however, be consistent with the presence of weak osmium-osmium bonds in the cluster.

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Supplementary Material Available: Tables of atomic coordinates, temperature factors, and bond lengths and angles for **1** (4 pages). Ordering information is given on any current masthead page.

Assembly of Vanadium-Iron-Sulfur Cubane Clusters from Mononuclear and Linear Trinuclear Reactants

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The spontaneous assembly from simple reactants of stable clusters containing the $MoFe_3S_4$ and WFe_3S_4 core units,[1] as well as their incorporation in a variety of double-[1-3] and single-cubane[1,4] structures, raises the issue of the scope of the generalized heterometal cluster core $MFe_3(\mu_3\text{-}S)_4$. The most likely new species would be isoelectronic with known clusters, all of which ultimately derive from $[MoS_4]^{2-}$ and $[WS_4]^{2-}$.[1] Consequently, initial investigations have involved systems based on $(NH_4)_3[VS_4]$,[5,6] which is the precursor to the "linear" trinuclear cluster $[VFe_2S_4Cl_4]^{3-}$ (**1**, Fe-V-Fe = 172.9 (1)°).[6] This species is particularly valuable synthetically because terminal chloride ligand substitution proceeds with retention of the VFe_2S_4 core structure,[6] as exemplified by the following preparation[8a] of a V-Fe-S cluster. A solution of $Li_2[Fe_2S_2(CO)_6]$[7] (2.9 mmol) in 100 mL of THF at -78 °C was treated with $(Et_4N)_3(\mathbf{1})$[6] (1.5 mmol) in 250 mL of acetonitrile. Addition of ether to the reaction mixture filtrate after a 16-h reaction at ~25 °C afforded black crystals of composition $(Et_4N)_3[VFe_6S_8(CO)_{12}]$[8b] (**3**, 31%; λ_{max} (ϵ_M) 316 (26 500), 416 (11 500), 526 (sh), 560 (12 100) nm (MeCN); ν_{CO} 1955, 1998, 2035 cm^{-1} (MeCN)). Diffraction-quality crystals have not been obtained. However, analytical data, the presence of a perturbed $[VS_4]^{3-}$ chromophore[6] in the UV/visible spectrum, and analogy to $[MoFe_3S_6(CO)_6]^{2-}$[2c] (**2**), which is prepared by the substitution of terminal chlorides in $[S_2MoS_2FeCl_2]^{2-}$ with $[Fe_2S_2(CO)_6]^{2-}$, establish structure **3**. While **3**, as **2**, may be subject to cubane cluster formation by oxidative decarbonylation,[2c] more direct routes were investigated.

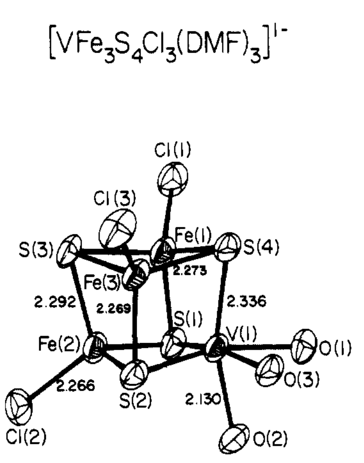
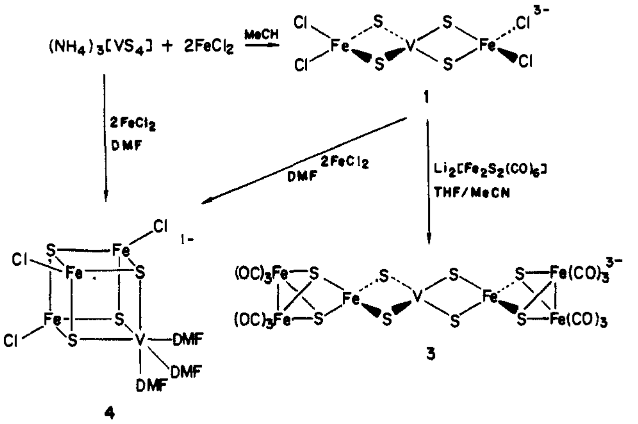


Figure 1. Structure of $[VFe_3S_4Cl_3(DMF)_3]^{1-}$ (**4**), showing 50% probability ellipsoids and mean values of bond distances under idealized trigonal symmetry. Of the DMF ligands, only the oxygen atoms are shown. Ranges of interatomic distances (Å): V-S, 2.331 (3)-2.340 (3); V-O, 2.112 (6)-2.145 (6); V-Fe, 2.771 (2)-2.781 (2); Fe-S(3), 2.287 (3)-2.301 (3); type Fe(3)-S(4), 2.265 (2)-2.281 (3); type Fe(3)-S(2), 2.263 (3)-2.276 (3); Fe-Cl, 2.260 (3)-2.275 (2).



