

tendencies of Fe and Mo atoms in $(\mu_3\text{-S})_3$ 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.

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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; $(\text{Et}_4\text{N})_3[\text{Mo}_2\text{Fe}_7\text{S}_8(\text{SEt})_{12}]$, 73589-29-4; $[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{SEt})(\text{dmpe})]^-$, 106589-85-9; $[\text{MoFe}_3\text{S}_4\text{Cl}_2(\text{SEt})_2(\text{dmpe})]^-$, 106589-86-0; $[\text{MoFe}_3\text{S}_4\text{Cl}(\text{SEt})_3(\text{dmpe})]^-$, 106589-87-1; $[\text{MoFe}_3\text{S}_4\text{Cl}_4(\text{dmpe})]^-$, 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 $[\text{V}_2\text{Fe}_6\text{S}_8\text{Cl}_4(\text{C}_2\text{H}_4\text{S}_2)_2]^{4-}$

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Reaction of the linear trinuclear cluster $[\text{VFe}_2\text{S}_4\text{Cl}_4]^{3-}$ (**6**) with FeCl_2 in DMF affords the first example of a new set of heterometal MFe_3S_4 cubane-type clusters, $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ (**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 $\text{sol} = \text{MeCN} < \text{DMF} \leq \text{Me}_2\text{SO}$. With ≥ 3 equiv of RS^- and RO^- , substitution occurs at the Fe sites only, giving $[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{sol})_3]^-$ (**2**) and $[\text{VFe}_3\text{S}_4(\text{OR})_3(\text{sol})_3]^-$ ($\text{R} = p\text{-C}_6\text{H}_4\text{Me}$). One Et_3P molecule binds weakly at the V site of **1**. The V-substituted clusters $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{bpy})(\text{DMF})]^-$ (**3**) and $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{MeCN})]^-$ (**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), $[\text{V}_2\text{Fe}_6\text{S}_8\text{Cl}_4(\text{edt})_2]^{4-}$ (**5**) is formed. $(\text{Me}_4\text{N})_2(\text{Et}_4\text{N})_2[\text{V}_2\text{Fe}_6\text{S}_8\text{Cl}_4(\text{edt})_2] \cdot 2\text{MeCN}$ crystallizes in monoclinic space group $P2_1/c$, with $a = 11.536$ (**5**) Å, $b = 14.903$ (**8**) Å, $c = 20.284$ (**8**) Å, $\beta = 90.24$ (**4**)°, and $Z = 2$. The anion is a centrosymmetric double cubane in which $\text{VFe}_3\text{S}_4\text{Cl}_2(\text{edt})$ subclusters of unexceptional dimensions are connected by Fe-($\mu\text{-S}$)-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 $[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{edt})]^{3-}$ (**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 $[\text{VFe}_3\text{S}_4\text{Cl}_n(\text{SR})_{3-n}(\text{Me}_2\text{SO})_3]^-$ ($n = 1, 2$). 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 $\text{M} = \text{V}, \text{Mo},$ and W . Further, the formation of the isoelectronic cores $[\text{VFe}_3\text{S}_4]^{2+}$, $[\text{MoFe}_3\text{S}_4]^{3+}$, and $[\text{WFe}_3\text{S}_4]^{3+}$ 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 one¹⁻⁸ and two⁹⁻¹¹ cubane-type $\text{MFe}_3(\mu_3\text{-S})_4$ and $\text{WFe}_3(\mu_3\text{-S})_4$ 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 $\text{MM}'_3\text{S}_4$. As one probable example, incubation of *Desulfotribio gigas* ferredoxin and Co(II) affords a new cluster of likely com-

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position $\text{CoFe}_3\text{S}_4^{13}$ and cubane stereochemistry. Such a cluster could be readily formed by insertion of the heterometal into the vacant metal site of a $\text{Fe}_3(\mu_3\text{S})(\mu\text{-S})_3$ protein cluster. A similar type of reaction between $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ and metallic Fe in aqueous ammoniacal solution has recently afforded $[\text{FeMo}_3\text{S}_4(\text{NH}_3)_9(\text{H}_2\text{O})]^{4+}$, which has a cubane-type structure¹⁴ and is thus a member with inverted metal composition of the $\text{MM}'_3\text{S}_4$ cluster family.

As has been briefly reported,¹⁵ the recent synthesis of $[\text{VFe}_3\text{S}_4\text{Cl}_4]^{3-16}$ provides entry to a new set of V-Fe-S heterometal clusters. The most fundamental member of the set is assembled from mono- and trinuclear precursors, and as will be seen, substantial structural rearrangement of the latter is required in the course of product formation. The clusters contain the previously unknown cubane-type core $[\text{VFe}_3\text{S}_4]^{2+}$, which is isoelectronic with the $[\text{MoFe}_3\text{S}_4]^{3+}$ cores of many single and double cubanes. Consequently, this favorable circumstance permits an analysis of comparative properties such as detailed structural¹⁷ and electronic features.¹⁸ These matters will be described separately. Here we report the synthesis and selected reactions of this new set of heterometal clusters, together with the structure of a double-cubane reaction product.

In this paper the numerical designations refer to the cluster or the entire compound, as appropriate.

Experimental Section

Preparation of Compounds. All operations were performed under a pure dinitrogen atmosphere; solvents were degassed prior to use. Anhydrous FeCl_2 (99.99%) was obtained from Cerac and DMF (high purity, 0.03% H_2O) from Burdick & Jackson. Acetonitrile was distilled from CaH_2 and stored over 3-Å molecular sieves. $(\text{NH}_4)_3\text{VS}_4$,¹⁶ $(\text{Et}_4\text{N})_3[\text{VFe}_2\text{S}_4\text{Cl}_4]$,¹⁶ 1,2-bis(dimethylphosphino)ethane¹⁹ (dmpe), disodium ethane-1,2-dithiolate^{20,21} (Na_2edt), and 5,5'-dimethyl-2,2'-bipyridyl²² (5,5'-Me₂bpy) were prepared as described. 2,2'-Bipyridyl (bpy) and 4,4'-dimethyl-2,2'-bipyridyl (4,4'-Me₂bpy) were obtained from Aldrich.

(Me₄N)[VFe₃S₄Cl₃(DMF)₃]·2DMF (1). A slurry of 3.0 g (13 mmol) of $(\text{NH}_4)_3\text{VS}_4$ and 2.0 g (13 mmol) of Me_4NBr in 300 mL of DMF was treated with 6.6 g (52 mmol) of anhydrous FeCl_2 . An intense wine-red solution was formed initially, which turned dark brown after ~2-h reaction time. After being stirred for ~16 h, the reaction mixture was filtered to remove NH_4Br and an insoluble black solid. Addition of 100 mL of ether to the dark brown filtrate followed by cooling to -20 °C afforded 5.7 g of crude product as a black microcrystalline solid. Recrystallization of this material from DMF/ether afforded 4.4 g (39%) of pure product as a black crystalline solid. Analytical data and the ¹H NMR spectrum are most consistent with a DMF disolvate formulation. Anal. Calcd for $\text{C}_{19}\text{H}_{47}\text{Cl}_3\text{Fe}_3\text{N}_6\text{O}_5\text{S}_4\text{V}$: C, 25.56; H, 5.31; Fe, 18.77; N, 9.41; S, 14.37; V, 5.71. Found: C, 24.55; H, 5.12; Fe, 19.09; N, 9.29; S, 14.41; V, 5.77. Chloride analytic results (11.91% for disolvate) were repeatedly high by several percent, for reasons unknown. Absorption spectrum (DMF): essentially featureless with a gradual rise from 800 to 250 nm.

(Ph₄P)[VFe₃S₄(S-p-C₆H₄Me)₃(DMF)₃] (2). A solution of 2.7 g (3.1 mmol) of **1** in 100 mL of DMF was treated with 1.4 g (9.4 mmol) of $\text{Na}(\text{S-p-C}_6\text{H}_4\text{Me})$, to afford an immediate color change from dark brown to an intense yellow-brown. After the mixture was stirred for 5 min, 1.3 g (3.1 mmol) of Ph_4PBr was added to the reaction mixture, which was then stirred for an additional 3 h and filtered to remove NaCl and Me_4NBr . Following the addition of ~20 mL of ether, the yellow-brown

filtrate was cooled to -20 °C and filtered to remove a white solid. This procedure was repeated twice to achieve separation of the product from the foregoing salts. Ether (~150 mL) was layered upon the DMF filtrate, and the mixture was cooled to -20 °C. The crude product was obtained as 1.1 g of black crystalline solid. A second crop was obtained from the filtrate. The combined crops (2.1 g) were recrystallized from DMF/ether, collected by filtration, washed with ether, and dried in vacuo to afford 1.6 g (40%) of pure product as a black crystalline solid. Anal. Calcd for $\text{C}_{54}\text{H}_{62}\text{Fe}_3\text{N}_3\text{O}_3\text{PS}_3\text{V}$: C, 50.87; H, 4.90; Fe, 13.14; N, 3.31; P, 2.43; S, 17.60; V, 4.00. Found: C, 50.66; H, 5.00; Fe, 12.96; N, 3.40; P, 2.37; S, 17.48; V, 4.08. Absorption spectrum (DMF): λ_{max} (ϵ_M , $\text{M}^{-1}\text{cm}^{-1}$) 433 (15 600), 360 (sh, 17 000), 263 (sh, 51 300) nm. Best results were obtained when the product cluster was isolated from the reaction mixture in times not exceeding 5 h.

