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Phosphine Cleavage of Iron(III)-Bridged Double Cubanes: A New Route to $MoFe_3S_4$ Single Cubanes

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Reaction of the Fe(III)-bridged double-cubane cluster $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ (**1**) with ~6 equiv of 1,2-bis(dimethylphosphino)ethane (dmpe) in benzene at 40 °C afforded a 33% yield of black $(Et_4N)[MoFe_3S_4(SEt)_4(dmpe)]$ (**5**). Treatment of **5** with 5.6 equiv of PhCOCl in acetonitrile gave black $(Et_4N)[MoFe_3S_4Cl_4(dmpe)]$ (**6**) (94%). Compound **5** (**6**) crystallizes in orthorhombic space group $Pbc2_1$ ($P2_1ab$) with $a = 12.867$ (3) (13.458 (4)) Å, $b = 21.334$ (7) (14.175 (5)) Å, $c = 28.539$ (8) (15.835 (5)) Å, and $Z = 8$ (4). With use of 5171 (2852) unique data having $I > 3\sigma(I)$, the structure of **5** (**6**) was refined to $R = 6.6\%$ (5.6%). Clusters **5** and **6** contain the cubane-type $[MoFe_3(\mu_3\text{-}S)_4]^{3+}$ core of precursor **1**, indicating bridge cleavage of the latter with dmpe. In the two inequivalent clusters **5**, each Fe atom exists in a distorted tetrahedral $Fe(\mu_3\text{-}S)_3(SR)$ unit, and the distorted octahedral $Mo(\mu_3\text{-}S)_3P_2S$ coordination unit is completed by a chelated dmpe and a terminal ethanethiolate ligand. The clusters are mainly differentiated by the asymmetric skew and envelope conformations of the chelate rings. Cluster **6** is structurally very similar to **5** with chloride in place of each thiolate ligand in the former and an asymmetric skew chelate ring conformation. Core dimensions of **5** and **6** do not clearly reflect idealized C_s core symmetry (neglecting chelate ring nonplanarity) and vary among the clusters in an unsystematic way. Despite these variations, cores have indistinguishable volumes (9.55-9.57 Å^3). The Fe-Cl and Mo-SEt/Cl bond lengths are not inconsistent with the mean oxidation state description $Mo^{3+} + 3Fe^{2.67+}$; at the least, the former distances indicate an oxidation state no less than $Fe^{2.5+}$. In the solid and solution phases the clusters have a $S = {}^3/_2$ ground state. ^1H NMR spectra are well resolved and are consistent with rapid chelate ring conversion between enantiomeric skew configurations and a stereochemically rigid cluster structure of idealized C_s symmetry. Reaction of **5** with acyl halides and benzenethiol proceeds in two stages. The three Fe sites are immediately substituted, followed by a much slower reaction at the Mo site. A similar pattern of reactivity is observed in the system **6**/4(RS^-) ($R = p\text{-}C_6H_4CH_3$) in acetonitrile. These are the first examples of the substitution reactions of Mo-SR/Cl terminal groups with electrophiles or nucleophiles. It was previously shown that $Mo-(\mu\text{-}SR)_3-Mo$ groups are unreactive toward these electrophiles. The four possible permutations of chloride and thiolate binding at Fe and Mo sites have been achieved. The present results and those obtained from an earlier reactivity study of $[MoFe_3S_4Cl_3(al_2cat)(THF)]^{2-}$, which contains labile ligands at all metal sites, provide a rather detailed picture of the relative substitutional tendencies of Fe and Mo atoms in $(\mu_3\text{-}S)_3$ binding sites in the same clusters. These results may have utility in interpreting the ligand-binding reactions of the FeMo cofactor of nitrogenase.

Introduction

Cluster species containing a single $MoFe_3S_4$ cubane-type core unit are currently accessible only by cleavage reactions of preassembled double-cubane clusters. Thus the Fe(III)-bridged cluster $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$[2,3] (**1**) in Figure 1 reacts smoothly with 3,6-disubstituted catechols R'_2catH_2 to afford the doubly bridged clusters **2** as the initial product, with Fe(III) removed in the form of $[Fe(R'_2cat)_3]^{3-}$. These double cubanes are readily cleaved by coordinating solvents to afford the solvated single cubanes $[MoFe_3S_4(SR)_3(R'_2cat)(solv)]^{2-}$ (**3**), which are precursors to the ligated clusters $[MoFe_3S_4(SR)_3(R'_2cat)L]^{2-,3-}$ (**4**).[4-7] The structural and reaction chemistry of these single cubanes and related clusters $[MoFe_3S_4Cl_3(R'_2cat)(solv)]^{2-}$,[6] in which thiolate is replaced by chloride, have been explored at length in this laboratory, and many of the leading results are summarized elsewhere.[8] These efforts were motivated in significant measure by the apparent resemblance of the Mo coordination environment to that in the native Mo-Fe-S cluster of nitrogenase.[9,10] The solvated chloro clusters have been particularly useful in establishing relative binding affinities at Fe and Mo sites for a number of ligands including R_3P, RS^-, RO^-, and CN^-, information that may be valuable in interpreting the ligand-binding reactions of the FeMo cofactor of nitrogenase.

More recently, we have sought access to new types of $MoFe_3S_4$ single cubanes lacking the catecholate(2-) ligand present in **3** and **4**, in order to ascertain the influence of ligand variation at the Mo site on cluster properties. Of the latter, we are particularly concerned with the effect on metal site binding affinities, redox behavior, and electronic properties. In a more general sense, these $MoFe_3S_4$ clusters are part of a growing class of heterometal MM'_3S_4 cubanes that also include the VFe_3S_4[11] and $FeMo_3S_4$[12] types. Here we report the cleavage of double cubane **1** with a bifunctional phosphine and characterization and reactions of the resultant phosphino-ligated single cubanes.

Experimental Section

Preparation of Compounds. All operations were carried out under a pure dinitrogen atmosphere; solvents were degassed immediately before use. 1,2-Bis(dimethylphosphino)ethane (dmpe) was prepared by a published method.[13] Dmpe-d_{12}, $(CD_3)_2PCH_2CH_2P(CD_3)_2$, was prepared similarly from $Cl_2PCH_2CH_2PCl_2$ and CD_3MgI.

$(Et_4N)(S\text{-}p\text{-}C_6H_4CD_3)$. This compound was required for ^1H NMR signal assignments. *p*-Bromobenzotribromide was photochemically prepared in 90% yield from *p*-bromotoluene and bromine[14] by using a 275-W lamp. The tribromide was converted to $p\text{-}BrC_6H_4CD_3$ (61%) by reduction with Zn/DOAc in ether.[15] This compound was converted to $p\text{-}CD_3C_6H_4SH$ by reaction with magnesium, sulfur, and $LiAlH_4$ in ether.[16]

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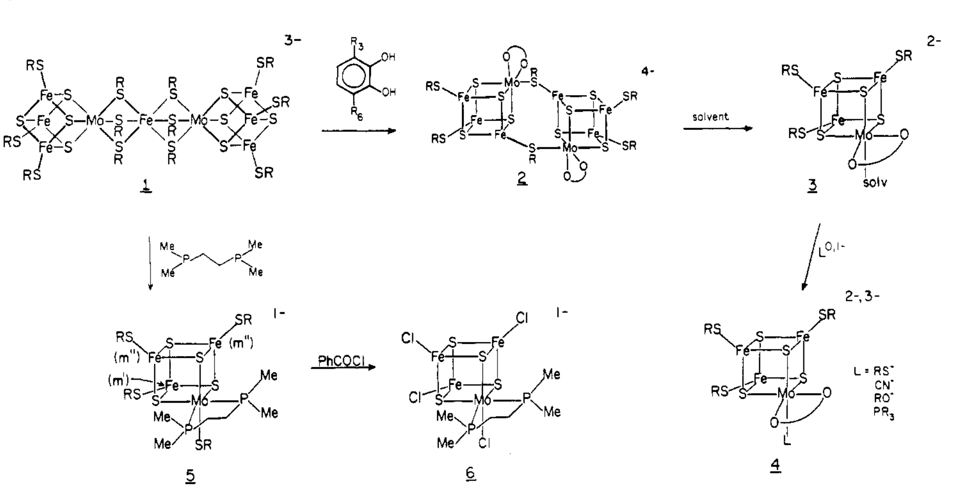

Figure 1. Synthetic routes to $MoFe_3S_4$ single-cubane clusters (**3**–**6**) initiated by bridge cleavage of $[Mo_2Fe_7S_8(SEt)_{12}]^{3-}$ (**1**).

