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A Novel Molybdenum−Iron−Sulfur Cluster. Synthesis, Structure, and Properties of $[Et_4N]_2[MoFe_4S_4(SC_6H_{11})_7]\cdot{}^1/_2CH_3CN$

Changneng Chen, Tingbin Wen, Wenjie Li,[†] Hongpin Zhu, Yihui Chen, Qiutian Liu,* and Jiaxi Lu

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter,
Chinese Academy of Sciences, Fuzhou, Fujian 350002, China

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A reaction system consisting of $FeCl_2$, $NaSC_6H_{11}$, $(NH_4)_2MoS_4$, and Et_4NBF_4 in methanol affords a novel Mo−Fe−S cluster $[Et_4N]_2[MoFe_4S_4(SC_6H_{11})_7]\cdot{}^1/_2CH_3CN$ (**1**). The compound crystallizes in the monoclinic space group C_2/c, $a = 50.762(5)$ Å, $b = 12.230(1)$ Å, $c = 33.228(4)$ Å, $\beta = 130.428(10)°$, $V = 15703(3)$ Å^3, and $Z = 8$. The structure of the anion is composed of a single $MoFe_3S_4$ cubane unit and a $Fe(SC_6H_{11})_4$ subunit. All the four Fe atoms are tetrahedrally coordinated, and the Mo atom is octahedrally coordinated. The metal formal oxidation levels were deduced as $2Fe^{(III)} + 2Fe^{(II)} + Mo^{(III)}$ by structural parameters and Mössbauer effect. The effective magnetic moment of the cluster diminishes smoothly with the decreasing of temperature in the range 1.5−300 K showing an antiferromagnetic spin-exchange interaction operating in the cluster.

Introduction

In nature the activation and the reduction of dinitrogen to ammonia are known to be catalyzed by nitrogenase. The recent crystal structure studies on FeMo protein of *Azotobacter vinelandii* and *Clostridium pasteurianum* have revealed the identity of FeMo-cofactor[1] which is essential for substrate binding and activation. The FeMo-cofactor was modeled as an elongated $MoFe_7S_9$ cluster containing two incomplete cuboidal subunits MFe_3S_3 (M = Fe or Mo) linked by three μ_2-S bridges. The Mo atom occupies a unique position at the pole of the cluster and is also coordinated by a homocitrate that serves as a bidentate-(O,O)-ligand through the central carboxylate and the hydroxyl groups and an imidazole group from a histidine residue. In the last two decades, attempts to obtain analogues of the active site in nitrogenase have resulted in the syntheses and characterization of a large number of Fe/Mo/S clusters containing one or two $MoFe_3S_4$ cubane structural units as possible structural or functional models for the active site. These clusters, including their analogues of vanadium,[2] were synthesized, and their reactions have been studied in detail,[3−13] such as double cubanes: $[Mo_2Fe_6S_9(SR)_8]^{3-}$,[3] $[Mo_2Fe_6S_8(SR)_9]^{3-}$,[3,4] $[Mo_2Fe_6S_8(OMe)_3(SR)_6]^{3-}$,[5] $[Mo_2Fe_7S_8(SR)_{12}]^{3-,4-}$,[6] $[Mo_2Fe_6S_8(SR)_6(3,6\text{-}R_2cat)_2]$,[4−7] (cat = catecholate) $\{[MoFe_3S_4Cl_2(Cl_4cat)]_2(\mu_2\text{-}S)(\mu_2\text{-}L)\}^{n-}$ ($L = N_2H_4$, $n = 4$; $L = OH^-$, CN^-, N^{3-}, $n = 5$; and $L = S^{2-}$, $n = 6$),[8] $[(MoFe_3S_4Cl_4)_2(\mu\text{-}C_2O_4)]$,[4−9] $\{[(MoFe_3S_4Cl_2)(C_2O_4)]_2(\mu\text{-}S)(\mu\text{-}CN)\}$,[5−9] and $\{[(meida)MoFe_3S_4Cl_2]_2S\}^{4-}$ (meida = *N*-methylimidodiacetate(2-));[10] single cubanes: $[MoFe_3S_4(R_2dtc)_5]$ ($R_2 = Me_2$, Et_2, C_5H_{10}, C_4H_8; M = Mo, W),[11] $[MoFe_3S_4(Et_2dtc)_5]^-$,[11] $[Mo(3,6\text{-}R_2cat)(L')Fe_3S_4(L)_3]^{2-,3-}$ ($L = RS^-$, Cl^-; R = allyl, n-Pr, L′ = DMSO, DMF, CH_3CN, PR_3, RS^-, CN^-, RO^-),[12] $[(media)MoFe_3S_4(SR)_3]^{2-}$ (R = Et, p-C_6H_4F),[10] $[(MoFe_3S_4Cl_4)C_2O_4)]^{3-}$,[9] $[MoFe_3S_4Cl_3(mida)]^{2-}$ (mida = methyliminodiacetate),[9] $[MoFe_3S_4(EtS)_3Fe(C_6H_4O_2)_3]^{3-}$,[13] and so on.