A slurry of $(NH_4)_3[VS_4]$ (12 mmol) and equimolar Me_4NBr in 300 mL of DMF was allowed to react with 52 mmol of anhydrous $FeCl_2$,[8a] giving an intense red solution which slowly turned brown. After 16 h, workup of the reaction mixture as above afforded black crystalline $(Me_4N)[VFe_3S_4Cl_3(DMF)_3]\cdot 2DMF$[8b] (anion **4**, 50%). The absorption spectrum lacked UV/visible features characteristic of perturbed $[VS_4]^{3-}$, indicating reduction of V(V) and incorporation in the product. This compound crystallizes in monoclinic space group $P2_1/c$ with a = 12.479 (4) Å, b = 10.638 (3) Å, c = 29.422 (9) Å, β = 92.56 (2)°, and Z = 4. The crystal structure was solved and refined by standard procedures.[9] The stereochemistry of anion **4**, shown in Figure 1, is that of a cubane-type cluster whose $[VFe_3S_4]^{2+}$ core is isoelectronic and nearly isostructural with the $[MoFe_3S_4]^{3+}$ core found in numerous single and double cubanes,[1-4] including $[MoFe_3S_4Cl_3(al_2cat)(THF)]^{2-}$[4e] (**5**, al₂cat = 3,6-diallylcatecholate). The cluster closely approaches trigonal symmetry

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(8) (a) All reactions and manipulations were conducted under a pure dinitrogen atmosphere. (b) All new compounds gave satisfactory elemental analyses.

(9) Suitable crystals were obtained by diffusion of ether into a DMF solution. Diffraction data were collected at ~25 °C on a Nicolet P3F four-circle automated instrument with graphite-monochromatized Mo Kα radiation. An empirical absorption correction was applied. With use of 2889 unique data (5° ≤ 2θ ≤ 40°, $I \geq 3\sigma(I)$), the structure was solved by a combination of direct methods (MULTAN) and Fourier techniques and refined to $R(R_w)$ = 6.0 (7.9)%. The anion and cation were refined anisotropically, and the DMF solvate molecules were refined isotropically, by using block cascade least-squares refinement.

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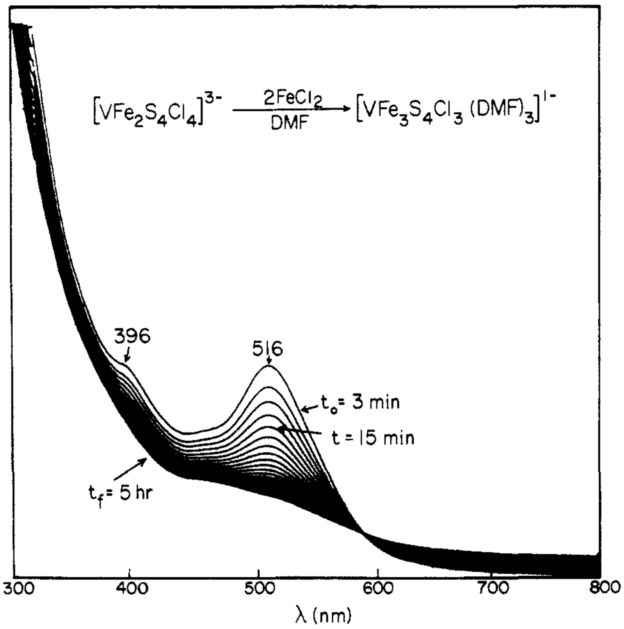

Figure 2. Spectrophotometric time course of the reaction of 3.2 mM $[VFe_2S_4Cl_4]^{3-}$ (**1**) and 6.9 mM $FeCl_2$ in DMF solution at ~25 °C.