Table I. Crystallographic Data[a] for $(Et_4N)[MoFe_3S_4(SEt)_4(dmpe)]$ (**5**) and $(Et_4N)[MoFe_3S_4Cl_4(dmpe)]$ (**6**)

	5	6
formula	$C_{22}H_{56}Fe_3MoNP_2S_8$	$C_{14}H_{36}Cl_4Fe_3MoNP_2S_4$
M_r	916.64	814.01
a, Å	12.867 (3)	13.458 (4)
b, Å	21.334 (7)	14.175 (5)
c, Å	28.539 (8)	15.835 (5)
V, Å^3	7834 (4)	3021 (2)
space group	$Pbc2_1$	$P2_1ab$
d_{calcd} (d_{obsd}),[b] g/cm^3	1.55 (1.54)	1.79 (1.80)
Z	8	4
abs coeff μ, cm^{-1}	19.0	25.5
max/min transmission	0.93/0.64	0.84/0.55
crystal dimens, mm	0.8 × 0.3 × 0.3	1.2 × 0.5 × 0.3
scan range,[c] deg	1.4	1.2
data collcd	$+h,+k,+l$ ($5.0° \le 2\theta \le 50.0°$)	$+h,+k,+l$ ($2.0° \le 2\theta \le 55.0°$)
total no. of reflcns	9576	4147
no. of unique data ($I > 3\sigma(I)$)	5171	2852
no. of variables	864	244
R (R_w), %[d]	6.6 (8.3)	5.6 (6.9)

[a] For both compounds: orthorhombic crystal system; Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å); scan speed, 5.0–29.3 deg min^{-1} (ω scans); background/scan time ratio, 0.25. [b] Measured by flotation in cyclohexane/1,2-dibromoethane. [c] Value given is x in $x + (2\theta_{K\alpha_2} - 2\theta_{K\alpha_1})$. [d] $R = [\sum||F_o| - |F_c||/\sum|F_o|]$; $R_w = [\sum w(|F_o|^2 - |F_c|^2)/\sum w|F_o|^2]^{1/2}$. Weighting scheme: Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1979**, *A35*, 698.

The compound contained 98% deuterium in the methyl group (NMR). The thiol was treated with equimolar NaOEt in ethanol, the solvent was removed, and the residue was extracted with acetonitrile. Addition of ether to the acetonitrile solution caused separation of the thiolate salt, which was obtained as a white microcrystalline solid.

$(Et_4N)[MoFe_3S_4(SEt)_4(dmpe)]$ (5). Dmpe (0.22 mL, 1.67 mmol) was added to a suspension of 0.50 g (0.26 mmol) of $(Et_4N)_3[Mo_2Fe_7S_8(SEt)_{12}]$[3] in 40 mL of benzene. The reaction mixture was stirred overnight on a water bath at 40 °C. During this period the mixture became dark greenish brown, the cluster salt dissolved, and a brown amorphous precipitate formed. The mixture was filtered and the filtrate was reduced in volume to ~10 mL. About 20 mL of ether was added to this solution, causing the separation of a microcrystalline solid. This material was collected by filtration, washed with ether, and dried in vacuo, affording the pure product as 0.17 g (33%) of black microcrystalline solid. Anal. Calcd. for $C_{22}H_{56}Fe_3MoNP_2S_8$: C, 28.83; H, 6.16; Fe, 18.28; Mo, 10.47; N, 1.53; P, 6.76; S, 27.98. Found: C, 28.94; H, 6.27; Fe, 18.32; Mo, 9.76; N, 1.55; P, 6.54; S, 27.86. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M, M^{-1} cm^{-1}) 283 (26 300), 402 (15 200) nm.

$(Et_4N)[MoFe_3S_4Cl_4(dmpe)]$ (6). $(Et_4N)[MoFe_3S_4(SEt)_4(dmpe)]$ (1.00 g, 1.09 mmol) was dissolved in 25 mL of acetonitrile. To this solution was added 0.64 mL (5.6 mmol) of benzoyl chloride, resulting in an immediate color change from dark greenish brown to brownish purple. The solution was stirred for 6 h and was reduced in volume to ~10 mL. The addition of 10 mL of ethanol caused the separation of black microcrystals, which were collected, washed with ether, and dried in vacuo. Recrystallization from acetonitrile/ethanol afforded 0.84 g (94%) of pure product as black microcrystals. Anal. Calcd. for $C_{14}H_{36}Cl_4Fe_3MoNP_2S_4$: C, 20.66; H, 4.46; Cl, 17.42; Fe, 20.58; Mo, 11.79; N, 1.73; P, 7.61; S, 15.90. Found: C, 20.64; H, 4.36; Cl, 17.15; Fe, 20.77; Mo, 11.78; N, 1.89; P, 7.47; S, 15.90. Absorption spectrum (acetonitrile): λ_{max} (ϵ_M, M^{-1} cm^{-1}) 258 (22 300), 334 (sh, 6700), 560 (1550) nm.

Collection and Reduction of X-ray Data. Black single crystals of $(Et_4N)[MoFe_3S_4(SEt)_4(dmpe)]$ (**5**) and $(Et_4N)[MoFe_3S_4Cl_4(dmpe)]$ (**6**) were grown by slow cooling of 2:1:1 acetonitrile/2-propanol/ether (v/v) and 2:1 acetonitrile/methanol (v/v) solutions, respectively, to −20 °C and maintenance of these solutions at this temperature for several days. Crystals of suitable size were sealed in glass capillaries under dinitrogen. Data collections were performed at ambient temperature on a Nicolet R3m four-circle diffractometer equipped with a Mo X-ray source and a graphite monochromator. Crystal and data collection parameters are summarized in Table I. The orientation matrices and unit cell parameters were derived from a least squares fit of 25 machine-centered reflections with 2θ values between 20 and 25° for **5** and 16 and 30° for **6**. No significant decay of three check reflections measured every 123 reflections was observed for either compound over the duration of data collection. Intensity data were corrected for the Lorentz polarization effect. Data reductions and empirical absorption corrections were performed by the programs XTAPE and XEMP, respectively, of the SHELXTL structure determination program package (Nicolet XRD Corp., Madison, WI). Both compounds crystallize in the orthorhombic system. Space group $Pbc2_1$ of **5** is consistent with the systematic absences $0kl$ ($k \neq 2n$) and $h0l$ ($l \neq 2n$) and intensity statistics. Space group $P2_1ab$ of **6** is determined by the systematic absences $hk0$ ($k \neq 2n$) and $h0l$ ($h \neq 2n$) and by intensity statistics. Both space groups were confirmed by successful solutions and refinements of the structures.

Structure Solutions and Refinements. Mo and Fe atoms were found by the direct-methods program MULTAN using the phase set with the highest combined figure of merit. Subsequent alternating least-squares refinements and difference Fourier maps revealed all other non-hydrogen atoms. The structures were refined by the blocked-cascade least-squares method, with the function R (Table I) being minimized. Atomic scattering factors were taken from a standard source.[17] An extinction correction was introduced for **6** but was not significant for **5**.

The asymmetric unit of compound **5** consists of two anions and two cations. The ethyl groups of S(2) and S(3) (anion 1) and S(2′) and S(3′) (anion 2) are disordered. Anisotropic refinement of Mo, Fe, P, and S atoms and isotropic refinement of C and N atoms converged at R = 7.3%. Further inspection of the difference maps indicated that ca. 5% of the anions were slightly disordered in terms of heavy-atom positions. This aspect was not successfully modeled. The disordered thiolate groups were modeled in terms of two orientations with occupancy factors summing to unity. Owing to limitations on the data, all C–C bond lengths were constrained to 1.52 Å and P–C distances to 1.84 Å, the mean value determined in the initial refinement. All atoms except disordered C atoms were anisotropically described. The heavy atoms, but not the carbons, are approximately related by a center of symmetry for the two anions. Attempted refinement in centrosymmetric space group $Pbcm$ resulted in high esd's for coordinates and unrealistic bond lengths because of randomly oriented thiolate groups that are inconsistent with this

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Table II. Positional Parameters (×10^4) for $[MoFe_3S_4(SEt)_4(dmpe)]^-$