Here we report a novel type of single $MoFe_3S_4$ cubane-like cluster $[MoFe_3S_4(SC_6H_{11})_3Fe(SC_6H_{11})_4]^{2-}$ which contains a $Fe(SC_6H_{11})_4$ unit linking to the cubane skeleton through three SR bridges. The synthesis, structure, and properties of the cluster compound are also included in this paper.

Experimental Section

All experimental procedures were carried out under dinitrogen atmosphere, and standard Schlenk technique was used. All solvents were degassed before use. The chemicals in this research were used as purchased without further purification. $(NH_4)_2MoS_4$ was obtained by literature method.[14] White hygroscopic powder $NaSC_6H_{11}$ was obtained through refluxing cyclohexanethiol with sodium metal in THF.

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* To whom correspondence should be addressed.

[†] Present address: Department of Physics, Fuzhou University, Fuzhou, Fujian 350002, China.

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Preparation of $[Et_4N]_2[MoFe_3S_4(SC_6H_{11})_3Fe(SC_6H_{11})_4]\cdot{}^1/_2CH_3CN$ (1). A solution of $NaSC_6H_{11}$ (2.76 g, 20 mmol) in 25 mL of methanol was added dropwise to a slurry of $FeCl_2$ (0.63 g, 5 mmol) in 25 mL of methanol for 30 min at room temperature, resulting in a large amount of yellow-brown precipitates. Then 0.26 g (1 mmol) of $(NH_4)_2MoS_4$ was added. A gradual color change from brown-red to dark brown was observed. After being stirred for 22 h, the reaction solution was filtered, and 0.66 g (3 mmol) of Et_4NBF_4 was added to the filtrate. The filtrate was evaporated to dryness. The residue was dissolved in 25 mL of CH_3CN and was filtered again to remove the yellow insoluble solid. After 2 days of storage of the solution at 4 °C, dark brown crystals (0.98 g, yield 63.8%) of compound **1** were collected by filtration, washed with acetonitrile/ether (1:3 v/v), and dried in vacuo. Anal. Calcd for $C_{59}H_{118.5}Fe_4MoN_{2.5}S_{11}$: C, 46.16; H, 7.72; N, 2.28. Found: C, 46.13; H, 7.67; N, 2.28. Far-IR (cm^{-1}): 473(s), 440 (s), 408 (sh), 388 (s), 374 (s), 354 (s), 338 (s), 322 (sh), 310 (sh). UV, λ_{max} (ϵ, $M^{-1}cm^{-1}$, CH_3CN): 290 nm (12 300), 330 nm (11 700).

Preparation of $(Me_3PhCH_2N)_2[MoFe_3S_4(SC_6H_{11})_3Fe(SC_6H_{11})_4]$. The procedure in the preceding preparation was utilized in the synthesis of this compound with the use of Me_3PhCH_2NBr (0.46 g, 2 mmol) instead of Et_4NBF_4. A satisfactory elemental analyses were given, and the structure of the product was identified by X-ray diffraction,[15] in which seven disordered carbon atoms of the ligands were found.

Preparation of $[Et_4N]_3[Mo_2Fe_6S_8(SC_6H_{11})_9]$ (2). A procedure with the intention of obtaining anion **1** as an intermediate and of studying its reaction was performed as follows: A solution of $NaSC_6H_{11}$ (1.38 g, 10 mmol) in 12 mL of methanol was added dropwise to a slurry of $FeCl_2$ (0.32 g, 2.5 mmol) in 12 mL of methanol for 30 min at room temperature, resulting in a large amount of yellow-brown precipitate. A sample of 0.13 g (0.5 mmol) of $(NH_4)_2MoS_4$ was added, causing a color change from brown-red to dark brown. After stirring for 12 h and filtration, 0.30 g (1.43 mmol) of citric acid $C_6H_8O_7\cdot H_2O$ was added to the filtrate and stirred for 12 h at 50 °C, and then the reaction solution was filtered again. The filtrate was allowed to stand at 4 °C for several days to give black crystals. The product was collected by filtration, washed with CH_3CN/THF (1:3 v/v), and dried in vacuo, affording 0.58 g (yield 52%) of complex **2**. Anal. Calcd for $C_{78}H_{159}Fe_6Mo_2N_3S_{17}$: C, 42.37; H, 7.25; Fe, 15.16; Mo, 8.68; N, 1.90; S, 24.65. Found: C, 41.67; H, 7.11; Fe, 15.80; Mo, 8.38; N, 2.11; S, 25.51. The complex was further identified by X-ray structure determination to give a rough structure of double $Mo_2Fe_6S_8$ cubane skeleton.[16]

Crystal Structure Determination. Single crystals of compound **1** were obtained by diffusion of ether vapor into ether/acetonitrile (1:1, v/v) solution of **1**. A black, air-sensitive crystal with dimensions of 0.26 × 0.32 × 0.36 mm was sealed inside a glass capillary under dinitrogen atmosphere. Diffraction data were collected on a Siemens P4 four-circle diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator using $\theta - 2\theta$ scan mode with the scan speed of 6°/min in ω. The intensities were corrected for Lorentz-polarization effects and empirical absorption. The crystallographic data are summarized in Table 1.