(Me₄N)[VFe₃S₄Cl₃(bpy)(DMF)]·3DMF (3). A solution of 0.30 g (1.9 mmol) of 2,2'-bipyridyl in 20 mL of DMF was added dropwise to a stirred solution of 1.7 g (1.9 mmol) of **1** in 100 mL of DMF. An immediate color change from dark brown to purple-black ensued. After being stirred for ~20 h, the reaction mixture was filtered to remove an insoluble black solid. Ether (40 mL) was layered upon the purple-black filtrate, and the mixture was cooled to -20 °C. The crude product (1.2 g) was obtained as a purple microcrystalline solid. Recrystallization of this material from 2:1 v/v DMF/ether afforded 0.80 g (43%) of pure product as a purple microcrystalline product. Anal. Calcd for $\text{C}_{26}\text{H}_{48}\text{Cl}_3\text{Fe}_3\text{N}_7\text{O}_4\text{S}_4\text{V}$: C, 32.00; H, 4.96; Cl, 10.90; Fe, 17.17; N, 10.09; S, 13.14; V, 5.22. Found: C, 31.88; H, 5.10; Cl, 10.76; Fe, 16.99; N, 9.93; S, 13.06; V, 5.33. Absorption spectrum (DMF): λ_{max} (ϵ_M , $\text{M}^{-1}\text{cm}^{-1}$) 509 (2900), 360 (sh, 5200), 299 (19 700) nm. Exposure of a DMF solution of the compound to dioxygen induces a rapid color change from purple-black to bright red.

(n-Pr₄N)[VFe₃S₄Cl₃(dmpe)(MeCN)]·3MeCN (4). Dmpe (360 μL , 2.2 mmol) was added dropwise to a slurry of 2.0 g (2.2 mmol) of **1** in 100 mL of acetonitrile. After 30 min of stirring, 0.64 g (2.4 mmol) of *n*-Pr₄NBr was added to the yellow-brown homogeneous reaction mixture. After being stirred overnight, the mixture was filtered to remove Me_4NBr and cooled to -20 °C to achieve further separation of this salt from the product. After filtration, reduction of the filtrate volume to ~60 mL followed by the addition of 30 mL of ether and cooling to -20 °C afforded the crude product (1.6 g) as a black crystalline solid. This material was recrystallized twice from 2:1 v/v MeCN/ether, collected by filtration, and washed with ether to give 1.0 g (48%) of pure product as a black crystalline product. The ¹H NMR spectrum was consistent with a trisolvate formulation. The compound readily loses its solvate molecules and was dried (25 °C, 12 h) prior to analysis. Anal. Calcd for $\text{C}_{20}\text{H}_{47}\text{Cl}_3\text{Fe}_3\text{N}_3\text{P}_2\text{S}_4\text{V}$: C, 28.91; H, 5.70; Cl, 12.80; Fe, 20.17; N, 3.39; P, 7.46; S, 15.44; V, 6.13. Found: C, 28.79; H, 5.80; Cl, 12.67; Fe, 20.26; N, 3.42; P, 7.38; S, 15.34; V, 6.37. Absorption spectrum (MeCN): λ_{max} (ϵ_M , $\text{M}^{-1}\text{cm}^{-1}$) 530 (sh, 1400), 450 (sh, 2300), 370 (sh, 4500) nm.

(Me₄N)₂(Et₄N)₂[V₂Fe₆S₈Cl₄(C₂H₅S₂)₂] (5). A slurry of 1.8 g (2.0 mmol) of **1** in 200 mL of acetonitrile was treated with 0.28 g (2.0 mmol) of Na_2ed and 0.67 g (4.0 mmol) of Et_4NCl , after which the mixture became homogeneous. When the mixture was stirred for ~15 min, the solution color changed from dark brown to green-brown, and the product began to separate as a black microcrystalline solid. This material was collected by filtration from the reaction mixture after stirring for 16 h, washed with 3 × 50 mL of 1:1 v/v MeCN/ether, and dried in vacuo to afford 1.3 g of black microcrystalline product. The crude product was dissolved in 150 mL of 4:1 (v/v) DMF/MeCN, and the solution was filtered to remove a black insoluble solid. Layering of ether upon the green-brown filtrate, followed by cooling to -20 °C, gave 0.61 g (42%) of pure product as a black microcrystalline product. The ¹H NMR spectrum indicated that the product is an acetonitrile disolvate. The compound readily loses its solvate molecules and was dried (25 °C, 5 h) prior to analysis. Anal. Calcd for $\text{C}_{28}\text{H}_{72}\text{Cl}_4\text{Fe}_6\text{N}_4\text{S}_{12}\text{V}_2$: C, 23.54; H, 5.08; Cl, 9.93; Fe, 23.46; N, 3.94; S, 26.93; V, 7.13. Found: C, 23.66; H, 4.98; Cl, 9.92; Fe, 23.55; N, 4.06; S, 26.95; V, 7.08. Absorption spectrum (DMF): essentially featureless with a gradual rise from 800 to 250 nm.

Collection and Reduction of X-ray Data. Single crystals of compound **5** as the disolvate were obtained by diffusion of ether vapor into a 4:1 v/v DMF/MeCN solution. Because this compound desolvates readily and converts to an amorphous solid, crystals were removed from the mother liquor with a glass fiber probe, immediately immersed in epoxy, and quickly transferred to a capillary tube. The latter was flame-sealed under a dinitrogen atmosphere. Data were collected at ~25 °C with use of a Nicolet P3F four-circle automated diffractometer equipped with a Mo X-ray tube and a graphite monochromator. Data collection parameters are summarized in Table I. The final orientation matrix and unit cell parameters were obtained from the least-squares refinement of 25 machine-centered reflections with $17^\circ \leq 2\theta \leq 25^\circ$. Selected ω scans were

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Table I. Summary of Crystal Data, Intensity Collection, and Structure Refinement Parameters for $(\text{NMe}_4)_2(\text{NEt}_4)_2[\text{V}_2\text{Fe}_6\text{S}_8\text{Cl}_4(\text{edt})_2] \cdot 2\text{MeCN}$

formula	$\text{C}_{32}\text{H}_{78}\text{Cl}_4\text{Fe}_6\text{V}_2\text{N}_6\text{S}_{12}$
M_r	1510.87
a , Å	11.536 (5)
b , Å	14.903 (8)
c , Å	20.284 (8)
β , deg	90.24 (4)
cryst syst	monoclinic
V , Å ³	3487 (3)
Z	2
d_{calcd} , g/cm ³	1.36
d_{obsd} , g/cm ³	a
space group	$P2_1/c$
cryst dimens, mm	$0.50 \times 0.40 \times 0.30$
radiation	$\text{Mo K}\alpha_1$ ($\lambda = 0.71069$ Å)
abs coeff μ , cm ⁻¹	19.80
transmission factors (max/min)	0.94/0.62
scan speed, deg/min	3.00–29.3 (ω scan)
scan range, deg	$2.00 + (2\theta_{\text{K}\alpha_1} - 2\theta_{\text{K}\alpha_2})$
bkgd/scan time ratio	0.25
data colld, deg	3–40 ($+h, +k, \pm l$)
total no. of reflns	3985
R_{merge} , %	2.71
no. of unique data ($F_o^2 > 3.0\sigma F_o^2$)	1996
no. of variables	206
R , %	6.31
R_w , %	8.33 ^c

^a Accurate density could not be obtained owing to apparent loss of MeCN solvate molecules. ^b R_{merge} is defined by $R_{\text{merge}} = [(\sum N_i \sum_{j=1}^{N_i} (F_j - F_i)^2) / (\sum (N_i - 1) \sum_{j=1}^{N_i} F_j^2)]^{1/2}$, where N_i is the number of reflections in a given set, F_j is one member of the set, and F_i is the mean. ^c $R = [\sum (|F_o| - |F_c|) / \sum |F_o|]$. ^d $R_w = [\sum w(|F_o|^2 - |F_c|^2) / \sum w|F_o|^2]^{1/2}$. ^e Weighting scheme for least-squares refinement: Carruthers, J. R.; Watkin, D. J. *Acta Crystallogr., Sect. A: Cryst. Phys., Diff., Theor. Gen. Crystallogr.* **1979**, *A35*, 698.

symmetrical with half-widths of 0.5–0.8°. These somewhat broad peak profiles are indicative of appreciable mosaic spread, which is presumably a consequence of partial solvate loss. All crystals, whether mounted under mother liquor or epoxy, displayed similar peak profiles. Three standard reflections monitored after every 63 observations showed no signs of decay over the course of data collection. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied with use of the programs XTAPE and XEMP of the SHELXTL structure determination package.²³ Intensity data were also corrected for secondary extinction. Machine parameters used in the intensity collection and crystal data are collected in Table I. The systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$) uniquely identify the space group as $P2_1/c$.