atom	x/a	y/b	z/c
	Cluster 1		
Mo	9849 (1)[a]	7392.8 (7)	−718 (2)
Fe(1)	10727 (3)	7291 (1)	−1593 (2)
Fe(2)	8630 (2)	7372 (1)	−1519 (2)
Fe(3)	9644 (3)	6322 (1)	−1225 (2)
S(11)	8296 (4)	6806 (2)	−857 (3)
S(12)	11189 (4)	6709 (2)	−955 (3)
S(13)	9808 (4)	8119 (2)	−1348 (3)
S(14)	9521 (5)	6686 (3)	−1962 (3)
S(1)	12079 (5)	7603 (3)	−2032 (3)
S(2)	7234 (5)	7882 (3)	−1808 (3)
S(3)	9458 (6)	5272 (3)	−1144 (3)
S(4)	10063 (4)	6956 (3)	89 (3)
P(1)	8734 (5)	8165 (3)	−292 (3)
P(2)	11128 (3)	8158 (2)	−383 (3)
C(1)	10409 (16)	8837 (6)	−157 (8)
C(2)	9502 (14)	8608 (11)	138 (6)
C(3)	7976 (18)	8741 (10)	−625 (7)
C(4)	7670 (13)	7810 (8)	45 (7)
C(5)	12091 (15)	7856 (11)	34 (8)
C(6)	12042 (17)	8556 (11)	−777 (8)
C(1)S(1)[b]	12704 (38)	6904 (17)	−2259 (12)
C(2)S(1)	13296 (39)	6574 (20)	−1870 (16)
C(1)S(2)	6252 (17)	7276 (11)	−1896 (10)
C(2a)S(2)	6707 (26)	6636 (10)	−1781 (15)
C(2b)S(2)	6748 (29)	6820 (15)	−2244 (13)
C(1a)S(3)	10797 (24)	5146 (49)	−1356 (21)
C(2a)S(3)	10832 (65)	5218 (48)	−1886 (21)
C(1b)S(3)	10161 (21)	4862 (16)	−1613 (10)
C(2b)S(3)	11264 (22)	5109 (18)	−1655 (14)
C(1)S(4)	9995 (10)	6103 (8)	25 (6)
C(2)S(4)	10023 (16)	5779 (8)	500 (6)
	Cluster 2		
Mo′	4850 (1)	4919.3 (8)	441 (2)
Fe(1′)	3631 (3)	4929 (1)	1227 (2)
Fe(2′)	5729 (2)	4821 (1)	1303 (2)
Fe(3′)	4590 (2)	3852 (1)	945 (2)
S(11′)	6149 (4)	4219 (2)	688 (3)
S(12′)	3283 (4)	4362 (2)	580 (2)
S(13′)	4838 (4)	5682 (2)	1056 (3)
S(14′)	4492 (5)	4237 (3)	1697 (3)
S(1′)	2243 (5)	5449 (3)	1527 (3)
S(2′)	7082 (6)	5119 (4)	1743 (3)
S(3′)	4419 (5)	2811 (2)	892 (3)
S(4′)	4948 (4)	4425 (3)	−377 (3)
P(1′)	6309 (4)	5624 (2)	85 (3)
P(2′)	3721 (4)	5718 (2)	−3 (3)
C(1′)	4525 (11)	6304 (14)	−301 (16)
C(2′)	5686 (12)	6182 (10)	−316 (8)
C(3′)	7004 (17)	6126 (10)	503 (7)
C(4′)	7331 (20)	5305 (18)	−295 (11)
C(5′)	2889 (22)	5444 (11)	−484 (8)
C(6′)	2848 (22)	6203 (14)	353 (10)
C(1)S(1′)	1219 (15)	4832 (10)	1570 (8)
C(2)S(1′)	1315 (22)	4474 (11)	2029 (9)
C(1a)S(2′)	8176 (39)	4558 (29)	1844 (13)
C(1b)S(2′)	7405 (63)	4356 (25)	2013 (30)
C(2a)S(2′)	8682 (31)	4394 (22)	1378 (17)
C(2b)S(2′)	8406 (64)	4100 (37)	1804 (37)
C(1a)S(3′)	5106 (13)	2506 (11)	1418 (5)
C(1b)S(3′)	5613 (34)	2507 (31)	1170 (18)
C(2a)S(3′)	6268 (12)	2581 (16)	1342 (10)
C(2b)S(3′)	5790 (62)	2809 (42)	1646 (20)
C(1)S(4′)	5007 (28)	3587 (15)	−276 (10)
C(2)S(4′)	4972 (14)	3175 (10)	−711 (7)

[a] Esd given in parentheses in this and succeeding tables. [b] Thiolate labeling as in S(*n*)–C(1)S(*n*)–C(2)S(*n*).

Table III. Positional Parameters (×10^4) for $[MoFe_3S_4Cl_4(dmpe)]^-$

atom	x/a	y/b	z/c
Mo	2847 (2)	5309 (5)	1575.6 (5)
Fe(1)	2558 (2)	4595 (1)	3142 (1)
Fe(2)	4091 (2)	5853 (1)	2848 (1)
Fe(3)	4160 (2)	4051 (1)	2211 (1)
S(1)	4596 (3)	5416 (2)	1545 (2)
S(2)	2546 (3)	3724 (2)	1944 (2)
S(3)	2434 (3)	6139 (2)	2805 (2)
S(4)	4163 (4)	4490 (3)	3606 (2)
Cl(1)	1358 (4)	4143 (3)	4000 (3)
Cl(2)	4995 (5)	7069 (4)	3257 (3)
Cl(3)	5085 (4)	2814 (3)	1923 (3)
Cl(4)	2929 (3)	4828 (2)	65 (2)
P(1)	2676 (1)	6931 (2)	878 (2)
P(2)	1010 (2)	5348 (2)	1195 (2)
C(1a)[a]	777 (3)	6304 (4)	396 (5)
C(2a)	1331 (2)	7188 (4)	652 (6)
C(3a)	3274 (7)	7930 (2)	1484 (4)
C(4a)	3366 (7)	7082 (4)	−146 (4)
C(5a)	476 (3)	4245 (3)	711 (6)
C(6a)	131 (2)	5573 (7)	2097 (3)
C(1b)	663 (4)	6563 (5)	814 (12)
C(2b)	1474 (7)	6998 (5)	270 (10)
C(3b)	2809 (13)	7963 (2)	1624 (3)
C(4b)	3698 (7)	7254 (6)	118 (9)
C(5b)	591 (4)	4519 (10)	332 (9)
C(6b)	123 (2)	5053 (14)	2078 (5)

[a] C(*n*a) and C(*n*b) are carbon atoms in the major and minor conformations, respectively, of the Mo(dmpe) rings.

symmetry group. In the final stages of refinement, hydrogen atoms were included at a C–H distance of 0.96 Å, with thermal parameters 1.2 times those of the bonded C atoms. The asymmetric unit of compound **6** contains one anion and one cation. Anisotropic refinement of Mo, Fe, P, and S atoms and isotropic refinement of C and N atoms converged at $R = 6.8\%$. A subsequent difference Fourier map revealed additional significant electron density in the vicinity of the cation and the C atoms of dmpe. Cation disorder was modeled in terms of different ethyl group orientations in a 3:1 ratio. The dmpe ligands were interpreted in terms of two skew chelate ring conformations in the ratio 82:18. The C–C (1.52 Å) and P–C (1.88 Å) distances were constrained, and the minor conformation was refined, assuming the same value of a given angle as in the major conformation. The P–C distances used here and with compound **5** are within the range of values in numerous dmpe complexes including several of Mo.[18] All carbon atoms were refined isotropically. The possibility of a centrosymmetric space group was also considered. $Z = 4$ in *Pmab* requires the molecule to reside on a special position. In this case the only possible model is a mirror plane running through the molecule, which requires disorder in the dmpe group equally on each side of the plane. Refinement according to this model was erratic, converging to unreasonable bond lengths with high esd's. Also, the anion is not aligned properly for a mirror plane with respect to the *a* axis, which would be the axis having the mirror plane perpendicular to it in centrosymmetric space group *Pmab*. All these considerations support the choice of the noncentrosymmetric space group. Hydrogen atoms were introduced in the final refinement as with compound **5**. After the final refinement, the difference map showed only a few Fourier ripples around the metal atoms with heights <0.8 e/Å^3. Final *R* factors are given in Table I. Positional parameters of anions are listed in Tables II and III; other crystallographic data are deposited.[19]

Other Physical Measurements. All measurements were performed under strictly anaerobic conditions. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer with Me_4Si as the internal standard. Magnetic susceptibilities in solution were determined by the NMR method;[20] solvent susceptibilities[21a] and diamagnetic corrections[21b] were taken from tabulated values. Electrochemical measurements were made at ambient temperature by using standard PAR instrumentation with a glassy-carbon working electrode, a SCE reference electrode, and 0.2 M (n-Bu_4N)(ClO_4) supporting electrolyte. DMF (Burdick & Jackson, as received) and acetonitrile (distilled from CaH_2) were stored over 3-Å molecular sieves.

Results and Discussion

Synthesis of Single Cubanes. The procedure shown in Figure 1 for the preparation of the solvated single cubanes **3** depends

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(18) (a) Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1983**, *22*, 1507. (b) Campbell, F. L., III; Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1985**, *24*, 177.

(19) See paragraph at the end of this article concerning supplementary material available.

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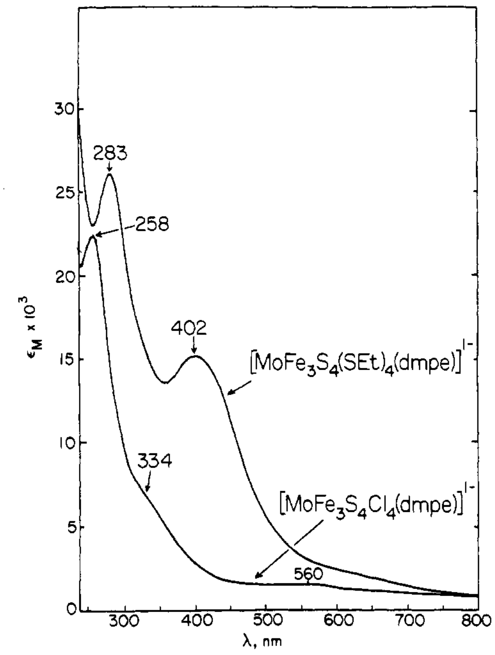
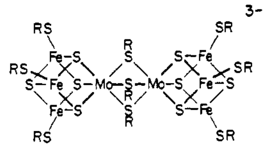


Figure 2. Absorption spectra of $[MoFe_3S_4(SEt)_4(dmpe)]^-$ and $[MoFe_3S_4Cl_4(dmpe)]^-$ in acetonitrile solutions.

importantly on the affinity of catecholate for Fe(III), which is present in the bridge of precursor double cubane **1**. Other potential ligands for this bridge component such as ethylenediamine, *N*,*N'*-dimethylethylenediamine, 2,6-dithiahexane, and sodium 2-aminoethoxide either did not react or produced a complicated mixture containing the familiar and well-studied triply thiolate-bridged double cubanes $[Mo_2Fe_6S_8(SR)_9]^{3-}$ [8] (**7**) as the only



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readily identifiable cluster product. However, dmpe behaved entirely differently. A heterogeneous reaction system in benzene containing the initial molar ratio dmpe:$[Mo_2Fe_7S_8(SEt)_{12}]^{3-} \approx$ 6:1 afforded in 33% yield the Et_4N^+ salt of the cluster $[MoFe_3S_4(SEt)_4(dmpe)]^-$ (**5**). Bridge cleavage of **1** removes the elements of $[Fe(SEt)_4]^-$. This reaction may have been assisted by the formation of a species such as $Fe(dmpe)_2(SEt)_2$, analogous to $Fe(dmpe)_2Cl_2$,[22-24] with Fe(II) produced by thiolate reduction.