The structure was solved by direct methods. Sixteen atoms (Mo, Fe, S) in the skeleton were located from an E-map, while the remaining non-hydrogen atoms were located in succeeding difference Fourier syntheses. Non-hydrogen atoms except for those of the CH_3CN solvate molecule were refined anisotropically by full-matrix least-squares techniques. The atoms N(3), C(61), and C(62) of the CH_3CN were disordered with the occupancy factors of 0.5 for each and were refined isotropically. Hydrogen atoms were introduced at calculated positions (C−H = 1.00 Å) with isotropic thermal parameters. All calculations were performed on an IBM PC/486 computer with the Siemens SHELXTL P4/PC program package. Selected atomic coordinates with their thermal parameters are listed in Table 2.

Table 1. Crystallographic Data for $[Et_4N]_2[MoFe_4S_4(SC_6H_{11})_7]\cdot{}^1/_2CH_3CN$

chemical formula	$C_{59}H_{118.5}Fe_4MoN_{2.5}S_{11}$
fw	1535.0
space group	$C2/c$
a, Å	50.762(5)
b, Å	12.230(1)
c, Å	33.228(4)
β, deg	130.428(10)
V, Å^3	15703(3)
Z	8
T, °C	21
λ, Å	0.71073
ρ_{calc}, g/cm^3	1.30
μ, cm^{-1}	12.03
R^a	0.068
$R_w{}^b$	0.079

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum[w(|F_o{}^2 - F_c|)]^2/\sum w(F_o)^2\}^{1/2}$, $w^{-1} = \sigma^2(F) + 0.0008F^2$.

Table 2. Selected Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for **1**

atom	x	y	z	$U_{eq}{}^a$
Mo(1)	1383(1)	3513(1)	7520(1)	64(1)
Fe(1)	1900(1)	4654(1)	7659(1)	76(1)
Fe(2)	1244(1)	5311(1)	6919(1)	74(1)
Fe(3)	1453(1)	3407(1)	6779(1)	77(1)
Fe(4)	1157(1)	2096(1)	8034(1)	86(1)
S(1)	1851(1)	2811(1)	7615(1)	81(1)
S(2)	946(1)	3717(1)	6595(1)	76(1)
S(3)	1559(1)	5330(1)	7804(1)	74(1)
S(4)	1635(1)	5111(1)	6804(1)	92(1)
S(5)	1695(1)	2985(1)	8494(1)	82(1)
S(6)	942(1)	3845(1)	7661(1)	75(1)
S(7)	1195(1)	1451(1)	7404(1)	83(1)
S(8)	2421(1)	5440(1)	8218(1)	107(1)
S(9)	952(1)	6893(1)	6651(1)	115(1)
S(10)	1444(1)	2201(1)	6267(1)	126(1)
S(11)	991(1)	982(1)	8378(1)	115(1)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Other Physical Measurement. All measurements were performed under anaerobic conditions. Mössbauer spectrum was measured at liquid-nitrogen and room temperature with a constant-acceleration spectrometer. The source was ^{57}Co in a Pd matrix and was held at room temperature. Parameters were calibrated with natural-abundance-iron foil at room temperature. The infrared spectrum was recorded on a Magna 750 spectrophotometer and UV−vis spectrum on a Shimadzu UV-300 spectrophotometer. Variable-temperature magnetic susceptibilities in the temperature range 1.5−300 K were measured on a model CF-1 superconducting extracting sample magnetometer at a magnetic field of 5.0 T with powdered sample kept in capsule for weighing. A correction for the diamagnetism of compound **1** was estimated from Pascal's constants to be -508×10^{-6} cm^{-3} mol^{-1}. Cyclic voltammetric measurement was performed on a CV-1B cyclic voltammeter in a three-electrode cell with platinum working and auxiliary electrodes and an SCE reference electrode. The supporting electrolyte was $Bu^n{}_4NClO_4$ (0.1 mol/dm^3) and scan rate 200 mV/s.