Structure Solution and Refinement. The direct-methods program MULTAN was used to locate the heavy atoms. Trial positions of the V, Fe, and core S atoms were taken from the E map derived from the phase set with the highest combined figures of merit. The program CRYSTALS was employed in structure refinement. The remaining nonhydrogen atoms were located by Fourier refinement with a few intervening cycles of least-squares refinement. Atom scattering factors were taken from tabulated values.²⁴ Isotropic refinement converged at $R = 16.8\%$. The cluster anion was well-behaved and was anisotropically refined by using blocked least-squares treatment. The asymmetric unit consists of one-half of the anion, two cations, and one MeCN solvate molecule. The remaining atoms are generated by inversion symmetry. Both the Me_4N^+ cation and the MeCN solvate molecule are disordered, and no suitable model for the disorder was found. The methyl carbon atoms of the Et_3N^+ cation are moderately disordered. The geometry of the solvate molecule is very irregular and could not be corrected by application of observational constraints to bond lengths and angle. All atoms except cation C atoms and those of the solvate molecule were refined anisotropically. In the final stages of the refinement, hydrogen atoms were placed at a H–C distance of 1.0 Å, with isotropic thermal parameters 1.2 times those of bonded carbon atoms. Unique data used in the refinement and final R values are included in Table I. Positional parameters of the anion are listed in Table II.²⁵

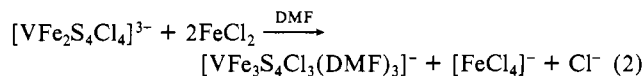
Table II. Positional Parameters ($\times 10^4$) for $[\text{V}_2\text{Fe}_6\text{S}_8\text{Cl}_4(\text{edt})_2]^{4-}$

atom	x/a	y/b	z/c
V(1)	3597 (2)	–991 (2)	9111 (1)
Fe(1)	5368 (2)	–1347 (2)	9977 (1)
Fe(2)	3677 (2)	–2597 (2)	9753 (1)
Fe(3)	5184 (2)	–2245 (2)	8807 (1)
S(2)	5659 (4)	–2830 (3)	9832 (2)
S(4)	3235 (4)	–2412 (4)	8674 (2)
S(3)	5508 (4)	–752 (4)	8931 (2)
Cl(1)	6174 (5)	–2877 (5)	7973 (3)
S(1)	3438 (4)	–1242 (3)	10231 (2)
Cl(2)	2640 (5)	–3722 (4)	10214 (3)
S(11)	6770 (4)	–591 (3)	10569 (2)
C(2)	6875 (16)	–1130 (14)	11360 (9)
C(1)	7788 (17)	–670 (14)	11752 (9)
S(12)	7580 (4)	554 (4)	11766 (2)

Other Physical Measurements. All measurements were performed under strictly anaerobic conditions. ¹H NMR spectra were recorded on a Bruker WM-300 or WM-500 spectrometer with Me_4Si as the internal standard. CD_3CN and $(\text{CD}_3)_2\text{SO}$ were dried by trap-to-trap distillation from CaH_2 under reduced pressure and stored over 3-Å molecular sieves. Magnetic susceptibilities in solution were determined by the NMR method;²⁶ solvent susceptibilities²⁷ and diamagnetic corrections²⁸ 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 ($n\text{-Bu}_4\text{N}$)(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 $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ (1). This cluster is readily assembled at ambient temperature in a DMF reaction system containing the reactant molar ratio $\text{FeCl}_2:\text{[VS}_4]^{3-} = 4:1$. The reactions are summarized in Figure 1, which also includes structural formulas of $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ and other clusters isolated in this work. The cubane-type structures of these species are described in detail separately.¹⁷ Two distinct steps, reactions 1 and 2, have been detected in cluster formation by overall reaction 3. At the concentrations used here, reaction 1 generating the



“linear” cluster $[\text{VFe}_2\text{S}_4\text{Cl}_4]^{3-}$ (**6**: Fe–V–Fe = 172.9 (1)°) is complete within 2 h. This species has been isolated and is readily recognized in solution by its absorption spectrum.¹⁶ The properties of **6** are consistent with the formulation $\text{V(V)} + 2\text{Fe(II)}$. Reaction 2, which requires about 14 h for completion, involves, in effect, a two-electron reduction of V(V) by FeCl_2 , which produces 2 equiv of Fe(III), one of which is incorporated in the cluster. Spectral changes accompanying reaction 2 are given elsewhere.¹⁵

Reduction of tetrahedrally coordinated V(V) in **6** to or near the V(III) level, which is normally stabilized by six-coordination, must induce a structural rearrangement from a linear to a non-linear structure, presumably an incomplete cubane-type core. The product structure is completed by incorporation of a Fe atom and binding of three DMF molecules at the V site. Solvent binding is a significant stability feature inasmuch as the above system in acetonitrile, a generally weaker ligand than DMF, evidences no reaction after 3 days at room temperature. As shown elsewhere,¹⁸ the $[\text{VFe}_3\text{S}_4]^{2+}$ core of **1** is electronically delocalized and V is

(23) Nicolet XRD Corporation, Madison, WI.

(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

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

(26) Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 79.

(27) Gerger, W.; Mayer, U.; Gutmann, V. *Monatsh. Chem.* **1977**, *108*, 417.

(28) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 203.

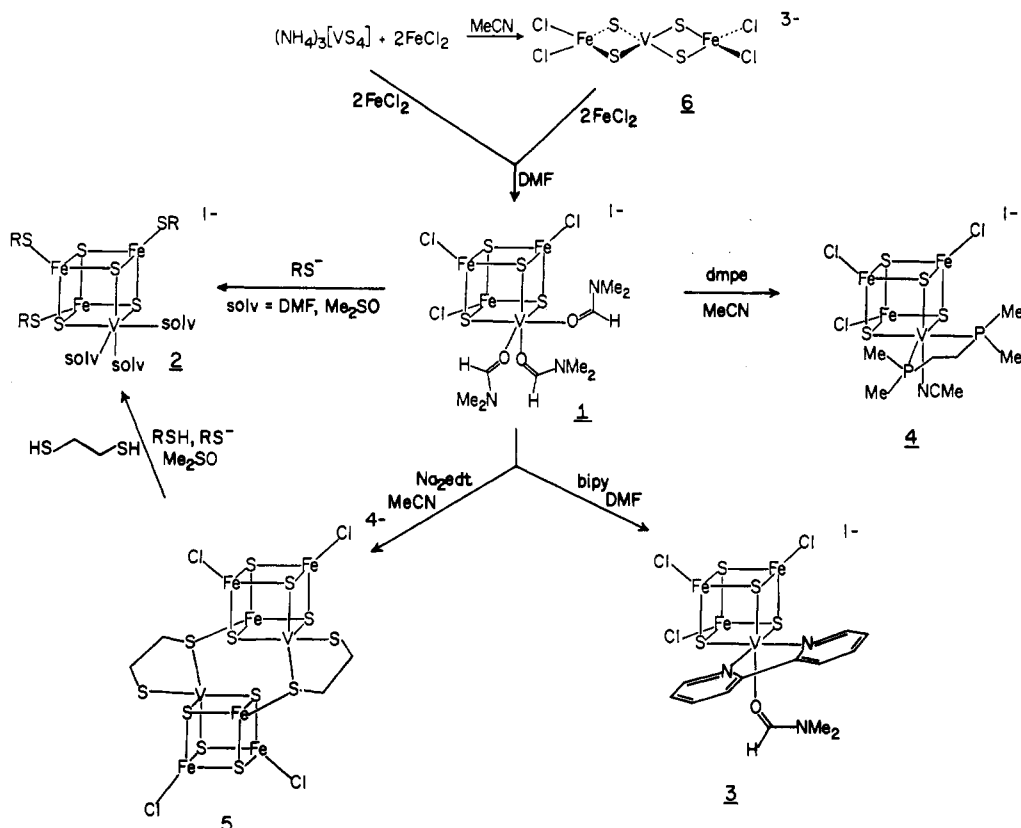


Figure 1. Synthesis of $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ (**1**) from $[\text{VFe}_2\text{S}_4\text{Cl}_4]^{3-}$ (**6**) and the reactions of **1** to afford single cubanes **2–4** and the doubly bridged double cubane **5**. Clusters **1–5** have been isolated; the generation of other cluster species in solution is described in the text.

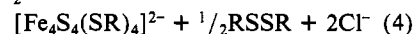
Table III. ^1H NMR Chemical Shifts, Magnetic Moments, and Redox Potentials at $\sim 297\text{ K}$