Reaction of $[MoFe_3S_4(SEt)_4(dmpe)]^-$ with 5 equiv of benzoyl chloride in acetonitrile abolished the absorption band at 402 nm, in a region characteristic of terminal Fe thiolate ligands in other $MoFe_3S_4$ clusters,[4,5] and caused development of a nearly featureless visible absorption spectrum, shown in Figure 2. This spectral change is typical of replacement of such ligands with chloride.[25] From the reaction mixture, the Et_4N^+ salt of $[MoFe_3S_4Cl_4(dmpe)]^-$ was isolated in 94% yield. Cluster **6** is formed in overall reaction 1.

$$[MoFe_3S_4(SEt)_4(dmpe)]^- + 4PhCOCl \rightarrow [MoFe_3S_4Cl_4(dmpe)]^- + 4PhCOSR \quad (1)$$

Clusters **5** and **6** are extremely air-sensitive and should be handled accordingly. While analogy with **3** and **4** suggested that the dmpe ligand is chelated and chloride and thiolate are bound at the Mo site, proof of cluster configurations required X-ray structural analysis.

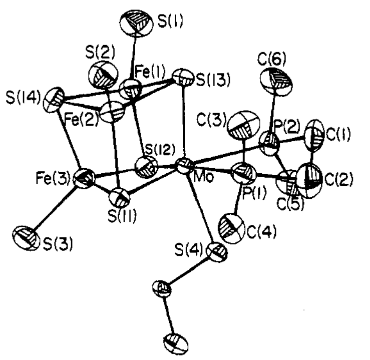

Figure 3. Structure of anion 1 of $[MoFe_3S_4(SEt)_4(dmpe)]^-$ showing the atom-labeling scheme and 50% probability ellipsoids.

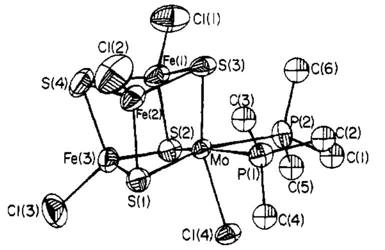

Figure 4. Structure of $[MoFe_3S_4Cl_4(dmpe)]^-$ showing the atom-labeling scheme and 50% probability ellipsoids. Isotropically refined C atoms are represented by spheres.

Cluster Structures. Crystals of only fair diffraction quality were obtained for $(Et_4N)[MoFe_3S_4(SEt)_4(dmpe)]$ and $(Et_4N)[MoFe_3S_4Cl_4(dmpe)]$. However, both were sufficient to allow definition of all chemically significant structural features. Structures are depicted in Figures 3 and 4. Interatomic distances and angles are collected in Tables IV and V. If dmpe chelate ring and ethyl group conformations are ignored, the idealized cluster symmetry is C_s. The tables are arranged such that dimensions related under this symmetry appear consecutively.

(a) Core Units. The cubane-type $[MoFe_3(\mu_3\text{-}S)_4]^{3+}$ cores of $[MoFe_3S_4(SEt)_4(dmpe)]^{1-}$ and $[MoFe_3S_4Cl_4(dmpe)]^-$ are built up from the fusion of $MoFeS_2$ and Fe_2S_2 nonplanar rhombs. Core interatomic distances are within the ranges of corresponding distances in isoelectronic structures,[4-8] the essential features of which have been summarized[8] and will not be repeated here. Corresponding individual distances in the two inequivalent $[MoFe_3S_4(SEt)_4(dmpe)]^-$ clusters can vary substantially, but mean values are within 0.03 Å. There do not appear to be any chemically significant differences in core structural aspects of these clusters and $[MoFe_3S_4Cl_4(dmpe)]^-$. Inspection of the distance data reveals that distortions from mirror symmetry are irregular and, with certain distance types, pronounced. Examples include the Mo–S(11,12) bond lengths in the two thiolate clusters, which differ by 0.035 and 0.024 Å, respectively. Despite the evident and unsystematic differences in individual dimensions of the three clusters, their core volumes (calculated from atom positional parameters) are indistinguishable: $[MoFe_3S_4(SEt)_4(dmpe)]^-$, 9.56 and 9.57 Å^3; $[MoFe_3S_4Cl_4(dmpe)]^-$, 9.55 Å^3. These are identical with the core volumes of $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4(al_2cat)]^{3-}$ (9.56 Å^3 [5]) and ca. 2.1% larger than that of $[MoFe_3S_4Cl_3(al_2cat)(THF)]^{2-}$ (**8**, 9.37 Å^3 [6]). The latter clusters are isoelectronic with **5** and **6**.

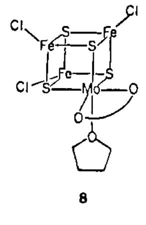

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Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[MoFe_3S_4(SEt)_4(dmpe)]^-$

dist/angle	cluster 1	cluster 2	dist/angle	cluster 1	cluster 2
Mo···Fe(1)	2.750 (3)	2.737 (3)	Fe(1)···Fe(3)	2.706 (4)	2.730 (4)
Mo···Fe(2)	2.775 (4)	2.714 (3)	Fe(2)···Fe(3)	2.726 (4)	2.731 (4)
Mo···Fe(3)	2.718 (3)	2.714 (3)	Fe(1)···Fe(2)	2.711 (4)	2.717 (4)
Mo–S(11)	2.392 (5)	2.350 (5)	Mo–P(1)	2.499 (6)	2.611 (5)
Mo–S(12)	2.357 (5)	2.374 (5)	Mo–P(2)	2.506 (5)	2.573 (4)
Mo–S(13)	2.375 (5)	2.393 (6)	P(1)···P(2)	3.348 (7)	3.487 (8)
Mo–S(4)	2.486 (8)	2.566 (8)	Fe(3)–S(11)	2.275 (6)	2.276 (6)
			Fe(3)–S(12)	2.286 (6)	2.258 (6)
Fe(1)–S(13)	2.237 (6)	2.287 (6)	Fe(3)–S(14)	2.249 (6)	2.301 (6)
Fe(2)–S(13)	2.253 (6)	2.277 (6)			
Fe(1)–S(14)	2.277 (7)	2.282 (7)	Fe(1)–S(1)	2.243 (6)	2.269 (7)
Fe(2)–S(14)	2.249 (6)	2.313 (7)	Fe(2)–S(2)	2.257 (7)	2.240 (7)
Fe(1)–S(12)	2.283 (6)	2.255 (6)	Fe(3)–S(3)	2.263 (6)	2.236 (6)
Fe(2)–S(11)	2.283 (6)	2.239 (6)			
P(1)–Mo–P(2)	76.2 (2)	80.4 (2)	S(13)–Fe(1)–S(14)	103.6 (2)	104.6 (2)
S(11)–Mo–S(12)	103.8 (2)	103.6 (2)	S(13)–Fe(2)–S(14)	103.8 (2)	103.7 (2)
S(4)–Mo–S(13)	161.2 (2)	161.4 (2)	S(12)–Fe(1)–S(13)	108.6 (2)	109.6 (2)
P(1)–Mo–S(13)	85.7 (2)	84.3 (2)	S(11)–Fe(2)–S(13)	108.8 (2)	110.0 (2)
P(2)–Mo–S(13)	82.9 (2)	84.7 (2)	S(12)–Fe(1)–S(14)	103.7 (2)	103.4 (2)
P(1)–Mo–S(11)	87.0 (2)	88.4 (2)	S(11)–Fe(2)–S(14)	102.6 (2)	103.9 (2)
P(2)–Mo–S(12)	91.9 (2)	86.2 (2)	S(1)–Fe(1)–S(12)	113.8 (3)	114.5 (3)
S(11)–Mo–S(13)	101.4 (2)	102.6 (2)	S(2)–Fe(2)–S(11)	114.0 (3)	114.5 (3)
S(12)–Mo–S(13)	101.6 (2)	102.2 (2)	S(11)–Fe(3)–S(14)	102.8 (2)	103.1 (2)
P(1)–Mo–S(4)	79.8 (2)	81.2 (2)	S(12)–Fe(3)–S(14)	104.5 (2)	102.6 (2)
P(2)–Mo–S(4)	82.1 (2)	81.4 (2)	S(11)–Fe(3)–S(12)	110.1 (2)	110.0 (2)
S(4)–Mo–S(11)	89.8 (2)	88.6 (2)	S(3)–Fe(3)–S(14)	115.4 (2)	114.3 (2)
S(4)–Mo–S(12)	90.1 (2)	89.3 (2)			
Mo–S(11)–Fe(3)	71.2 (2)	71.8 (2)	Mo–S(13)–Fe(2)	73.5 (2)	71.0 (2)
Mo–S(12)–Fe(3)	71.6 (2)	71.7 (2)	Mo–S(13)–Fe(1)	73.1 (2)	71.7 (2)
Mo–S(11)–Fe(2)	72.8 (2)	72.4 (2)	Fe(2)–S(14)–Fe(3)	74.6 (2)	72.6 (2)
Mo–S(12)–Fe(1)	72.7 (2)	72.5 (2)	Fe(1)–S(14)–Fe(3)	73.5 (2)	73.1 (2)
Fe(2)–S(11)–Fe(3)	73.4 (2)	74.4 (2)	Fe(1)–S(13)–Fe(2)	74.2 (2)	73.1 (2)
Fe(1)–S(12)–Fe(3)	72.7 (2)	74.5 (2)	Fe(1)–S(14)–Fe(2)	73.6 (2)	72.5 (2)