Results and Discussion

Synthesis and Reaction of $[Et_4N]_2[MoFe_4S_4(SC_6H_{11})_7]\cdot{}^1/_2CH_3CN$ (1). The title cluster as a black prism crystal was obtained with high yield of 60−75% in an assembly reaction system containing reactants $NaSC_6H_{11}$, $FeCl_2$, and $(NH_4)_2MoS_4$ in molar ratio of 20:5:1 at room temperature in CH_3OH solution (Scheme 1). Compound **1** is soluble in strong polar, weak polar, or nonpolar organic solvents, such as DMF, CH_3OH, CH_3CN,

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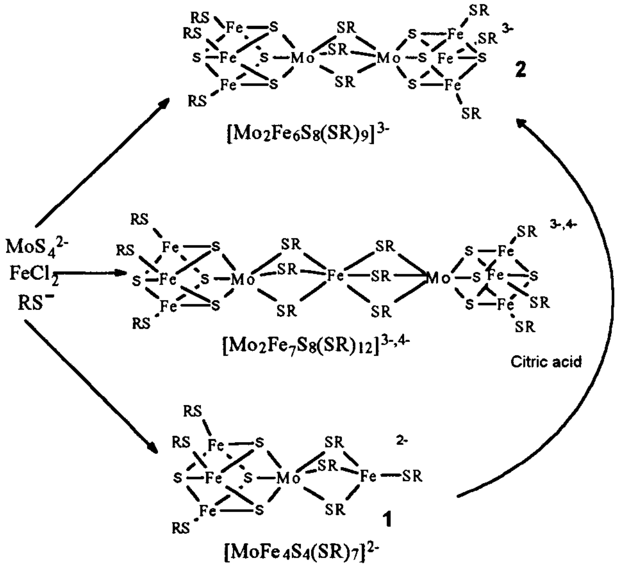
(16) Crystal data for $[Et_4N]_3[Mo_2Fe_6S_8(SC_6H_{11})_9]$: fw = 2211.08, monoclinic, a = 18.58(6) Å, b = 16.62(6) Å, c = 18.61(5) Å, β = 59.99(18)°, and V = 4978 Å^3. Mean Mo−S$_{core}$, 2.338(6) Å, and mean Fe−S$_{core}$, 2.260(7) Å.

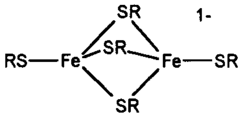
Scheme 1. Structure and Reaction Scheme for Related $MoFe_3S_4$ Single and Double Cubanes



THF, etc., and very sensitive to air even in the solid state. To our knowledge, the reaction system of $RSNa/FeCl_{2-3}/MoS_4^{2-}$ in MeOH(MeONa) has been successfully used to obtain a series of $[Mo_2Fe_6S_8(SR)_9]^{3-}$ [3,4] and $[Mo_2Fe_7S_8(SR)_{12}]^{3-,4-}$ [6] double cubane clusters.

$$2MoS_4^{2-} + 11RS^- + 6FeCl_2 \rightarrow [Mo_2Fe_6S_8(SR)_9]^{3-} + RSSR + 12Cl^- \quad (1)$$

However, cyclohexanethiolate leads to a novel Fe/Mo/S cluster different from those reported in previous works.[3−6] It is interesting to know why the novel cluster can be formed even though we have not enough evidence that would contribute to our understanding of the clustering mechanism. The key innovation is the use of a bulky thiolate which may give rise to the formation of new structures. For example, t-BuS$^-$ has been reported to result in a new $Fe^{(II)}$/S cluster $[Fe_2(SBu^t)_5]^-$ [17] which



is a highly reactive ferrous thiolate, but has not yet been used as an iron source in the preparation of Mo/Fe/S clusters. According to the reaction procedure[17] used to give $[Fe_2(SR)_5]^-$, an experimental method was designed to make the reaction of $[Fe_2(SR)_5]^-$ (R = t-Bu, C_6H_{11}, and C_5H_9) with MoS_4^{2-} and the title complex **1**; therefore, the following was obtained:

$$2MoS_4^{2-} + 8FeCl_2 + 16C_6H_{11}S^- \rightarrow 2[MoFe_4S_4(SC_6H_{11})_7]^{2-} + C_6H_{11}SSC_6H_{11} + 16Cl^- \quad (2)$$

though other isostructural complexes such as $[MoFe_4S_4(SBu^t)_7]^{2-}$ were not isolated. However, this work has not yet afforded the direct evidence of the $[Fe_2(SR)_5]^-$ intermediate before it can be detected in the reaction system. Compared to the reported methods for the syntheses of Mo/Fe/S double-cubane clusters,[3−6] the large excess of $NaSC_6H_{11}$ (RS^-:metal salts = 20:6 in mole ratio) used in this work could also be a favorable factor to the formation of **1** with a higher RS/metal ratio than those of other Mo/Fe/S cubane clusters. In the reaction of **1** with organic acid, such as citric acid, o-HSC_6H_4COOH, etc., the product isolated is a double cubane with two $MoFe_3S_4$ subunits bridged by three cyclohexanethiolate ligands. A reasonable assumption is suggested that compound **1** undergoes dissociation promoted by the organic acid to give $[(L)_3MoFe_3S_4(SR)_3]^0$ (L = solvent) and $[(RS)_3MoFe_3S_4(SR)_3]^{3-}$ and then combination with each other to get the double cubane.