cluster ^a	solvent	μ, μ_B	^1H NMR chem shifts, ^c ppm	$E_{1/2}$, ^b V
$[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ (1)	DMF			-0.02 (ox) [-1.38 (red)]
$[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{MeCN})_3]^-$	MeCN	4.18		+0.12 (ox) [-1.15 (red)]
$[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{solV})_2(\text{PEt}_3)]^-$	MeCN		12.3 (CH_2), 2.9 (Me)	
$[\text{VFe}_3\text{S}_4\text{Cl}_2(\text{SR})(\text{Me}_2\text{SO})_3]^-$	Me_2SO		5.56 (<i>p</i> -Me)	
$[\text{VFe}_3\text{S}_4\text{Cl}(\text{SR})_2(\text{Me}_2\text{SO})_3]^-$	Me_2SO		10.3 (meta H), 7.60 (<i>p</i> -Me)	
$[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{Me}_2\text{SO})_3]^-$ (2)	Me_2SO	4.11	12.9 (meta H), 11.6 (<i>p</i> -Me)	
$[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{DMF})_3]^-$ (2)	DMF			-0.31 (ox), -1.35 ^d (red)
$[\text{VFe}_3\text{S}_4(\text{OR})_3(\text{Me}_2\text{SO})_3]^-$	Me_2SO		15.9 (meta H), 13.4 (<i>p</i> -Me)	
$[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{bpy})(\text{DMF})]^-$ (3)	DMF	4.16	15.7 (4,4'), 10.5 (3,3'), 5.93 (5,5')	[+0.38 (ox)]; -1.20 ^d , -1.41 ^d (red)
$[\text{VFe}_3\text{S}_4\text{Cl}_3(4,4'\text{-Me}_2\text{bpy})(\text{DMF})]^-$	DMF		10.4 (3,3'), 5.66 (5,5'), -3.96 (4,4')	
$[\text{VFe}_3\text{S}_4\text{Cl}_3(5,5'\text{-Me}_2\text{bpy})(\text{DMF})]^-$	DMF		15.4 (4,4'), 10.5 (3,3'), 4.04 (5,5')	
$[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{MeCN})]^-$ (4)	MeCN	4.25	13.2 (Me), 11.8 (CH), 6.91 (CH)	+0.03 (ox) [-1.28 (red)]
$[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{Me}_2\text{SO})]^-$	Me_2SO		15.6 (CH), 11.6 (Me), 10.6 (CH)	
$[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{edt})]^{3-}$ (14)	Me_2SO		20.2 (CH_2), 12.3 (meta H), 10.6 (<i>p</i> -Me)	
$[\text{V}_2\text{Fe}_6\text{S}_8\text{Cl}_4(\text{edt})_2]^{4-}$ (5)	DMF		30.6 (CH_2), -6.9 (CH_2)	[-0.28, -0.13 (ox)]
	Me_2SO		30.3 (CH_2), -8.3 (CH_2)	
$[\text{MoFe}_3\text{S}_4(\text{SR})_3(\text{al}_2\text{cat})(\text{Me}_2\text{SO})]^{2-f}$ (12)	Me_2SO	4.09 ^e	12.9 (meta H), 11.9 (<i>p</i> -Me)	-1.17 (red)
$[\text{MoFe}_3\text{S}_4\text{Cl}_4(\text{dmpe})]^{-g}$ (8)	MeCN	4.12	11.8 (Me), 10.7 (CH), 8.54 (Me), 6.84 (CH)	-0.71 (red)

^a R = *p*-C₆H₄Me. ^b Values vs. SCE; potentials in brackets are E_{pc} or E_{pa} values for irreversible processes. ^c Ortho hydrogen resonances are usually shifted upfield of 0 ppm and are broad. ^d Quasi-reversible. ^e R = Ph. ^f Reference 2. ^g Reference 7.

reduced below the V(IV) level. This synthesis expands the types of heterometal MFe_3S_4 cubane clusters to those with $\text{M} = \text{V}, \text{Mo}$, and W . Further, the cores of the latter two types, $[\text{MFe}_3\text{S}_4]^{3+}$, are isoelectronic with $[\text{VFe}_3\text{S}_4]^{2+}$. Like **1**, the Mo and W clusters are also formed by an assembly process involving simple reactants.^{8,9} These usually include $[\text{MS}_4]^{2-}$, FeCl_3 , and thiolate in alcohol solvents, which constitute a redox-buffered system that without exception yields clusters with the $[\text{MFe}_3\text{S}_4]^{3+}$ core. Evidently, these 51e cores represent a stability plateau with early transition metals as the heteroatom²⁹ and weak field terminal ligands.

The prior reaction most closely related to the synthesis of $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ is reaction 4 (R = Et), by which the linear $[\text{Fe}_3\text{S}_4(\text{SR})_4]^{3-} + \text{FeCl}_2 + \text{RS}^- \rightarrow$



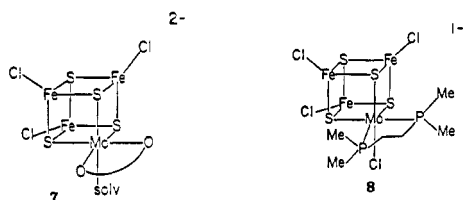
trinuclear cluster ($\text{Fe}-\text{Fe}-\text{Fe} = 172.9$ (1)^o) is converted to a cubane cluster.³⁰ The clusters mentioned at the outset do not appear to be derived from linear precursors. $[\text{FeMo}_3\text{S}_4(\text{NH}_3)_9(\text{H}_2\text{O})]^{4+}$ is formed by the incorporation of a Fe atom into a cubane fragment.¹⁴ An analogous process is likely to be responsible for the formation of the protein CoFe_3S_4 cluster¹³ and for reconstitution of Fe_4S_4 clusters in aconitase³¹ and *D. gigas* ferredoxin

(29) Preparation of analogous $\text{M} = \text{Nb}$ and Ta clusters may be less straightforward owing to the greater resistance to reduction of the M(V) state and the absence of the simple thiometalates $[\text{MS}_4]^{2-}$: Sola, J.; Do, Y.; Berg, J. M.; Holm, R. H. *Inorg. Chem.* **1985**, *24*, 1706.

(30) Hagen, K. S.; Watson, A. D.; Holm, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 3905.

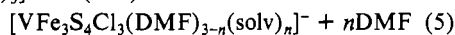
II.³² All evidence, including protein crystallography,³³ indicates that the precursor Fe_3S_4 clusters do not have a linear structure.

Reactions of $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$. On the basis of reactivity properties of isoelectronic MoFe_3S_4 single cubanes^{1-4,6,7} such as 7 and 8 and of $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$,³⁴ cluster 1 should exhibit substitutional



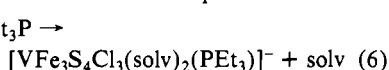
lability at all metal sites. This matter has been investigated with use of ligands that do not cause core degradation at a rate competitive with ligand substitution. The reactions leading to clusters 2-5 are presented in Figure 1. Solution properties of these and other clusters are collected in Table III. An immediate difference between 1 and 7 is the presence of three labile sites at the V atom vs. one such site at the Mo atom. The bidentate ligands (catecholate, dmpe) arise in 7 and 8 as a consequence of their use in bridge cleavage of the double cubane precursors.^{2,7-9} No MoFe_3S_4 single cubanes containing three monodentate ligands at the Mo site have yet been prepared.

(a) Solvolysis. When 1 is placed in acetonitrile solution, one set of concentration-dependent isotropically shifted DMF resonances are observed. For example, at $[\mathbf{1}] = 37 \text{ mM}$, signals occur at 2.38, 2.44, and 7.42 ppm. Addition of DMF causes these signals to be shifted toward the free DMF chemical shifts of 2.72, 2.88, and 7.93 ppm. These observations are indicative of the fast exchange equilibria 5 ($n = 1-3$, solv = MeCN). In this solvent



the cluster species has $\mu = 4.18 \mu_B$, consistent with the $S = 3/2$ ground state of 7, 8, and related clusters.^{5,18} With solv = Me_2SO , reaction 5 goes to completion ($n = 3$). The product cluster $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{Me}_2\text{SO})_3]^-$ very slowly converts to $[\text{VFe}_2\text{S}_4\text{Cl}_4]^{3-}$ in Me_2SO solution. No such reaction was observed in DMF or acetonitrile solution. The order of binding affinity at the V site is $\text{MeCN} < \text{DMF} \leq \text{Me}_2\text{SO}$.

(b) Reaction with Triethylphosphine. An acetonitrile solution of 1 and 1 equiv of Et_3P develops broad, isotropically shifted signals at 12.3 and 2.9 (partially obscured) ppm, indicative of phosphine binding. The product of reaction 6 is interpreted in terms of



binding at the V site inasmuch as only exchange broadening was observed with additional phosphine. Bound Et_3P , with its cone angle of 132° ,³⁵ likely provides a steric barrier to further phosphine binding in competition with DMF and solvent. No reaction between the cluster and up to 30 equiv of Et_3P was observed in Me_2SO solution.

(c) Reaction with Thiolate. Reactions were investigated with NaSR ($\text{R} = p\text{-C}_6\text{H}_4\text{Me}$) because the isotropically shifted meta hydrogen and $p\text{-Me}$ signals facilitate monitoring by ^1H NMR. The reaction of $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{Me}_2\text{SO})_3]^-$ with 1.5-3.0 equiv of thiolate in Me_2SO solution is shown in Figure 2. The stepwise substitution processes 7 (solv = Me_2SO) are clearly evident,

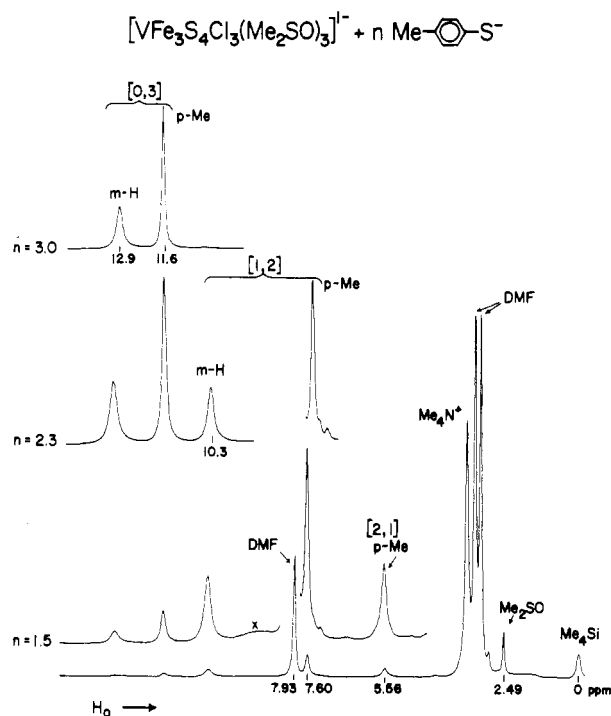
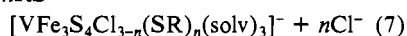