Table V. Selected Interatomic Distances (Å) and Angles (deg) for $[MoFe_3S_4Cl_4(dmpe)]^-$

Mo···Fe(1)	2.708 (2)	Mo–S(1)	2.359 (3)
Mo···Fe(2)	2.732 (2)	Mo–S(2)	2.355 (3)
Mo···Fe(3)	2.703 (2)	Mo–S(3)	2.342 (3)
Mo–P(1)	2.562 (3)	Fe(1)···Fe(3)	2.724 (3)
Mo–P(2)	2.545 (3)	Fe(2)···Fe(3)	2.748 (3)
P(1)···P(2)	3.212 (3)	Fe(1)···Fe(2)	2.767 (3)
Mo–Cl(4)	2.490 (2)		
Fe(1)–S(3)	2.260 (3)	P(1)–Mo–P(2)	78.0 (1)
Fe(2)–S(3)	2.268 (4)	S(1)–Mo–S(2)	103.7 (1)
Fe(1)–S(4)	2.286 (5)	S(3)–Mo–Cl(4)	161.2 (1)
Fe(2)–S(4)	2.277 (4)	P(1)–Mo–S(3)	83.4 (1)
Fe(1)–S(2)	2.263 (3)	P(2)–Mo–S(3)	87.4 (1)
Fe(2)–S(1)	2.260 (4)	P(1)–Mo–S(1)	91.3 (1)
Fe(3)–S(1)	2.278 (4)	P(2)–Mo–S(2)	85.0 (1)
Fe(3)–S(2)	2.261 (4)	S(1)–Mo–S(3)	102.8 (1)
Fe(3)–S(4)	2.296 (4)	S(2)–Mo–S(3)	103.5 (1)
		P(1)–Mo–Cl(4)	80.5 (1)
Fe(1)–Cl(1)	2.206 (4)	P(2)–Mo–Cl(4)	79.8 (1)
Fe(2)–Cl(2)	2.208 (4)	S(1)–Mo–Cl(4)	87.3 (1)
Fe(3)–Cl(3)	2.198 (4)	S(2)–Mo–Cl(4)	89.2 (1)
S(3)–Fe(1)–S(4)	102.1 (1)	Mo–S(1)–Fe(3)	71.3 (1)
S(3)–Fe(2)–S(4)	102.1 (2)	Mo–S(2)–Fe(3)	71.7 (1)
S(2)–Fe(1)–S(3)	108.5 (1)	Mo–S(1)–Fe(2)	72.5 (1)
S(1)–Fe(2)–S(3)	109.2 (1)	Mo–S(2)–Fe(1)	71.8 (1)
S(2)–Fe(1)–S(4)	103.6 (1)	Fe(2)–S(1)–Fe(3)	74.5 (1)
S(1)–Fe(2)–S(4)	103.9 (1)	Fe(1)–S(2)–Fe(3)	74.0 (1)
Cl(1)–Fe(1)–S(2)	110.7 (2)	Mo–S(3)–Fe(2)	72.7 (1)
Cl(2)–Fe(2)–S(1)	108.5 (2)	Mo–S(3)–Fe(1)	72.1 (1)
S(1)–Fe(3)–S(4)	102.4 (1)	Fe(2)–S(4)–Fe(3)	73.9 (1)
S(2)–Fe(3)–S(4)	103.7 (2)	Fe(1)–S(4)–Fe(3)	73.0 (1)
S(1)–Fe(3)–S(2)	109.6 (1)	Fe(1)–S(3)–Fe(2)	75.4 (1)
Cl(3)–Fe(3)–S(4)	114.5 (2)	Fe(1)–S(4)–Fe(2)	74.7 (1)

(b) Iron Sites. We have previously argued, using ^{57}Fe isomer shifts of a wide variety of Fe–S compounds, that (mean) oxidation states in clusters containing the $[MoFe_3S_4]^{3+}$ core approximate the description Mo^{3+} + $Fe^{2.67+}$.[26] It is shown elsewhere that on the same basis the core of $[MoFe_3S_4(SEt)_4(dmpe)]^-$ is similarly described.[27] Further, terminal Fe–SR/Cl distances in cubane-type clusters are generally responsive to Fe mean oxidation states.[8,28,29] As has been discussed,[11] increased Fe^{3+} character affords relatively shorter bond distances. These distances for $[MoFe_3S_4(SEt)_4(dmpe)]^-$ (2.250 (10), 2.248 (18) Å) and $[MoFe_3S_4Cl_4(dmpe)]^-$ (2.205 (5) Å), being marginally less than those in Fe–S clusters containing $Fe^{2.5+}$ with thiolate[28] and chloride[30] ligands, further support a mean oxidation state no less than $Fe^{2.5+}$.

(c) Molybdenum Sites. These sites in $[MoFe_3S_4(SEt)_4(dmpe)]^-$ and $[MoFe_3S_4Cl_4(dmpe)]^-$ have the common feature of Mo–dmpe chelate rings, although of somewhat differing conformations and dimensions. The structure of **6** provides confirmation of the presence of terminal chloride. Terminal Mo–ligand bond distances are more difficult to interpret than Fe–Cl distances owing to the wide ranges of Mo–L separations in six-coordinate complexes with the same metal oxidation state, even when the trans effect of oxo ligands and apparent steric effects are taken into account. The Mo–SR distance of 2.600 (3) Å in $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4(al_2cat)]^{3-}$[5] is the longest measured Mo–S bond involving an anionic sulfur ligand. The values for $[MoFe_3S_4(SEt)_4(dmpe)]^-$ (2.486 (8), 2.566 (8) Å) are less long, presumably because ethanethiolate is more basic than an arenethiolate and catecholate has been replaced by dmpe. Both of these ligands are expected to be strong σ-donors, but dmpe, being uncharged, causes the Mo center to be less electron-rich and thus to form a tighter bond. These distances are well above the range of Mo(II–V)–SR dis-

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tances (2.30–2.40 Å[31,32]), as well as of Mo(VI)–SR bond lengths (2.39–2.44 Å[33]). The Mo–Cl distance of 2.490 (2) Å in $[MoFe_3S_4Cl_4(dmpe)]^-$ is one of the longest such distances known. It is closer to the Mo(II–V)–Cl (2.39–2.48 Å[34]) than to the Mo(VI)–Cl interval (2.30–2.40 Å[34a,35]). To this extent, the observed distance is consistent with an oxidation state near Mo^{3+}.

The two inequivalent $[MoFe_3S_4(SEt)_4(dmpe)]^-$ clusters are mainly differentiated by their chelate ring conformations. Cluster **1** exhibits the "asymmetric" skew (near-"half-chair") conformation[36] shown in Figure 3, with C(1) 0.33 Å on one side and C(2) 0.56 Å on the other side of the MoP(1,2) plane, and a P(1)C(2)C(1)P(2) dihedral angle of 61.2°. In cluster **2** (not shown) the chelate ring has the asymmetric envelope conformation[36] with one C atom virtually in the MoP_2 plane and the other 0.22 Å above it, and a PCCP angle of 18.1°. This situation is rather closely approached in the two inequivalent forms of $[W(\eta^3\text{-}C_3H_5)(\eta^6\text{-}PhMe)(dmpe)]^{+}$[37] and $[IrSe_4(dmpe)_2]^{+}$.[38] The structure of $[MoFe_3S_4Cl_4(dmpe)]^-$ was successfully refined in terms of a ~4:1 ratio of enantiomeric asymmetric skew conformations. In the major conformation, C(1) and C(2) are on opposite sides of the MoP(1,2) plane at 0.51 and 0.22 Å, respectively, with a P(1)C(2)C(1)P(2) dihedral angle of 51.5°. The existence in crystals of dmpe chelate rings with large methylene carbon thermal parameters, which have been attributed to disorder without further refinement or have been refined in terms of the presence of opposite skew ring conformations, is quite common.[18b,23,37,39] The most closely related example is the cubane cluster $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$ (**9**), whose structure was successfully refined on the basis of these conformations.[11]