Table 3. Selected Bond Distances (Å) in **1**

Mo(1)−Fe(1)	2.735(2)	Fe(1)−Fe(2)	2.674(2)
Mo(1)−Fe(2)	2.738(2)	Fe(1)−Fe(3)	2.722(1)
Mo(1)−Fe(3)	2.711(3)	Fe(2)−Fe(3)	2.721(3)
Mo(1)−S(1)	2.346(3)	Mo(1)−S(2)	2.362(2)
Mo(1)−S(3)	2.353(1)	Mo(1)−S(5)	2.600(2)
Mo(1)−S(6)	2.597(4)	Mo(1)−S(7)	2.634(1)
Fe(1)−S(1)	2.262(1)	Fe(1)−S(3)	2.231(4)
Fe(1)−S(4)	2.289(2)	Fe(1)−S(8)	2.237(2)
Fe(2)−S(2)	2.266(2)	Fe(2)−S(3)	2.259(2)
Fe(2)−S(4)	2.265(4)	Fe(2)−S(9)	2.243(2)
Fe(3)−S(1)	2.247(2)	Fe(3)−S(2)	2.260(4)
Fe(3)−S(4)	2.259(2)	Fe(3)−S(10)	2.230(3)
Fe(4)−S(5)	2.356(3)	Fe(4)−S(6)	2.356(1)
Fe(4)−S(7)	2.358(4)	Fe(4)−S(11)	2.266(3)

Table 4. Selected Bond Angles (deg) in **1**

S(1)−Mo(1)−S(2)	103.2(1)	S(1)−Mo(1)−S(3)	101.6(1)
S(2)−Mo(1)−S(3)	102.3(1)	S(1)−Mo(1)−S(5)	89.7(1)
S(2)−Mo(1)−S(5)	161.1(1)	S(3)−Mo(1)−S(5)	88.2(1)
S(1)−Mo(1)−S(6)	161.4(1)	S(2)−Mo(1)−S(6)	91.5(1)
S(3)−Mo(1)−S(6)	85.9(1)	S(5)−Mo(1)−S(6)	73.4(1)
S(1)−Mo(1)−S(7)	84.7(1)	S(2)−Mo(1)−S(7)	88.0(1)
S(3)−Mo(1)−S(7)	166.1(1)	S(5)−Mo(1)−S(7)	79.3(1)
S(6)−Mo(1)−S(7)	84.5(1)	S(1)−Fe(1)−S(3)	108.3(1)
S(1)−Fe(1)−S(4)	102.3(1)	S(3)−Fe(1)−S(4)	105.3(1)
S(1)−Fe(1)−S(8)	120.2(1)	S(3)−Fe(1)−S(8)	109.0(1)
S(4)−Fe(1)−S(8)	110.6(1)	S(2)−Fe(2)−S(3)	108.5(1)
S(2)−Fe(2)−S(4)	102.5(1)	S(3)−Fe(2)−S(4)	105.2(1)
S(2)−Fe(2)−S(9)	119.1(1)	S(3)−Fe(2)−S(9)	103.7(1)
S(4)−Fe(2)−S(9)	116.9(1)	S(1)−Fe(3)−S(2)	109.9(1)
S(1)−Fe(3)−S(4)	103.7(1)	S(2)−Fe(3)−S(4)	102.8(1)
S(1)−Fe(3)−S(10)	106.6(1)	S(2)−Fe(3)−S(10)	116.7(1)
S(4)−Fe(3)−S(10)	116.3(1)	S(5)−Fe(4)−S(6)	82.5(1)
S(5)−Fe(4)−S(7)	90.3(1)	S(6)−Fe(4)−S(7)	96.5(1)
S(5)−Fe(4)−S(11)	127.1(1)	S(6)−Fe(4)−S(11)	127.9(1)
S(7)−Fe(4)−S(11)	121.2(1)	Mo(1)−S(1)−Fe(1)	72.8(1)
Mo(1)−S(1)−Fe(3)	72.3(1)	Fe(1)−S(1)−Fe(3)	74.3(1)
Mo(1)−S(2)−Fe(2)	72.5(1)	Mo(1)−S(2)−Fe(3)	71.8(1)
Fe(2)−S(2)−Fe(3)	73.9(1)	Mo(1)−S(3)−Fe(1)	73.2(1)
Mo(1)−S(3)−Fe(2)	72.8(1)	Fe(1)−S(3)−Fe(2)	73.1(1)
Fe(1)−S(4)−Fe(2)	71.9(1)	Fe(1)−S(4)−Fe(3)	73.5(1)
Fe(2)−S(4)−Fe(3)	73.9(1)	Mo(1)−S(5)−Fe(4)	78.0(1)
Mo(1)−S(6)−Fe(4)	78.1(1)	Mo(1)−S(7)−Fe(4)	77.3(1)