Figure 2. ^1H NMR spectra for reactions of $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{Me}_2\text{SO})_3]^-$ (formed from 1) with $n = 1.5-3.0$ equiv of $\text{NaS-}p\text{-C}_6\text{H}_4\text{Me}$ in $\text{Me}_2\text{SO-}d_6$ solutions at 297 K. Signal assignments are indicated. Ortho hydrogen resonances (not shown) occur upfield and are broad; that of the [0,3] cluster is at -2.3 ppm.

particularly with the $p\text{-Me}$ signals whose intensities indicate roughly statistical formation of the species $[3-n, n]$ and which progressively shift downfield as n increases.³⁶ Isotropic shifts of the final product 2 (solv = Me_2SO) are closely comparable to those of the clusters $[\text{MoFe}_3\text{S}_4(\text{SR})_3(\text{cat})(\text{solv})]^{2-}$.² Quaternary cation salts of $[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{Me}_2\text{SO})_3]^-$ proved too soluble to isolate from Me_2SO . However, when reaction 7 with $n = 3$ equiv was carried out in DMF solution, the Ph_4P^+ salt of cluster 2 (solv = DMF) was readily isolated as black crystals. Reaction 7 in acetonitrile does not proceed cleanly; NMR spectra indicate breakdown of the VFe_3S_4 core and substantial formation of $[\text{Fe}(\text{SR})_4]^{2-}$ and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$.

The structure of $[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{DMF})_3]^-$ has not been determined by X-ray analysis. However, the following properties constitute a structure proof of 2: (i) in Me_2SO solution 3 equiv of DMF are released (NMR integration) in solvolysis reaction 5; (ii) $\mu = 4.11 \mu_B$ in Me_2SO solution, indicating that the core structure of 1 ($4.18 \mu_B$) has been maintained; (iii) the intense visible band at 433 nm, shown in Figure 3, has LMCT counterparts in the spectra of isoelectronic, Fe-SR substituted MoFe_3S_4 clusters of proven cubane-type structures,^{2,3,6,7} while chloro-ligated clusters lack this feature;^{4,7} (iv) meta hydrogen and $p\text{-Me}$ isotropic shifts are very similar to those of isoelectronic MoFe_3S_4 clusters of known structure.¹⁻³

Reaction 7 with $n > 3$ equiv of RS^- results in destruction of the core as opposed to formation of a stable cluster with thiolate ligands at the V site. The principal product is $[\text{Fe}(\text{SR})_4]^{2-}$, identified by its characteristic resonances at 34.3 ($p\text{-Me}$) and 22.5 (meta H) ppm. The fate of V upon cluster degradation was not determined; no V-containing species were observable by NMR. There was no evidence of reaction between 2 (solv = Me_2SO) and up to 30 equiv of Et_3P . $(\text{Et}_4\text{N})(\text{CN})$ (1 equiv) and this cluster liberated thiolate and formed an insoluble black precipitate.

- (31) (a) Kent, T. A.; Dreyer, J.-L.; Kennedy, M. C.; Huynh, B. H.; Emptage, M. H.; Beinert, H.; Münck, E. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 1096. (b) Kennedy, M. C.; Emptage, M. H.; Dreyer, J.-L.; Beinert, H. *J. Biol. Chem.* **1983**, *258*, 11098.
- (32) Moura, J. J. G.; Moura, I.; Kent, T. A.; Lipscomb, J. D.; Huynh, B. H.; LeGall, J.; Xavier, A. V.; Münck, E. *J. Biol. Chem.* **1982**, *257*, 6259.
- (33) Robbins, A. H.; Stout, C. D. *J. Biol. Chem.* **1985**, *260*, 2328.
- (34) Wong, G. B.; Bobrik, M. A.; Holm, R. H. *Inorg. Chem.* **1978**, *17*, 578.
- (35) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

- (36) The meta hydrogen resonance of [2,1] was not detected and may be obscured by signals at 7.6-7.9 ppm or contained in the broad feature \times (Figure 2).

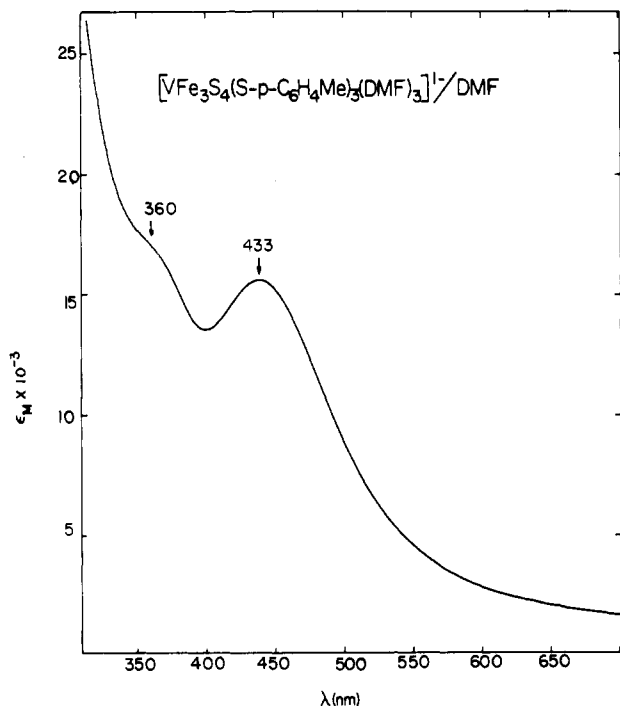
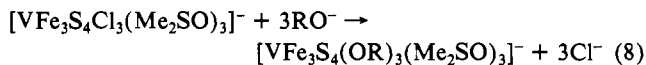


Figure 3. Absorption spectrum of $[\text{VFe}_3\text{S}_4(\text{S-}p\text{-C}_6\text{H}_4\text{Me})_3(\text{DMF})_3]^{1-}$ (**2**) in DMF solution.

(d) **Reaction with Cresolate.** Reaction 8 ($\text{R} = p\text{-C}_6\text{H}_4\text{Me}$) proceeds readily to afford an Fe-substituted cluster, so identified by its meta hydrogen and $p\text{-Me}$ shifts, which are somewhat larger



but occur in the same order as those of **2**. The isotropic shifts $[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{Me}_2\text{SO})_3]^-$: -5.80 (meta H), -9.36 ($p\text{-Me}$) ppm

$[\text{VFe}_3\text{S}_4(\text{OR})_3(\text{Me}_2\text{SO})_3]^-$: -9.27 (meta H), -11.3 ($p\text{-Me}$) ppm

are consistent with ligand \rightarrow core antiparallel spin transfer and dominant contact interactions. Among cluster species, similar behavior was originally observed for $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ ³⁷ and later for $[\text{Fe}_4\text{S}_4(\text{OR})_4]^{2-}$,³⁸ whose isotropic shifts are also larger than those of the analogous $p\text{-toluenethiolate}$ cluster. No further reaction occurred with >3 equiv of NaOR.

(e) **Reaction with 2,2'-Bipyridyl.** Reaction 9 with 1 equiv of bpy proceeds smoothly in DMF to afford product cluster **3**, which



has been isolated as its Me_4N^+ salt trisolvate in 43% purified yield. The indicated structure, in which bpy and DMF are coordinated at the V site, has been established by X-ray analysis.¹⁷ In solution, **3** is paramagnetic ($4.16 \mu_B$) and exhibits isotropically shifted proton resonances that were assigned by comparison with the 4,4'- and 5,5'- Me_2 bpy clusters generated in solution. NMR spectra are shown in Figure 4; the 6,6'-protons are apparently severely broadened by paramagnetic relaxation and were not detected.

(f) **Reaction with dmpe.** Reaction 10 in acetonitrile is analogous to reaction 9 and gives $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{MeCN})]^-$ (**4**), whose

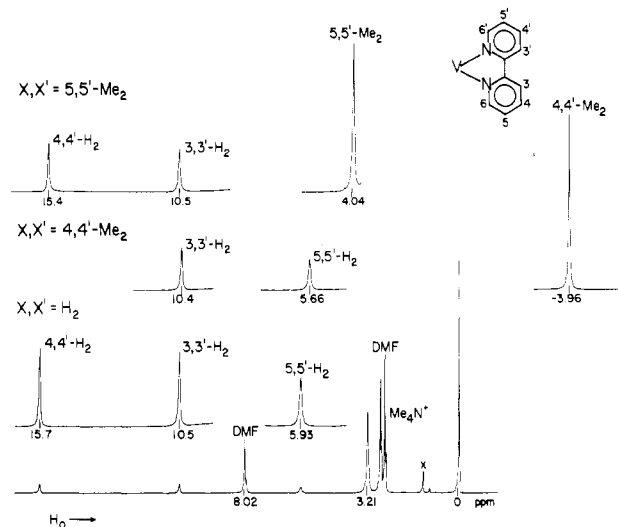
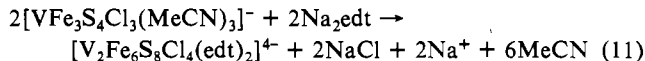


Figure 4. ^1H NMR spectra of $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{X},\text{X}'\text{-bpy})(\text{DMF})]^{1-}$ ($\text{X},\text{X}' = \text{H}_2$ (**3**), 4,4'- Me_2 , 5,5'- Me_2) in $\text{DMF-}d_7$ solutions at 297 K. Signal assignments and the bpy numbering scheme are indicated.