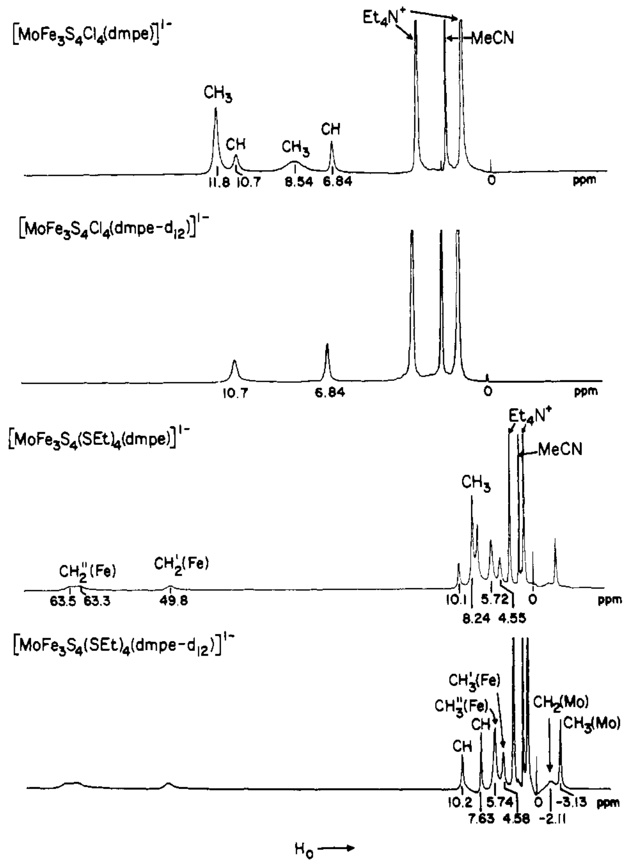
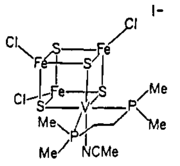


Figure 5. ^1H NMR spectra (297 K) of $[MoFe_3S_4Cl_4(dmpe)]^-$ (upper) and $[MoFe_3S_4(SEt)_4(dmpe)]^-$ (lower) and their dmpe-d_{12} variants in CD_3CN solutions. Signal assignments are indicated.



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The MoS_3P_2L coordination units (L = RS^-, Cl^-) are severely distorted octahedra. The S–Mo–S and S–Mo–L angles of 101–104° and 161°, respectively, are set by the core structure inasmuch as these values are entirely typical of all clusters with the $[MoFe_3S_4]^{3+}$ core.[8] The P–Mo–P bite angles of 76–80° are in the established range of 74–86° for dmpe complexes. Somewhat surprising is the large range of Mo–P bond lengths observed in the three clusters, 2.499 (6)–2.611 (5) Å. This may be due in part to the constraints placed on P–C and C–C bond lengths in the refinements. The shorter distances are associated with the asymmetric skew Mo–dmpe chelate ring conformation. There is no evident correlation of Mo–P bond lengths with nonbonded methyl C(3,6)–S(3),S(13) or C(4,5)–S(4),Cl(4) distances. These S and Cl atoms are the closest in the core units to the methyl C atoms.

^1H NMR Spectra. Our past work on clusters **3** and **4** has shown that NMR spectra are invaluable for detecting fluxional properties and monitoring substitution reactions at Mo and Fe sites.[4-8,25] This situation obtains because of the $S = {}^3/_2$ ground state of these clusters, which affords isotropically shifted spectra that in general are very well resolved. The solution magnetic moments at room temperature of $[MoFe_3S_4(SEt)_4(dmpe)]^-$ (3.97 μ_B, Me_2SO) and $[MoFe_3S_4Cl_4(dmpe)]^-$ (4.10 μ_B, acetonitrile) are consistent with a quartet state. Further, this spin state has been demonstrated

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(31) The bond distance ranges given here and subsequently refer to six-coordinate complexes, with the exception of several Mo(V)–chloro species. References cited support the stated distance ranges and are representative, not comprehensive.

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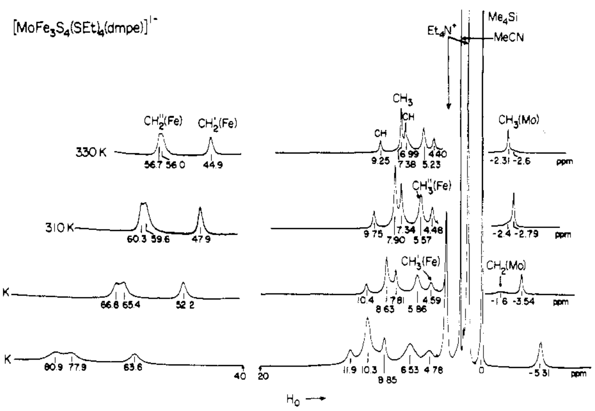

Figure 6. ^{1}H NMR spectra of $[MoFe_3S_4(SEt)_4(dmpe)]^-$ at 245–330 K in CD_3CN solution. Signal assignments are indicated. The spectral amplitude above 20 ppm is 2 times that at lower fields.

for both clusters in the crystalline phase by low-temperature magnetization and magnetic susceptibility measurements.[27]

Spectra of $[MoFe_3S_4Cl_4(dmpe)]^-$ and $[MoFe_3S_4(SEt)_4(dmpe)]^-$ in acetonitrile solutions at 297 K are shown in Figure 5. Methyl and methylene signals of dmpe could not securely be assigned without recourse to clusters derived from dmpe-d_{12}, whose spectra are also presented. The frozen skew Mo–dmpe ring conformation would generate eight signals, whereas rapid interchange of enantiomeric skew forms would average pairs of methylene protons and methyl groups on the same side of the MoP_2 plane. This would afford four signals, as observed for $[MoFe_3S_4Cl_4(dmpe)]^-$. One methyl (8.54 ppm) and one CH (10.7 ppm) resonance have larger line widths, suggestive of greater paramagnetic and/or exchange broadening. Owing to the near-Curie paramagnetism of the cluster,[27] these signals at 245 K are shifted downfield, to 11.0 (Me) and 12.7 (CH) ppm, but do not resolve into additional resonances. It is probable that the differential broadening is paramagnetic in origin and that the methyl and CH resonances affected arise from groups on the "core" (i.e., the Fe(1,2)S(3,4)) side of the MoP_2 plane, this being the region of closer proximity to the additional paramagnetic centers Fe(1,2).

The spectrum of $[MoFe_3S_4(SEt)_4(dmpe)]^-$ exhibits one methyl resonance at 8.24 ppm and two CH signals at 7.63 and 10.1 ppm due to dmpe. These features are also broadened and shifted to low field at 245 K (CH, 8.85 and 11.9 ppm; Me, 10.3 ppm) but do not split. The ratio of the integrated intensities of the overlapping 7.63 + 8.24 ppm signals to the nearly fully resolved signal at 10.1 ppm is 6.2:1, close enough to 7:1 to indicate that the two inequivalent methyl groups have degenerate chemical shifts over the temperature range examined. This puzzling behavior has also been observed for cluster **9** at 245–300 K.[11]

The clusters **3** are stereochemically nonrigid in a process that equilibrates Fe sites on (m') and off (m'') the mirror plane.[4a,5,6] These sites are illustrated with **5** (Figure 1). We have proposed that this process occurs by reorientation of catecholate chelate rings over three degenerate positions roughly coplanar with core faces, with accompanying solvent dissociation and rebinding. The sequence leads to time-averaged trigonal symmetry and is illustrated elsewhere.[6]

If with the present clusters trigonal averaging were faster than conformational interconversion, two dmpe signals would result, which is contrary to observation. A rigid structure is further supported by the appearance of two methylene proton resonances of the Fe–SEt groups of $[MoFe_3S_4(SEt)_4(dmpe)]^-$. At ambient temperature the broad feature centered near 63 ppm is twice as intense as the resonance at 50 ppm, consistent with effective C_s symmetry and supporting assignment to the m'' and m' sites, respectively. The full spectra of this cluster at other temperatures are shown in Figure 6. The CH_2'' feature is clearly split into a doublet, with the separation reaching 3 ppm at 245 K. The CH_2' signal remains a singlet at all temperatures. The C_s cluster symmetry further renders the CH_2'' protons within each group diastereotopic[40] while those of the CH_2' group are necessarily isochronous. Any process that causes trigonal averaging equilibrates sites m' and m'' and therewith removes these effects. The remaining feature of interest in the spectrum of this cluster is appearance of the methyl signal of the Mo–SEt group near −3 ppm and its shift to higher fields with decreasing temperature. This behavior whereby nuclei with large negative isotopic shifts[41] in ligands at Fe sites assume small negative or positive isotropic shifts at Mo sites has been previously observed.[5,6,42] If dominantly contact in origin, the shifts are suggestive of a different delocalization mechanism and/or lesser spin density on the Mo atom. The assignment of the broad upfield resonance to $CH_2(Mo)$ in Figures 5 and 6 is speculative.

Substitution Reactions. (a) Cluster 5. The formation of $[MoFe_3S_4Cl_4(dmpe)]^{1-}$ in reactions 1 has been found by ^{1}H NMR to proceed in the two stages represented by reactions 2 and 3.

$$[MoFe_3S_4(SEt)_4(dmpe)]^- + 3MeCOCl \rightarrow [MoFe_3S_4(SEt)Cl_3(dmpe)]^- + 3MeCOSEt \quad (2)$$

$$[MoFe_3S_4(SEt)Cl_3(dmpe)]^- + MeCOCl \rightarrow [MoFe_3S_4Cl_4(dmpe)]^- + MeCOSEt \quad (3)$$

(The use of acetyl chloride in these reactions instead of benzoyl chloride as in preparative reaction 1 is inconsequential.) In reaction 2 the Fe–SEt resonances of **5** are abolished and the remaining signals are those of dmpe (Me, 6.99 and 7.83 ppm; CH, 10.0 and 12.4 ppm) and the methyl group of Mo–SEt (−3.54 ppm).[43] At 256 K this signal appears at −4.86 ppm, consistent with the behavior in Figure 6. Thioester signals were also detected. Reaction 2 in acetonitrile or Me_2SO with 10 mM cluster at ambient temperature is immediate. Under the same conditions but with excess (≥2 equiv) of reagent, reaction 3 is much slower, at least 10 h being required to abolish the −3.54 ppm signal and generate the spectrum of $[MoFe_3S_4Cl_4(dmpe)]^-$ (Figure 5). Previously, we have shown that *bridging* thiolates in clusters **1** and **7** do not react with acetyl chloride under conditions that preserve subcluster core structure.[25] Evidently, as noted then, adjacent metal centers reduce the nucleophilicity of bridging sulfur atoms to the point that they do not react with electrophiles as strong as an acyl chloride. The occurrence of reaction 3 provides the initial demonstration of *terminal* Mo–SR reactivity, albeit at a relatively slow rate.