$$[MoFe_4S_4(SR)_7]^{2-} \rightarrow [L_3MoFe_3S_4(SR)_3] + [Fe(SR)_4]^{2-} \quad (3)$$

$$[MoFe_4S_4(SR)_7]^{2-} \rightarrow [(RS)_3MoFe_3S_4(SR)_3]^{3-} + [Fe(SR)L_3]^{+} \quad (4)$$

$$2\,[MoFe_4S_4(SR)_7]^{2-} \rightarrow [Mo_2Fe_6S_8(SR)_9]^{3-} + [Fe_2(SR)_5]^{-} \quad (5)$$

Structure of $[Et_4N]_2[MoFe_4S_4(SC_6H_{11})_7]\cdot{}^1/_2CH_3CN$. The crystal structure consists of discrete cations, the solvate molecule, and the anion. Structural features of all the organic portions including the ligands are unexceptional and will not be discussed further. Selected atomic distances and bond angles of **1** are listed in Tables 3 and 4, respectively. The structure of the anion and its framework is shown in Figure 1.

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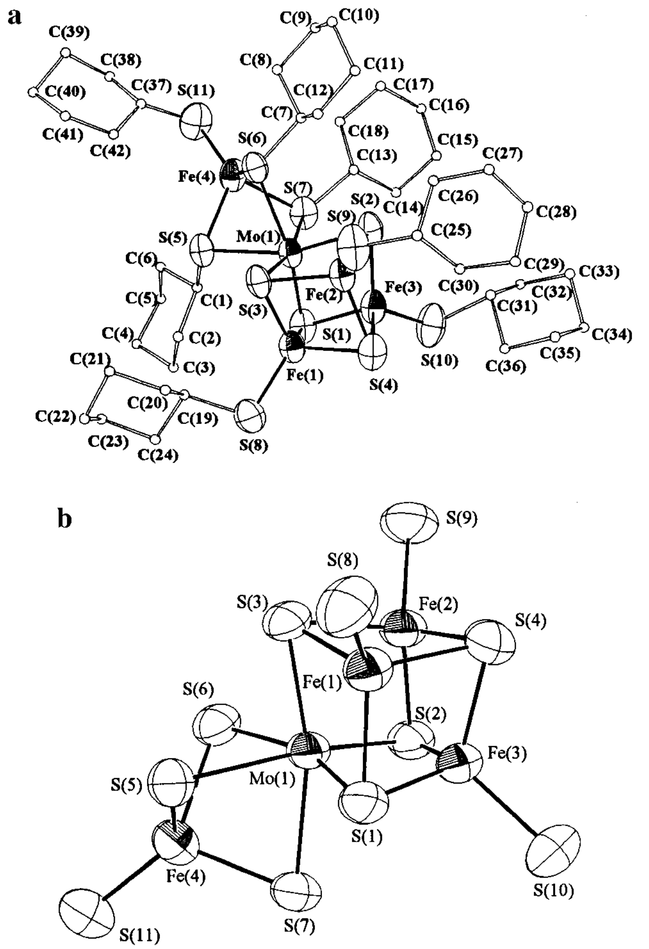

Figure 1. Structures of $[MoFe_4S_4(SC_6H_{11})_7]^{2-}$ (a) and its framework (b), showing the atom-labeling scheme. Thermal ellipsoids as drawn by ORTEP represent 50% probability surfaces.

