cycles. In an attempt to evaluate the possible involvement of the Fe sites in the catalytic reaction process, the [Fe$_4$S$_4$Cl$_4$]$^{2-}$ cluster[41] was tested as a potential catalyst. Under the same reaction conditions, no ammonia was detected above background limits (<3%). A catalytic disproportionation reaction (eq 2)

$$3N_2H_4 \rightarrow 4NH_3 + N_2 \qquad (2)$$
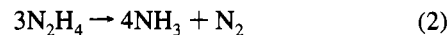
where N$_2$H$_4$ serves as both a substrate and a reducing agent, in the presence of **2** or **3**, did not proceed to any significant extent (about 4% conversion to NH$_3$ after 12 h). The coordinatively saturated Mo atom and the retention of the double cubane structure in solution (CH$_3$CN) raise questions concerning the possible binding site and mode of the N$_2$H$_4$ substrate. To address this point, **3** was allowed to react with 2 equiv of N$_2$H$_4$ in CH$_3$CN (see Experimental Section). The isolated cluster,[42] displayed ν(N−H) at 3292, 3232, and 3154 cm^{-1} and ν_{twist}-(N−H) at 1149 cm^{-1}. These vibrational frequencies are different from those associated with free N$_2$H$_4$[43] and are

(39) Results from our laboratory show that alterations in the Mo-coordinated polycarboxylate ligands of the [MoFe$_3$S$_4$]$^{3+}$ core dramatically influence ammonia production yields. A general trend we have observed is that as the number of "arms" of the carboxylate ligand increases, the efficiency of the catalyst improves.[40]

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(42) Cyclic voltammetric measurements on the product in CH$_3$CN show quasi-reversible reduction waves at −970 and −1200 mV cathodically shifted relative to **3**.

(43) Giguére, P. A.; Liu, I. D. *J. Chem. Phys.* **1952**, *20*, 136.

characteristic of metal-bound N_2H_4.[2gh,44] The far-infrared spectrum of the product (with vibrations at 320 (m), 340 (vs), 355 (vs), 390 (m), and 411 (m) cm^{-1}) is characteristic of a $MoFe_3S_4Cl_3$ structural core.[45] Moreover, its EPR spectrum (in CH_3CN glass) displayed the characteristic $S = {}^3/_2$ signal associated with a *single* cubane core. Lastly, metal-bound end-on bridging N_2H_4 is unlikely to be present in any steps of the catalytic process, since it has been proven that side-on μ_2-N_2H_4 is not reduced to any appreciable extent to $NH_4{}^+$.[13] Cluster **5** catalyzes the reduction of N_2H_4 as well. The yields are lower (100:1 ratio), time (percent conversion): 5 min (38), 30 min (45), 1 h (47), 12 h (65). Substrate access to Mo and subsequent activation of substrate on **5** can be envisioned by a change of the hapticity of the tridentate TDGA either by displacing the thioether S-donor atom or by protonation of a carboxyl arm.

Conclusions

Cluster **1** reacts readily with a variety of mercapto carboxylic acids. The Cl_4-cat ligand in **1** is protonated, and the mercapto carboxylate dianion is found coordinated to the Mo site in the end product. The cubane cluster products have the $[MoFe_3S_4Cl_3(SCH(R)COO)]_2{}^{4-}$ formulation. Cluster **1** also reacts with thiodiglycolic acid, which is incorporated in the final single cubane product in a tridentate fashion.

Compounds **2** and **3** have been structurally characterized as their Et_4N^+ salts. Their core is composed of two $MoFe_3S_4$ cubane structural subunits linked with two mercapto carboxylates through the bridging deprotonated thiol group while the carboxyl groups are found to be monodentate. $Mo\cdots Mo$ separations are 3.916(3) Å for **2** and 3.899(3) Å for **3**. The closest core $S\cdots S$ contact is 3.370(9), Å and the $S\cdots S$ distance between the thiolato bridges is 3.300(7) Å. Preliminary crystallographic results show cluster **5** as a single $MoFe_3S_4$ cubane core with the diacid coordinated to the Mo *via* two carboxyl and thioether functionalities.[21]

In CH_3CN glasses, **2**−**4** do not show EPR signals at temperatures as low as 4 K. These, combined with the electrochemical results in the same solvent (multiplicity of redox waves), indicate that there is strong electronic coupling between the two $MoFe_3S_4$ subunits.

Clusters **3** and **5** are efficient catalysts in the reduction of N_2H_4 (a product of nitrogenase function under N_2 obtained by quenching the functioning enzyme with acid or alkali[46]) to NH_3 in the presence of $Co(Cp)_2$ and Lut·HCl as reductant and proton source, respectively, with good turnover values. Cluster **3** gives a 66% conversion (N_2H_4:catalyst = 100:1) after 1 h and 71%

after 12 h. Cluster **5** gives 38% and 65% yields, respectively, under the same conditions. The lack of catalytic activity for the Fe_4S_4 cubanes in similar reactions and under identical conditions strongly suggests that the Mo heterometal is the site of substrate activation and reduction. The Osaka group has reported studies on reductions of a variety of nitrogenase substrates by electrochemically generated reduced forms of the $[Fe_4S_4(SR)_4]^{2-}$ and $[Mo_2Fe_6S_8(SR)_9]^{3-}$ clusters.[47] There was no discussion on the possible involvement of the Mo heterometal in the above processes; however, under the conditions used in those experiments, the Mo site is unlikely to be available (*e.g,* by protonation of a μ-SPh ligand) for substrate coordination. It appears that, for certain substrates, the Mo atom in nitrogenase is involved in substrate reduction in a process that requires availability of (at least) one site on the Mo atom. Evidence that may implicate the Mo atom as the site of substrate activation/inhibition in the FeMo-co[3b] includes (a) the profound effects in dinitrogen reduction brought about by skeletal alterations in the Mo-bound homocitrate ligand[10] and (b) EXAFS analyses[48] showing that CN^-, a nitrogenase inhibitor,[49] binds to the Mo site of the nitrogenase cofactor. Continuation of our studies will focus on the role of the Mo-coordinated carboxylate ligands in the catalytic process. The results may shed some light on the possible role and involvement of homocitrate in the function of the nitrogenase cofactor. It was suggested recently that, just as in the $[WH_2(\eta^2\text{-OOCCH}_3)(dppe)_2]^+$ complex, where loss of the carboxylate ligand is followed by N_2 coordination, dissociation of the homocitrate ligand from the Mo atom in the nitrogenase cofactor may precede substrate binding.[50]

Supporting Information Available: Table S1, containing listings of positional parameters, thermal parameters, and selected bond distances and angles for $[MoFe_3S_4Cl_3(SCH_2COO)]_2{}^{4-}$, **2**, and infrared spectra of **3** before and after the catalytic cycle (20 pages). Ordering information is given on any current masthead page. Listings of positional and thermal parameters and selected bond distances and angles for $[MoFe_3S_4Cl_3(SCH(CH_3)COO)]_2{}^{4-}$, **3**, have been deposited as supplementary material with a previous publication.[12]

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(45) Representative spectra have been deposited with the supporting information.

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