(b) Cluster 6. This cluster contains labile ligands at all metal sites. In this respect it is similar to **8**, whose axial ligand (solvent, as in **3**) is even more labile. The substitution reactions (4) with

$$[MoFe_3S_4Cl_4(dmpe)]^- + nRS^- \rightarrow [MoFe_3S_4Cl_{4-n}(SR)_n(dmpe)]^- + nCl^- \quad (4)$$

p-tolylthiolate (n = 1–4) have been examined by ^{1}H NMR in acetonitrile solution at room temperature. Spectra are shown in Figure 7 together with the cluster substitution products $[4 - n,n]^z$, where z = s (symmetrical, C_s symmetry) and u (unsymmetrical). At $n < 3$ equiv of thiolate, the spectra are quite complex because of mixtures of reaction products and the attendant large numbers of signals. The situation was improved by use of $[MoFe_3S_4Cl_4(dmpe\text{-}d_{12})]^-$, and all reactions were repeated with p-$CD_3C_6H_4S^-$ (not shown) to prove assignments of methyl signals.[44] Because of spectral complexity, only the methyl resonances of each reaction

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(40) These observations do not prove that the doublet components arise from the same methylene group. However, it is reasonable to assume that chemical shift differences between m' and m'' sites will be much larger than between inequivalent protons of CH_2'' groups. The former shift difference for $[MoFe_3S_4(SEt)_3(al_2cat)(CN)]^{3-}$ is 60 ppm![5]

(41) $(\Delta H/H_0)_{iso} = (\Delta H/H_0)_{dia} - (\Delta H/H_0)_{obsd}$.

(42) Mascharak, P. K.; Smith, M. C.; Armstrong, W. H.; Burgess, B. K.; Holm, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 7056.

(43) The Mo–SCH_2CH_3 resonance apparently is the broad feature at ca. −1.7 ppm.

(44) Even with $[MoFe_3S_4Cl_4(dmpe\text{-}d_{12})]^-$, products $[3,1]^z$ and $[2,2]^z$ can generate a total of 12 resonances. These account for the large majority of signals in the ca. 4–13 ppm region of $n < 3$ reaction systems.

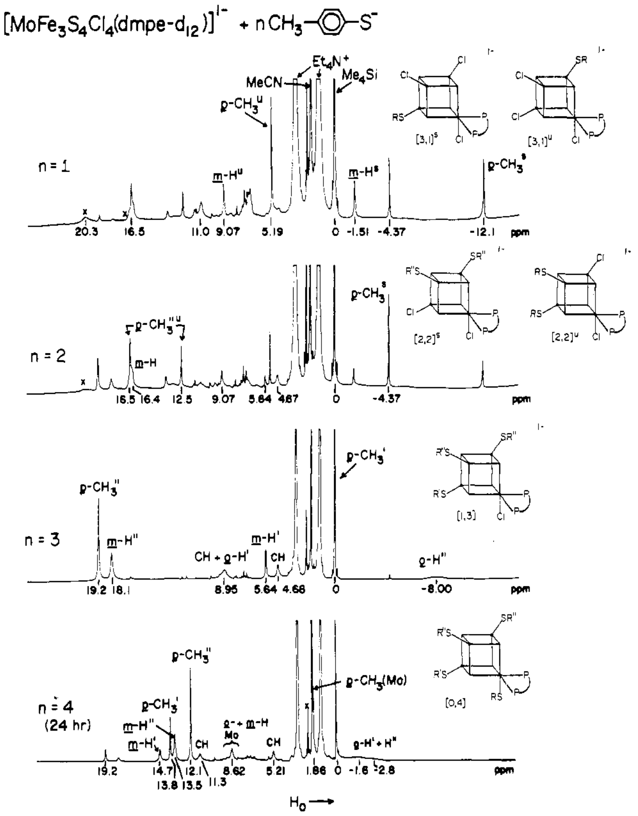

Figure 7. ^{1}H NMR spectra of reaction systems containing initially $[MoFe_3S_4Cl_4(dmpe\text{-}d_{12})]^-$ and n = 1–4 equiv of $(Et_4N)(S\text{-}p\text{-}C_6H_4CH_3)$ in CD_3CN solution at 297 K. Cluster reaction products $[4 - n,n]^z$ are depicted and signal assignments are indicated (× = unassigned signal). The bottom spectrum was recorded 24 h after reactants were mixed. Other spectra were recorded within 10 min of mixing.

product could be definitely assigned. However, this is sufficient for product identification. Assignments were made as in the study of the reactions of **8**,[6] viz., by assuming a roughly statistical product distribution and using relative signal intensities.

At n = 1 equiv, the major products are $[3,1]^s$ and $[3,1]^u$, whose meta proton and p-Me signals are assigned on the basis of a statistical weight of 2 for the latter. From p-Me signal intensities, the molar ratio $[3,1]^u$:$[3,1]^s$ = 1.6:1. In the n = 2 equiv system, signals of the [3,1] clusters have diminished in intensity and the p-Me resonances of $[2,2]^s$ and $[2,2]^u$ are identifiable because the latter requires two equally intense signals. The molar ratio $[2,2]^u$:$[2,2]^s$ = 1.6:1, compared to 2:1 for purely statistical formation. At n = 3 equiv, the spectrum simplifies to that of [3,1], all signals of which (except possibly the ortho H′, inferred by the relative intensity of the 8.95 ppm feature) are readily assigned. Introduction of a fourth equivalent of thiolate results in a very slow reaction. After 10 min the resonances of free thiolate are evident. These gradually diminish in intensity until after about 24 h the final spectrum, unquestionably that of [0,4], appears. Nearly all signals of this cluster can be securely assigned. Those of ring protons of the Mo–SR group are perhaps least certain because a reliable signal integration could not be obtained due to residual background intensity. These protons in $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4(al_2cat)]^{3-}$ occur in a similar region but at higher field (7.1–7.3 ppm).

Thiolate substitution reaction 5, with benzenethiol as the electrophile, was also examined. With n = 3 equiv substitution of the three thiolates at Fe sites was immediate in acetonitrile or Me_2SO solution. Product cluster $[MoFe_3S_4(SEt)(SPh)_3(dmpe)]^-$

$$[MoFe_3S_4(SEt)_4(dmpe)]^- + nPhSH \rightarrow [MoFe_3S_4(SEt)_{4-n}(SPh)_n(dmpe)]^- + nEtSH \quad (5)$$

was readily identified from its NMR spectrum: 14.4 (meta H′), 13.7 (meta H″), −2.90 (para H′), −3.26 (Mo–SCH_2CH_3), −4.22 (para H″) ppm in acetonitrile.[45] In the n = 4 equiv system, conversion of the n = 3 product to $[MoFe_3S_4(SPh)_4(dmpe)]^-$ was only 50% complete after 1 week. These results again emphasize the relatively slow reactivity of a terminal Mo–SR group with electrophiles.

Reactions of $[MoFe_3S_4Cl_4(dmpe)]^-$ with other ligands such as Et_3P, CN^-, N_3^-, and pyridine either gave no reaction or small perturbations on the dmpe signals suggestive of binding at the Mo site. Addition of thiolate to these systems in order to provide evidence of binding by the generation of signals attributable to a C_s cluster led to decomposition and/or complicated spectra that could not be interpreted.

Summary. The following are the principal findings and conclusions of this investigation.

(1) The Fe(III)-bridged double cubane **1** is cleaved by excess dmpe to afford the single cubane $[MoFe_3S_4(SEt)_4(dmpe)]^-$ (**5**) in moderate (33%) purified yield. Other than catechols, dmpe is the only reagent known to cleave **1** to a single cubane. In both cases, product clusters contain the cleavage reagent chelated to the Mo site.

(2) Reaction of **5** with a small excess of PhCOCl in acetonitrile causes substitution of thiolate at *all* metal sites, affording $[MoFe_3S_4Cl_4(dmpe)]^-$ (**6**) in 94% yield.

(3) Clusters **5** and **6** contain cubane-type $[MoFe_3(\mu_3\text{-}S)_4]^{3+}$ cores, trigonally distorted Fe sites, and $Mo(\mu_3\text{-}S)_3P_2L$ units (L = RS^-, Cl^-) severely distorted from the octahedral. Core dimensions vary irregularly among **6** and the two crystallographically inequivalent clusters **5**, and do not conform well to idealized C_s symmetry. Core volumes are indistinguishable. Terminal Fe–SEt/Cl bond lengths indicate a mean oxidation state no less than $Fe^{2.5+}$. The Mo–Cl distance is not inconsistent with an oxidation state near Mo^{3+}. Mo–dmpe chelate rings exhibit large thermal motions of C atoms, a frequent feature of dmpe complexes. The asymmetric skew conformation was found in **6** and in one cluster of **5**.