The anion structure contains a $MoFe_3S_4(SC_6H_{11})_3$ cuboidal unit and an $Fe(SC_6H_{11})_4$ subunit, while the $MoFe_3S_4$ core is composed of both distorted tetrahedra $MoFe_3$ and S_4 interlocking with each other. The Mo atom has a distorted octahedral coordination geometry, which is similar to that of the Mo atom in $[Mo_2Fe_6S_8(SEt)_9]^{3-}$ [3a] and $[Mo_2Fe_7S_8(SPh)_{12}]^{4-}$.[18] The $MoFeS_2$ and Fe_2S_2 units in the $MoFe_3S_4$ core are nonplanar rhombs. Each Fe atom in the cuboidal core is coordinated by one cyclohexanethiolate ligand and three μ_3-S atoms located at the center of the distorted tetrahedron with S−Fe−S bond angles ranging from 102.3(1)° to 120.2(1)°. It is noteworthy that the Fe(4) atom in the $Fe(SC_6H_{11})_4$ subunit connecting to the $MoFe_3S_4$ core has a significantly distorted tetrahedral coordination with the bond angles around the Fe(4) ranging from 82.5° to 127.9°. The Mo−S (mean 2.354(5) Å) and Fe−S (mean 2.260(5) Å) in **1** are comparable to those in other $MoFe_3S_4$ double cubane clusters[3,18−19] and **2**.[16] Three Fe atoms in the $MoFe_3S_4$ unit have their $Fe-S_{terminal}$ bond distances ranging from 2.230(3) Å to 2.243(2) Å, very close to those of the double cubanes $[Mo_2Fe_6S_8(SR)_9]^{3-}$ and $[Mo_2Fe_7S_8(SR)_{12}]^{3-}$, implying identical Fe oxidation states for all these $MoFe_3S_4$ cubane clusters, of which the double cubanes were reported to have a Fe mean oxidation state of +2.67.[3,19] The Fe(4)−S(11) distance of 2.266(3) Å is obviously longer than other three $Fe-S_{terminal}$ distances (mean 2.237(4) Å) of the cuboidal core, indicating that Fe(4) has a lower oxidation state than that of the other three. Compared with compound $[Fe^{II}_2(SC_4H_9)_5]^-$ [17] in which $Fe^{(II)}$ atoms locate in a similar environment to that of Fe(4) of **1**, the $Fe(4)-S_{terminal}$ and $Fe(4)-S_{bridge}$ (mean 2.356(8) Å) bond distances are close to the corresponding bond distances (mean $Fe-S_{terminal}$, 2.261(8) Å and mean $Fe-S_{bridge}$, 2.369(8) Å) of $[Fe^{II}_2(SC_4H_9)_5]^-$, indicating that the Fe(4) oxidation state is 2+.

Table 5. Isomer Shifts (mm/s) and Quadrupole Splittings (mm/s) for **1** and Related Compounds at 77 K

compounds	δ	ΔE_Q	ref
$[Et_4N]_2[MoFe_4S_4(SC_6H_{11})_7]\cdot{}^1/_2CH_3CN$	0.71	2.68	this work
	0.31	0.98	
	0.57	1.05	
$[Et_4N]_3[Mo_2Fe_7S_8(SEt)_{12}]$	0.29	0.78	22
	0.32	1.17	
	0.31	2.18	
$[Me_3NBz]_3[Mo_2Fe_7S_8(SEt)_{12}]$	0.29	0.74	22
	0.32	1.10	
	0.31	2.13	
$[Bu^n_4N]_4[Mo_2Fe_7S_8(SCH_2Ph)_{12}]$	0.30	0.96	22
	0.85	1.90	
$[Et_4N]_3[Mo_2Fe_6S_9(SEt)_8]$	0.27	0.95	3
$[Et_3NBz]_3[Mo_2Fe_6S_8(SEt)_9]$	0.27	0.98	3
	0.32	1.33	

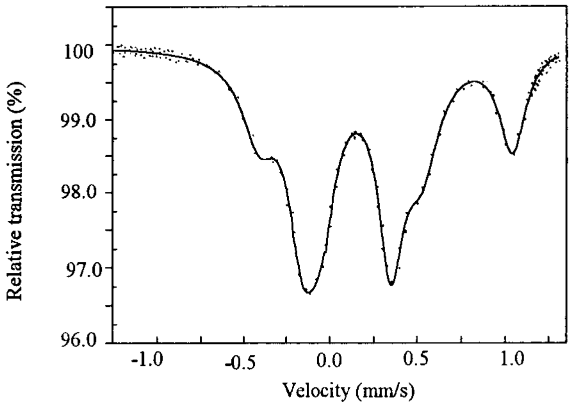

Figure 2. Mössbauer spectrum of $[Et_4N]_2[MoFe_4S_4(SC_6H_{11})_7]\cdot{}^1/_2CH_3CN$ at liquid-nitrogen temperature. Solid line represents the least-squares fits for the experimental data.

Electronic Absorption Spectra. The absorption spectrum in acetonitrile solution shows two peaks at 290 and 330 nm, resembling those of $[Mo_2Fe_6S_8(SR)_9]^{3-}$ [3] and $[Fe_4S_4(SR)_4]^{2-}$.[20] Referring to related assignments,[3,20,21] the two bands are considered to arise from RS → core charge-transfer excitations.

Mössbauer Spectrum. Mössbauer parameters obtained by least-squares fitting with the experimental data are shown in Table 5 together with the data of other related clusters. The Mössbauer spectrum of cluster **1** is shown in Figure 2.