structure has been proven by an X-ray determination.¹⁷ The cluster was obtained in 48% purified yield as its trisolvate $n\text{-Pr}_4\text{N}^+$ salt. As for related clusters, the solution magnetic moment of **4** ($4.25 \mu_B$) is indicative of a $S = 3/2$ ground state. In Me_2SO solution, acetonitrile is displaced from the V site forming $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{Me}_2\text{SO})]^-$, whose dmpe proton shifts are rather different from those in acetonitrile (Table III). In both solvents the NMR spectra consist of two methylene and one methyl signal. Assignments were proven by examination of the cluster prepared from $(\text{CD}_3)_2\text{PCH}_2\text{CH}_2\text{P}(\text{CD}_3)_2$.⁷ The dmpe chelate ring in the solid state is in the "asymmetric" skew ("half-chair") conformation, in which all methylene protons and methyl groups are inequivalent. Rapid interchange between the enantiomeric skew forms would average pairs of methylene protons and methyl groups. This is apparently the case for cluster **8**, which exhibits two methylene and two methyl resonances at ambient temperature.⁷ The observed spectral pattern of **4** is, however, inconsistent with this behavior unless it is assumed that the two inequivalent methyl groups have essentially degenerate chemical shifts. The intensity ratio of the signals (ppm, Me_2SO) (11.6 + 10.6):15.6 = 7.2:1 indicates that this is apparently the case. (At 231 K two barely resolved methyl signals near 15.0 and 15.4 ppm are observed.) We are unable to suggest a feasible dynamic process that does not simultaneously equilibrate two methylene protons and two methyl groups.³⁹

In acetonitrile solution, cluster **4** in the presence of ~ 10 equiv of Et_3P exhibits small shifting and sharpening of its signals (12.9, 11.0, 7.16 ppm), implying binding at the V site but less strongly than with **1**. No reaction is observed in Me_2SO solution with 30 equiv of the phosphine. The reaction systems $4/\text{CN}^-$, $4/\text{RS}^-$, and $3/\text{RS}^-$ in Me_2SO show complicated NMR spectra that have not been successfully interpreted and give evidence of cluster degradation. No firm conclusions as to preferred binding sites of these ligands could be drawn.

(g) **Reaction with Ethane-1,2-dithiolate.** We have recently demonstrated that edt binds strongly to all first-transition-series metal ions in common oxidation states by forming tight chelate rings to a common metal center.^{20,40} Here, reaction 11 in ace-



(37) (a) Holm, R. H.; Phillips, W. D.; Averill, B. A.; Mayerle, J. J.; Herskovitz, T. *J. Am. Chem. Soc.* **1974**, *96*, 2109. (b) Reynolds, J. G.; Laskowski, E. J.; Holm, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 5315. $(\Delta H/H_0)_{\text{iso}} = (\Delta H/H_0)_{\text{dia}} - (\Delta H/H_0)_{\text{obsd}}$.

(38) Cleland, W. E.; Holtman, D. A.; Sabat, M.; Ibers, J. A.; DeFotis, G. C.; Averill, B. A. *J. Am. Chem. Soc.* **1983**, *105*, 6021.

(39) Rupture of a V-P bond, rotation about the C-C bond, inversion at the P atom, and reformation of the V-P bond could average methyl groups but not protons of a CH_2 group. However, the inversion barrier (e.g., ~ 30 kcal/mol for Me_3P) is far too high for this mechanism to be operative here; cf.: Baechler, R. D.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *92*, 3090 and references therein. Weston, R. E., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 2645.

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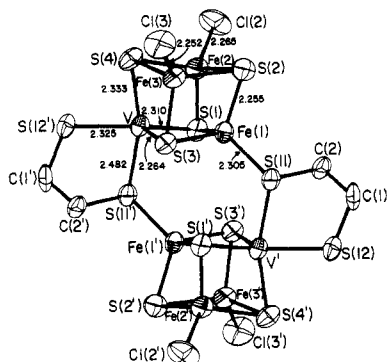
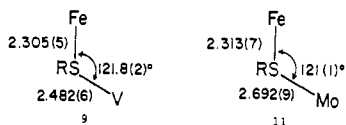


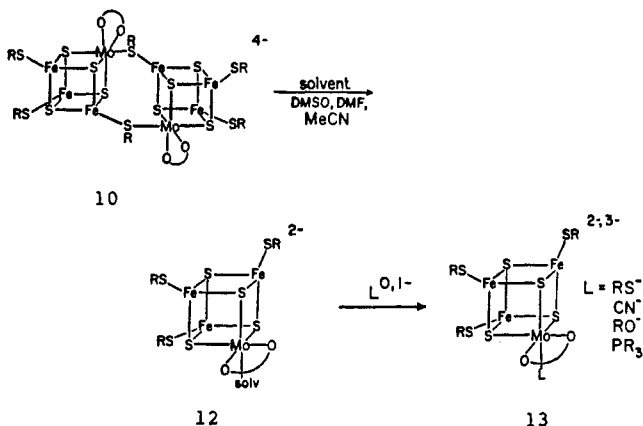
Figure 5. Structure of $[V_2Fe_6S_8Cl_4(edt)_2]^{4-}$ (**5**), showing 50% thermal ellipsoids, labeling scheme, and selected interatomic distances. Primed and unprimed atoms are related by a center of symmetry.

tonitrile proceeded readily to form a cluster whose simple formula, $[VFe_3S_4Cl_2(edt)]^{2-}$, does not conform to an acceptable single-cubane stoichiometry. The cluster was isolated in 42% purified yield as a mixed cation ($Me_4N^+ + Et_4N^+$) salt whose bis(acetonitrile) solvate formed single crystals suitable for X-ray structural analysis. The structure of the cluster is shown in Figure 5; metric parameters are collected in Table IV.

The cluster crystallizes as the doubly bridged double cubane **5**, in which the $VFe_3S_4Cl_2(edt)$ subclusters are connected via the fragment **9**. As such, it finds analogy with a series of Mo double



cubanes of composition $[Mo_2Fe_6S_8(SR)_6(cat)_2]^{4-}$,^{2,6} which have the structure **10** containing the bridge **11**. Because two structures



10 have been discussed in some detail^{2,6} and $[V_2Fe_6S_8Cl_4(edt)_2]^{4-}$ is similar in many aspects, the structure of the latter is briefly summarized.

(i) The double cubane has imposed centrosymmetry, such that the anion consists of two identical $VFe_3S_4Cl_2(edt)$ subclusters and bridges **9**. (ii) The $[VFe_3S_4]^{2+}$ cores have the cubane-type stereochemistry with angles and distances similar to those of the single cubanes **1**, **3**, and **4**, whose structures are reported in full elsewhere.¹⁷ The principal deviation from distance regularities is the $Fe(2)\cdots Fe(3)$ separation of 2.647 (4) Å, the shortest such distance in any MFe_3S_4 cubane, for which the usual values are ≥ 2.69 Å.⁸ Approximately tetrahedral coordination at $Fe(2,3)$ is completed by terminal chloride ligands. (iii) The VS_5 coordination unit is of irregular stereochemistry and contains three core sulfide atoms and bridging and terminal thiolate sulfur atoms from the same edt ligand. The $V-S(1-3)$ core distances average to 2.30 (4) Å compared to 2.178 (5) Å in **6**,¹⁶ a clear indication of reduction of $V(V)$ in the latter. The bridging $V-S(11')$ bond is 0.16 Å longer than the terminal $V-S(12')$ distance whose value (2.325

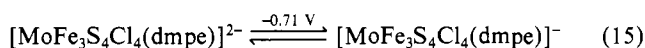
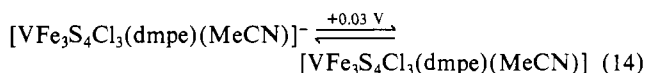
Table IV. Selected Interatomic Distances (Å) and Angles (deg) for $[V_2Fe_6S_8Cl_4(edt)_2]^{4-}$