(4) Clusters **5** and **6** have an $S = {}^3/_2$ ground state, as do all known clusters with the $[MoFe_3S_4]^{3+}$ core. The rapid electron spin relaxation of this state, whose EPR spectra can be observed only below ca. 20 K,[10] affords well-resolved ^{1}H NMR spectra.

(5) The chelate rings in **5** and **6** undergo rapid interconversion between enantiomeric asymmetric skew conformations. The clusters are otherwise stereochemically rigid inasmuch as their NMR spectra conform to C_s symmetry.

(6) Reaction of **5** with MeCOCl or PhSH results in immediate RS^-/Cl^- substitution at the three Fe sites, followed by much slower substitution at the Mo site, which proceeds to completion with a small excess of the acyl chloride. Similarly, **6** with RS^- undergoes rapid substitution at the Fe sites and then a much slower substitution at the Mo site. These are the first indications that a terminal Mo–SR group is reactive toward electrophiles (without cluster destruction) and that a terminal Mo–Cl group in a cluster undergoes a nucleophilic substitution reaction. In contrast, the less nucleophilic bridging thiolates in **1** and **7** are unreactive to these electrophiles.

The present results, together with those based on cluster **8**,[6] provide a fairly comprehensive picture of the relative substitutional

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(45) Isotropically shifted spectra of this and other clusters are well resolved and, as has been shown, are structurally diagnostic. In addition, they exhibit some unusual features. The isotropic shifts[41] of the m'' ligands are larger than for the m' ligands in the cases of **5** and [1,3], but the reverse is true for [0,4] (Figure 7), $[MoFe_3S_4(SEt)(SPh)_3(dmpe)]^-$, and all examples of **4**.[5-7] Further, in the substitution reactions 4, p-Me isotropic shifts of $[3,1]^z$ and $[2,2]^s$ are positive and those of $[2,2]^u$, [1,3], and [0,4] are negative. Also, dmpe shifts are quite sensitive to the ligands at all metal sites. We cannot explain these behavioral features but speculate that the magnetic anisotropy and the location of the principal magnetic axes may be extremely sensitive to the specific ligand set. This would have the effect of producing different dipolar contributions[46] to the observed isotropic shifts $(\Delta H/H_0)_{iso} = (\Delta H/H_0)_{contact} + (\Delta H/H_0)_{dipolar}$. In particular, it is difficult to see why the sign of the p-Me isotropic shift would change without a dipolar contribution.

(46) Horrocks, W. D., Jr. In *NMR of Paramagnetic Molecules*; La Mar, G. N., Horrocks, W. D., Jr., Holm, R. H., Eds.; Academic: New York, 1973; Chapter 4.

tendencies of Fe and Mo atoms in (μ_3-S)$_3$ binding sites in the same cluster. These should prove useful in interpreting ligand binding reactions of the FeMo cofactor of nitrogenase.[47] The four possible permutations of chloride and thiolate binding at Fe/Mo sites have been realized with the dmpe clusters. Solvent or another labile neutral ligand has not yet been introduced at the Mo site in these clusters. With catecholate clusters (**3**, **4**, **8**) the combinations Cl^-/RS^-, solvent and RS^-/RS^-, solvent have been achieved. Chloride does not bind to the Mo sites of **3** or **8** in acetonitrile even at 100-fold excess. Consequently, the dmpe clusters may have a generally greater binding affinity at the Mo site provided a suitably labile ligand can be introduced. While **3** will bind anionic pseudosubstrates of nitrogenase,[7] it has no affinity for dinitrogen or acetylenes when in the oxidized or reduced state. While containing a nonphysiological ligand type, oxidized or reduced dmpe clusters may be useful in binding and perhaps reducing enzyme substrates in a sulfur-rich environment similar to that deduced for nitrogenase from X-ray absorption spectroscopy.[9,10] These clusters undergo chemically reversible one-electron reductions at −1.48 (**5**) and −0.71 V (**6**) vs. SCE in acetonitrile solution.

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Registry No. **5**, 106626-03-3; **6**, 106589-84-8; $(Et_4N)_3[Mo_2Fe_7S_8(SEt)_{12}]$, 73589-29-4; $[MoFe_3S_4Cl_3(SEt)(dmpe)]^-$, 106589-85-9; $[MoFe_3S_4Cl_2(SEt)_2(dmpe)]^-$, 106589-86-0; $[MoFe_3S_4Cl(SEt)_3(dmpe)]^-$, 106589-87-1; $[MoFe_3S_4Cl_4(dmpe)]^-$, 106589-83-7.

Supplementary Material Available: Tables of X-ray structural data for compounds **5** and **6** giving full sets of positional parameters, thermal parameters, and calculated hydrogen atom positional parameters (14 pages); tables of calculated and observed structure factors for **5** and **6** (74 pages). Ordering information is given on any current masthead page.

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Heterometallic Clusters: Synthesis and Reactions of Vanadium-Iron-Sulfur Single- and Double-Cubane Clusters and the Structure of $[V_2Fe_6S_8Cl_4(C_2H_4S_2)_2]^{4-}$

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Reaction of the linear trinuclear cluster $[VFe_2S_4Cl_4]^{3-}$ (**6**) with $FeCl_2$ in DMF affords the first example of a new set of heterometal MFe_3S_4 cubane-type clusters, $[VFe_3S_4Cl_3(DMF)_3]^-$ (**1**), which was isolated as its Me_4N^+ salt. This reaction involves reduction of V(V) in **6** by Fe(II) to generate an incomplete VFe_2S_4 cubane fragment, into which a Fe atom is incorporated. Cluster **1** is notably reactive, undergoing substitution at all metal sites. It is solvolyzed at the V site, the order of binding affinity being solv = MeCN < DMF $\lesssim$ Me_2SO. With ≥3 equiv of RS^- and RO^-, substitution occurs at the Fe sites only, giving $[VFe_3S_4(SR)_3(solv)_3]^-$ (**2**) and $[VFe_3S_4(OR)_3(solv)_3]^-$ (R = *p*-C_6H_4Me). One Et_3P molecule binds weakly at the V site of **1**. The V-substituted clusters $[VFe_3S_4Cl_3(bpy)(DMF)]^-$ (**3**) and $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$ (**4**) were isolated from the reaction of **1** with 2,2′-bipyridyl and 1,2-bis(dimethylphosphino)ethane, respectively. With disodium ethane-1,2-dithiolate (Na_2edt), $[V_2Fe_6S_8Cl_4(edt)_2]^{4-}$ (**5**) is formed. $(Me_4N)_2(Et_4N)_2[V_2Fe_6S_8Cl_4(edt)_2]\cdot 2MeCN$ crystallizes in monoclinic space group $P2_1/c$, with a = 11.536 (5) Å, b = 14.903 (8) Å, c = 20.284 (8) Å, β = 90.24 (4)°, and Z = 2. The anion is a centrosymmetric double cubane in which $VFe_3S_4Cl_2(edt)$ subclusters of unexceptional dimensions are connected by Fe-(μ-S)-V bridges with Fe-S = 2.305 (5) Å, V-S = 2.482 (6) Å, and Fe-S-V = 121.8 (2)°. The bridge structure is maintained in coordinating solvents but is cleaved by RS^- to give $[VFe_3S_4(SR)_3(edt)]^{3-}$ (**14**), which does not bind excess RS^- or Et_3P at the V site, presumably because of steric constraints. Cluster **5** is also cleaved by RSH to give $[VFe_3S_4Cl_n(SR)_{3-n}(Me_2SO)_3]^-$ (n = 1, 2). With the exception of **3**, the single cubanes undergo a chemically reversible one-electron oxidation but tend to be irreversibly reduced. The synthesis of **1** and its derivatives expands the set of heteronuclear MFe_3S_4 cubane-type clusters to include those with M = V, Mo, and W. Further, the formation of the isoelectronic cores $[VFe_3S_4]^{2+}$, $[MoFe_3S_4]^{3+}$, and $[WFe_3S_4]^{3+}$ by cluster assembly reactions involving electron transfer indicates a special stability associated with these 51e, $S = {}^3/_2$ configurations. Ligand substitution and redox properties of the isoelectronic V and Mo clusters are compared. Structural and electronic features of cluster **1** and its derivatives are reported separately.

Introduction

Extensive investigations have been carried out in this laboratory on many aspects of the chemistry of clusters containing one[1-8] and two[8-11] cubane-type $MoFe_3(\mu_3\text{-}S)_4$ and $WFe_3(\mu_3\text{-}S)_4$ core units. This research has been motivated to a considerable extent by the apparent resemblance of the Mo coordination environments in the former clusters to that in the native Mo-Fe-S cluster of nitrogenase.[12] There is, however, another significant aspect of these clusters: their ease of formation and stability presage the existence of a more extensive set of MFe_3S_4 clusters, members of the generalized family of heterometal cubane-type clusters MM'_3S_4. As one probable example, incubation of *Desulfovibrio gigas* ferredoxin and Co(II) affords a new cluster of likely com-

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