The isomer shifts of ^{57}Fe in cluster **1** at liquid nitrogen temperature are 0.71 mm/s, 0.31 mm/s, and 0.57 mm/s, and the quadrupole splitting of 2.68(2), 0.98(2), and 1.05(2) mm/s at 77 K with intensity ratio of 1:2:1. It appears that there are three types of Fe atoms in cluster **1**, of which Fe(4) in the $Fe(SC_6H_{11})_4$ unit is considered to be responsible for the data of $\delta(\Delta E_Q) = 0.71(2.68)$ mm/s. The data are comparable to those for $[Mo_2Fe_7S_8(SCH_2Ph)_{12}]^{4-}$ (0.85(1.90) mm/s)[22] and $[Fe(SPh)_4]^{2-}$

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(0.64(3.24) mm/s),[23] indicating the Fe(4) oxidation state of 2+. The other two types in Mössbauer data are described as the Fe with mean oxidation state between 2+ and 3+ since their isomer shifts 0.31 and 0.57 mm/s are close to, though somewhat larger than, the shifts of other cluster complexes[3,13,19,22] with a $[MoFe_3S_4]^{3+}$ core which were reported to have a mean Fe oxidation state of 2.67+ in their cuboidal core. The Fe mean oxidation state in the core of **1** would be lower than the value of 2.67+, if it was obtained from an empirical formula,[4a,5b,24]

$$\delta = 1.44 - 0.43s\ (\delta = \text{IS},\ s = \text{formal oxidation state})$$

which used to be used to estimate the Fe formal oxidation state in tetrahedral FeS_4 sites. However, the influence of the core electronic structure on the Mössbauer data is complicated and some examples with large isomer shifts, 0.49 and 0.35 mm/s, for the $Fe^{(III)}{}_2Fe^{(II)}$ system have been found for the $MoFe_3S_4$ complexes.[25] In accordance with the discussion of the structural parameters and the fact that the most of the $MoFe_3S_4$ cubane clusters containing thiolate ligands showed their Fe oxidation states as $Fe^{2.67+}$, we prefer to describe the formal oxidation state as $2Fe^{(III)} + Fe^{(II)}$ rather than as $Fe^{(III)} + 2Fe^{(II)}$ for the $MoFe_3S_4$ core of **1**.

Magnetic Property. The molar magnetic susceptibility data (χ_M) were obtained from determination for the crystal sample of **1**, and the effective magnetic moments (μ_{eff}) were calculated in the temperature range determined. As the temperature is decreased, the molar susceptibility increases steadily. The effective magnetic moments are 6.66 μ_B at 300 K, 5.28 μ_B at 100 K, and 4.86 μ_B at 25 K, showing a diminutive trend with the decreasing of temperature. This implies the presence of intramolecular antiferromagnetic exchange interaction. However, it is difficult to suggest a spin model for cluster **1** on the basis of $2Fe^{(III)} + 2Fe^{(II)} + Mo^{(III)}$ oxidation states, because any reasonable assumptions of the ground spin state for each paramagnetic site will lead to a great deviation of spin-only magnetic moment from the experimental μ_{eff} value at room temperature. Successful fitting of the magnetic data for this $MoFe_4S_4$ cluster which contains highly delocalized electrons in the cuboidal core must be studied further to explain the exchange interaction between the metal sites. The present result only indicates that the antiferromagnetic interaction is dominant in the title complex.

Electrochemical Behavior. Cyclic voltammetry of complex **1** in CH_3CN reveals irreversible reduction waves at −0.72 V and −1.00 V on the cathodic scan and irreversible oxidation at 0.8 V on the return scan. A series of irreversible redox processes indicate the instability of complex **1** in the solution and make the assignment difficult. The cyclic voltommetric results for **1** are obviously different from that of $[MoFe_4S_4(SEt_3)(C_6H_4O_2)_3]^{3-}$ which showed three pairs of redox peaks (−1.31 V, qr; −1.74 V, irr; −0.25 V, qr, qr = quasireversible, irr = irreversible)[13] in acetonitrile. However, the reductions at −0.72 V and −1.0 V seem to be comparable with those of $[Mo_2Fe_7S_8(SR)_{12}]^{3-,4-}$ showing their reductions[19,22] at −0.89 V and −1.11 V associated to the reductions of the bridged $Fe(SR)_6$ and the $MoFe_3S_4$ core, respectively. Some single $MoFe_3S_4$ cubanes have also showed their reductions[9,26] of the cuboidal core in the range of −0.83 V to −1.1 V in CH_3CN. Irreversible oxidation at +0.8 V can be associated to the redox-active thiolate ligands. Similar irreversible oxidation behaviors have been observed for $[Mo_2Fe_6S_8(SR)_9]^{3-}$ [3,26] and other complexes[27] with thiolate ligands.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, bond distances and angles, and anisotropic thermal parameters for complex **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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