$VFe_3S_4Cl_2(edt)$ Subcluster	
V-S(1)	2.310 (5)
V-S(3)	2.264 (5)
V-S(4)	2.333 (6)
V-S(12')	2.325 (6)
V...Fe(1)	2.742 (4)
V...Fe(2)	2.727 (4)
V...Fe(3)	2.691 (4)
Fe(1)...Fe(2)	2.734 (4)
Fe(1)...Fe(3)	2.732 (4)
Fe(2)...Fe(3)	2.647 (4)
S(12')-V-S(1)	138.5 (2)
S(12')-V-S(3)	113.5 (2)
S(1)-V-S(3)	105.3 (2)
S(12')-V-S(4)	82.0 (2)
S(1)-V-S(4)	102.2 (2)
S(3)-V-S(4)	104.7 (2)
S(1)-Fe(1)-S(3)	104.6 (2)
S(1)-Fe(1)-S(2)	104.0 (2)
S(3)-Fe(1)-S(2)	104.2 (2)
S(1)-Fe(2)-S(2)	103.1 (2)
S(3)-Fe(3)-S(2)	103.4 (2)
S(1)-Fe(2)-S(4)	106.2 (2)
S(3)-Fe(3)-S(4)	106.4 (2)
S(2)-Fe(2)-S(4)	107.7 (2)
S(2)-Fe(3)-S(4)	107.2 (2)
Cl(2)-Fe(2)-S(2)	112.5 (2)
Cl(3)-Fe(3)-S(2)	113.5 (2)
Cl(2)-Fe(2)-S(4)	111.9 (2)
Cl(3)-Fe(3)-S(4)	111.6 (2)
Cl(2)-Fe(2)-S(1)	114.8 (2)
Cl(3)-Fe(3)-S(3)	114.2 (2)
Fe(1)-S(1)	2.292 (5)
Fe(1)-S(3)	2.306 (5)
Fe(2)-S(1)	2.257 (6)
Fe(3)-S(3)	2.270 (6)
Fe(3)-S(4)	2.278 (5)
Fe(2)-S(2)	2.317 (5)
Fe(3)-S(2)	2.318 (6)
Fe(1)-S(2)	2.255 (6)
Fe(2)-S(4)	2.263 (6)
Fe(2)-Cl(2)	2.265 (6)
Fe(3)-Cl(3)	2.252 (6)
C(1)-C(2)	1.486 (25)
C(1)-S(12)	1.839 (21)
V-S(1)-Fe(1)	73.1 (2)
V-S(3)-Fe(1)	73.7 (2)
V-S(4)-Fe(3)	71.4 (2)
V-S(4)-Fe(2)	72.8 (2)
V-S(1)-Fe(2)	73.3 (2)
V-S(3)-Fe(3)	72.8 (2)
Fe(1)-S(2)-Fe(2)	73.4 (2)
Fe(1)-S(2)-Fe(3)	73.4 (2)
Fe(1)-S(1)-Fe(2)	73.9 (2)
Fe(1)-S(1)-Fe(3)	73.3 (2)
Fe(2)-S(2)-Fe(3)	69.7 (2)
Fe(2)-S(4)-Fe(3)	71.3 (2)
V'-S(12)-C(1)	110.0 (6)
S(12)-C(1)-C(2)	112.0 (4)
V-(edt)-Fe Bridge	
V-S(11')	2.482 (6)
Fe(1)-S(11)	2.305 (5)
V...V'	5.668 (6)
V...Fe(1')	4.119 (4)
V...S(1')	4.952 (6)
V...S(3')	4.853 (5)
S(11')-V-S(12')	80.5 (2)
S(11')-V-S(1)	83.2 (2)
S(11')-V-S(3)	93.5 (2)
S(11')-V-S(4)	161.6 (2)
S(11')...S(11)	5.003 (9)
S(11')...S(12')	3.108 (7)
S(11')-C(2')	1.798 (18)
V-S(11')-Fe(1')	121.8 (2)
V'-S(11')-C(2')	101.6 (7)
V...V'	5.668 (6)
V...Fe(1')	4.119 (4)
V...S(1')	4.952 (6)
V...S(3')	4.853 (5)
Fe(1)...Fe(1')	4.105 (5)
Fe(1)...S(1')	4.120 (6)
Fe(1)...S(3')	3.966 (6)
S(11)-Fe(1)-S(1)	122.0 (3)
S(11)-Fe(1)-S(3)	103.8 (2)
S(11)-Fe(1)-S(2)	116.3 (2)
S(11')-C(2')-C(1')	108.4 (14)

(6) Å) is somewhat shorter than terminal $V(III,IV)-S$ distances in other edt complexes (2.36–2.39 Å^{41,42}). (iv) $S\cdots S$ distances in the VS_5 unit between one of the edt $S(11,12)$ and one of the core atoms $S(1',3',4')$ fall in the range 3.06–3.49 Å. This is less than twice the van der Waals radius of $S(0)$ (1.85 Å⁴³), indicating that size and charge repulsion effects disfavor a sixth (anionic) sulfur ligand and, likely, any sixth ligand (*vide infra*). (v) The two bridge units **9** are parallel and nearly coplanar, and atom positional deviations from the unweighted least-squares plane of both are ≤ 0.15 Å. (vi) The distance of 3.637 (6) Å between $S(1')$ and $S(3)$ is the closest distance of approach between subclusters. (vii) Bridge units **9** and **11** have nearly identical angles and Fe-S distances. The difference of 0.21 Å between V-S and Mo-S

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to prepare isoelectronic V and Mo clusters with the same set of ligands. The negative potential shifts for thiolate vs. chloride terminal ligands is an entirely usual effect,^{34,45} and reflects the stronger electron-donor characteristic of the former. The closest approach to a meaningful comparative situation is with the redox couples 14 and 15, in which the isolated isoelectronic clusters also



have the same charge. In these couples, **4** is reversibly oxidized at $E_{1/2} = +0.03 \text{ V}$ and irreversibly reduced at $E_{p,c} = -1.28 \text{ V}$ ($i_{p,a} \sim 0$), whereas **8** is reversibly reduced at $E_{1/2} = -0.71 \text{ V}$ and shows several irreversible oxidation peaks beginning at about $+0.4 \text{ V}$.⁷

In redox reactions of clusters containing the $[\text{MoFe}_3\text{S}_4]^{3+,2+}$ cores, the $\sim 0.1 \text{ mm/s}$ change in isomer shift between the two oxidation levels indicates that electron density changes occur mainly at the Fe sites whose mean oxidation state before reduction approaches $\text{Fe}^{2.67+}$.^{5,47} The isomer shift difference between **4** and **8** is much smaller ($\sim 0.03 \text{ mm/s}$) but does suggest that the Fe sites are slightly more reduced in the V than in the Mo cluster. This behavior appears to be general at parity of Fe terminal ligand.¹⁸ On the basis of simple considerations, it would tend to promote reversible oxidation. Oxidation of $[\text{VFe}_3\text{S}_4]^{2+}$ clusters affords $[\text{VFe}_3\text{S}_4]^{3+}$ species in which the Fe mean oxidation state could conceivably approach that in stable, isolable $[\text{MoFe}_3\text{S}_4]^{3+}$ clusters (limiting value $\text{Fe}^{2.67+}$). The latter are reversibly reduced to $[\text{MoFe}_3\text{S}_4]^{2+}$ clusters in which the limiting mean oxidation state ($\text{Fe}^{2.33+}$) may indicate an extent of reduction only somewhat less than that of stable, isolable $[\text{VFe}_3\text{S}_4]^{2+}$ clusters. In short, the Fe mean oxidation levels in the isoelectronic cores $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ appear not to be identical,¹⁸ with the consequence that attempted formation of $[\text{VFe}_3\text{S}_4]^+$ species results in an Fe oxidation level (limiting value Fe^{2+}) that destabilizes the cluster, particularly when a labile ligand like chloride is present.⁴⁸ (Note that thiolate cluster **2** shows a quasi-reversible reduction at -1.35 V .) Cluster **3** does not fit this elementary interpretation. Its oxidation is irreversible and it evidences two quasi-reversible reductions at rather negative potentials. Presumably the electron-accepting ability of bpy stabilizes the reduced species. The cause of the irreversible oxidation is unclear.

Summary

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

(1) $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ (**1**) can be assembled from linear trinuclear ($[\text{VFe}_2\text{S}_4\text{Cl}_4]^{2-}$, **6**) and mononuclear (FeCl_2) reactants in a process that requires reduction of V(V) (by FeCl_2). It is proposed that the reduced intermediate is the fragment $\text{VFe}_2(\mu_3\text{-S})(\mu\text{-S})_3$, which is probably formed in a concerted manner with the incorporation of a Fe atom to complete the cubane-type $[\text{VFe}_3(\mu_3\text{-S})_4]^{2+}$ core. Reductive rearrangement of a linear precursor accompanied by metal atom incorporation is preceded only by reaction 4. While the $\text{M}_3(\mu\text{-S})_3(\mu_3\text{-S})$ topology is now well established (but only with $\text{M} = \text{Mo}^{51,52}$), just one such in-

corporation reaction by these units has been reported.¹⁴ (Indeed, the reverse reactions occur.⁵²) Several probable examples of this reaction in proteins^{13,31} have already been cited.

(2) The synthesis of **1** and its derivatives expands the set of heteronuclear MFe_3S_4 cubane-type clusters to include those with $\text{M} = \text{V}$, Mo , and W . Further, the formation of the isoelectronic cores $[\text{VFe}_3\text{S}_4]^{2+}$, $[\text{MoFe}_3\text{S}_4]^{3+}$, and $[\text{WFe}_3\text{S}_4]^{3+}$ by cluster assembly reactions involving electron transfer indicates a special stability associated with these $51e$, $S = 3/2$ configurations.

(3) Reactions of **1** in pure solvents result in displacements at the V site only, with the order of binding affinities being $\text{MeCN} < \text{DMF} \leq \text{Me}_2\text{SO}$.

(4) Reaction of **1** with ≥ 3 equiv of $p\text{-MeC}_6\text{H}_4\text{S}^-$ and $p\text{-MeC}_6\text{H}_4\text{O}^-$ results in substitution at the Fe sites only and the formation of $[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{solV})_3]^-$ (**2**), which has been isolated, and $[\text{VFe}_3\text{S}_4(\text{OR})_3(\text{solV})_3]^-$ ($\text{solV} = \text{DMF}, \text{Me}_2\text{SO}$), respectively. Both exhibit isotropic shift patterns consistent with dominant contact interactions resulting from ligand \rightarrow core antiparallel spin transfer.

(5) Reaction of **1** with 1 equiv of bpy and dmpe affords the V-substituted clusters $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{bpy})(\text{DMF})]^-$ (**3**) and $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{MeCN})]^-$ (**4**), respectively, which have been isolated.

(6) Reaction of **1** with 1 equiv of Na_2edt in acetonitrile yields the centrosymmetric double cubane $[\text{V}_2\text{Fe}_6\text{S}_8\text{Cl}_4(\text{edt})_2]^{4-}$ (**5**), which has been isolated, whose structure contains two $\text{Fe}(\mu\text{-S})\text{-V}$ bridges (**9**) joining two $\text{VFe}_3\text{S}_4\text{Cl}_2(\text{edt})$ subclusters that contain irregular VS_3 coordination units. Unlike the structurally analogous Mo clusters **10**, **5** remains intact in coordinating solvents. It is readily cleaved by 6 equiv of $p\text{-toluenethiolate}$ to $[\text{VFe}_3\text{S}_4(\text{SR})_3(\text{edt})]^{3-}$ (**14**) and by 4 equiv of $p\text{-toluenethiol}$ to the mixed-ligand species $[\text{VFe}_3\text{S}_4\text{Cl}_n(\text{SR})_{3-n}(\text{Me}_2\text{SO})_3]^-$ ($n = 1, 2$), again illustrating exclusive binding of unidentate thiolate at Fe sites. Thiolate binding at the V site has been observed only in the form of the $\text{V}(\text{edt})$ chelate ring.

(7) Single cubanes **1-4** are redox-active with a more pronounced tendency toward reversible oxidation than reversible reduction, as exemplified by **1**. In comparison, the isoelectronic Mo clusters (**7, 8, 12, 13**) all show reversible reductions but not always reversible oxidations. Differences in Fe mean oxidation level in the isoelectronic cores $[\text{VFe}_3\text{S}_4]^{2+,+}$ and $[\text{MoFe}_3\text{S}_4]^{3+,2+}$ may be responsible for the instability of reduced clusters of the former, especially with a labile ligand such as chloride.

(8) The order of solvent binding affinity of **1** and other V clusters is the same as that of Mo clusters **12, 24**. Exclusive thiolate binding at the Fe sites of **1** parallels the behavior of Mo cluster **7, 4** but the latter will bind an additional thiolate or other ligand at the Mo site to form species such as **8** and **13**.¹⁻⁴ Of the monodentate ligands examined, only Et_3P appeared to bind at the heteroatom. This phosphine has also been shown to bind at the Mo site of isoelectronic clusters.^{3,4}

Overall, it is evident from formation of insoluble solids and multiple species (detected by NMR) in various cluster/ligand reaction systems that the V clusters with chloride terminal ligands are more fragile than their isoelectronic Mo counterparts. Nonetheless, it has proven possible to develop a substantial reaction chemistry based on **1**, the initial example of a VFe_3S_4 cubane-type cluster. Structural¹⁷ and electronic¹⁸ properties of this new set of clusters are described elsewhere. These clusters remain sus-

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(48) Although $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ is not isoelectronic with the clusters under consideration, it is pertinent to note that it is reducible reversibly to $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{3-}$ (stable only on the cyclic voltammetry time scale) and irreversibly to $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{4-}$ (4Fe^{2+}). These reduced species are quite unstable, apparently because the increased electron density at the Fe sites promotes chloride dissociation and thereafter decomposition. $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ clusters are generally reversibly reducible to the 3-species (which can be isolated⁴⁹) and, under some conditions, to the 4-state.^{49,50} The stability difference compared to the chloride clusters is doubtless due to the stronger binding affinity of thiolate.

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ceptible to further manipulation based on the demonstrated lability to substitution at all metal sites. Significant progress in other aspects of V-Fe-S cluster chemistry has been made by Rauchfuss and collaborators.⁵³ Their objects of study are organometallic clusters with variant metal:sulfur compositions that do not include VFe₃S₄. Finally, we noted at the outset the similarity of the Mo coordination environment in MoFe₃S₄ cubane-type clusters and that in nitrogenase.^{12,54} It will be most interesting to learn if there is a meaningful relationship between the structures and reactivities

of the V site in VFe₃S₄ clusters and those of the recently discovered V-containing nitrogenase.⁵⁵

Acknowledgment. This research was supported by National Science Foundation Grants CHE 81-06017 and 85-21365. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247.

Supplementary Material Available: Tables of positional and thermal parameters, cation and solvate molecule dimensions, and calculated hydrogen atom positions for (Me₄N)₂(Et₄N)₂[V₂Fe₆S₈Cl₄(edt)₂]-2MeCN (4 pages); a table of calculated and observed structure factors for (Me₄N)₂(Et₄N)₂[V₂Fe₆S₈Cl₄(edt)₂]-2MeCN (18 pages). Ordering information is given on any current masthead page.

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Structural Chemistry of Vanadium-Iron-Sulfur Clusters Containing the Cubane-Type [VFe₃S₄]²⁺ Core

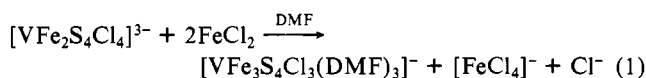
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The crystal structures of the compounds (Me₄N)[VFe₃S₄Cl₃(DMF)₃]-2DMF (**1**), (Me₄N)[VFe₃S₄Cl₃(bpy)(DMF)]-3DMF (**2**, bpy = 2,2'-bipyridyl), and (n-Pr₄N)[VFe₃S₄Cl₃(dmpe)(MeCN)]-3MeCN (**3**, dmpe = 1,2-bis(dimethylphosphino)ethane) have been determined. Compound **1** crystallizes in monoclinic space group *P*2₁/*c*, with *a* = 12.479 (4) Å, *b* = 10.638 (3) Å, *c* = 29.422 (9) Å, β = 92.56 (2)°, and *Z* = 4. Compound **2** was obtained in triclinic space group *P* $\bar{1}$, with *a* = 10.572 (3) Å, *b* = 12.132 (2) Å, *c* = 17.412 (4) Å, α = 78.64 (2)°, β = 80.18 (2)°, γ = 88.18 (2)°, and *Z* = 2. Compound **3** was found in monoclinic space group *C*2, with *a* = 35.47 (1) Å, *b* = 9.471 (3) Å, *c* = 12.611 (4) Å, β = 102.04 (2)°, and *Z* = 4. All three compounds contain cluster anions with the cubane-type [VFe₃(μ₃-S)₄]²⁺ core. They are the initial examples of this structural unit, which is isoelectronic with the [MFe₃S₄]³⁺ core of a variety of M = Mo and W single- and double-cubane clusters. The core unit of **1** exhibits idealized C_{3v} symmetry while the units of **2** and **3** approach C₃ symmetry, induced by chelate rings at the V sites. The cores have small and irregular dimensional differences and nearly constant volumes (9.50–9.64 Å³). The FeS₂Cl units are trigonally distorted tetrahedra, whose average Fe–Cl distances (**1**, 2.266 (8) Å; **2**, 2.249 (8) Å; **3**, 2.266 (16) Å) indicate a mean oxidation state no higher than Fe^{2.5+}. The V sites are six-coordinate with three DMF (**1**), bpy and DMF (**2**), and dmpe and MeCN (**3**) ligands. That in **1** is trigonally distorted, and those in **2** and **3** are distorted from octahedral in part by the restrictions of the chelate ligands. V–O bond distances in **1** (2.130 (17) Å) and **2** (2.112 (4) Å) indicate that the V oxidation state probably does not exceed 3+. Mean V–S distances in **1**–**3** are nearly constant and that of **3** (2.321 (6) Å) is 0.031 Å shorter than the Mo–S bond in [MoFe₃S₄Cl₄(dmpe)]⁻ (**4**). Clusters **3** and **4** have nearly identical terminal ligation and thus provide the most appropriate structural comparison. This difference is interpreted as compatible with any combination of effective oxidation states Mo^{3+,4+}/V^{3+,4+} in the isoelectronic cores of **3** and **4**. In conjunction with ⁵⁷Fe isomer shifts, certain structural parameters are of utility in an approximate description of (mean) oxidation states and charge distribution in the electronically delocalized [VFe₃S₄]²⁺ core.

Introduction

The first example of a new group of heterometal cubane-type clusters containing the [VFe₃S₄]²⁺ core has been synthesized by reaction 1.^{1,2} In this process, the V(V) atom of linear



[VFe₂S₄Cl₄]³⁻ is reduced by Fe(II) below the V(IV) level. The V atom in this oxidation level is not stable in the tetrahedral coordination of the trinuclear precursor, resulting in formation of a putative incomplete cubane core, VFe₂(μ₃-S)(μ-S)₃, which incorporates a Fe(III) atom and binds three DMF molecules at the V site. The product cluster, [VFe₃S₄Cl₃(DMF)₃]⁻ (**1**), belongs to the family of heterometal cubane clusters of generalized core formulation MM'₃(μ₃-S)₄. The only other authenticated examples

are those with M = Mo and W and M' = Fe,^{4,5} and M = Fe and M' = Mo.⁶

Cluster **1** is susceptible to ligand substitution at both the Fe and V sites, leading to a series of clusters that have been generated in solution and, in some cases, isolated.² Among the latter, all obtained as quaternary cation salts, in addition to **1** are [VFe₃S₄Cl₃(bpy)(DMF)]⁻ (**2**, bpy = 2,2'-bipyridyl) and [VFe₃S₄Cl₃(dmpe)(MeCN)]⁻ (**3**, dmpe = 1,2-bis(dimethylphosphino)ethane). While the stoichiometry of these clusters was highly suggestive of a cubane-type stereochemistry such as has been established for a considerable number of double⁷⁻¹⁵ and

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