with the pseudo-C_3 axis containing V(1) and S(3). Iron atoms occupy trigonally distorted FeS_3Cl sites. The near-Curie magnetic behavior of $(Me_4N)(\mathbf{4})\cdot 2DMF$ (μ = 3.87 (8.0 K), 3.92 (100 K), 3.99 (200 K), 4.13 μ_B (300 K)) demonstrates a $S = {}^3/_2$ ground state, in common with isoelectronic Mo clusters.[3c,4f] Like those clusters, **4** is electronically delocalized. The average Fe–Cl distance (2.266 (8) Å) is longer than that in $[Fe_4S_4Cl_4]^{2-}$[10] (2.216 (2) Å) and **5**[4e] (2.236 (15) Å), indicating a mean Fe oxidation state ≲2.5+.[11] Analysis of the ^{57}Fe Mössbauer spectrum at 4.2 K gives $\delta_{1,2}$ = 0.42–0.43 mm/s[12] (two-site fit), vs. $\delta \approx$ 0.40 mm/s for $[Fe_4S_4Cl_4]^{2-}$,[13] also consistent with this oxidation state.[14] The mean V–O distance (2.130 (17) Å) is in the V(II,III)–O, but not the V(IV)–O, range for neutral oxygen ligands.[15] We conclude that the $[V^{4+} + 3Fe^{2+}]$ charge distribution does not apply and that the V atom is more reduced and the Fe atoms are fractionally more oxidized than in this formulation.

Assembly of cluster **4** proceeds via **1**. As seen in Figure 2, the spectrum of authentic **1**[6] (λ_{max} 396, 516 nm) in a $2.2FeCl_2/\mathbf{1}$ system in DMF decays to an essentially featureless final spectrum (5 h) identical with that of isolated **4**. Cluster formation occurs by the reaction below, in which a cubane core is built from the linear $[VFe_2S_4]^{1+}$ core of **1** by Fe(II) insertion, rearrangement, and reduction (eq 1). A unique feature of **4** is the presence of

$$[VFe_2S_4Cl_4]^{3-} + 2FeCl_2 \rightarrow [VFe_3S_4Cl_3(DMF)_3]^{1-} + [FeCl_4]^{1-} + Cl^- \quad (1)$$

labile ligands at *all* terminal binding sites. In acetonitrile with $Me_2PCH_2CH_2PMe_2$ (1 equiv) **4** is converted to black $(Me_4N)[VFe_3S_4Cl_3(dmpe)(DMF)]$ (47%) by substitution at the V site. In Me_2SO **4** is solvolyzed to $[VFe_3S_4Cl_3(Me_2SO)_3]^{1-}$, which undergoes stoichiometric stepwise thiolate (and areneoxide) substitution at the Fe sites, terminating with $[VFe_3S_4(SR)_3(Me_2SO)_3]^{1-}$ (R = *p*-tolyl: λ_{max} (ϵ_M) 433 (10 900); 12.9 (*m*-H), 11.6 (*p*-Me), −2.3 (*o*-H) ppm). With ethane-1,2-dithiolate (1 equiv) in acetonitrile, **4** yields black $(Me_4N)_2(Et_4N)_2[VFe_3S_4Cl_2(edt)]_2$ (42%). X-ray structural analysis has shown the existence of a centrosymmetric double-cubane anion whose subclusters contain distorted trigonal bipyramidal $VS_3(edt)$ units and are linked by Fe–(μ_2-SR)–V bridges.[16]

The present work provides the only known route to VFe_3S_4 clusters. The final step in core assembly is the unique combination of trinuclear and mononuclear reactants, with the latter possibly extendable to metals other than Fe(II). The results above presage extensive manipulability of **4** by ligand substitution and redox reactions (E(1-/0) = +0.12 V vs. SCE). These matters, together with a more detailed evaluation of charge distribution and property comparisons with isoelectronic Mo clusters, will be the subjects of future reports. The only previously described V–Fe–S clusters are trinuclear[17] (V_2FeS_4, V_2FeS_3) and cubane-type[18] ($V_2Fe_2S_4$) organometallics unrelated to those described here.

Acknowledgment. This research was supported by NSF Grant CHE 81-06017. X-ray diffraction equipment was obtained by NIH Grant 1 S10 RR 02247. We thank Dr. G. C. Papaefthymiou for the Mössbauer spectral results.

Supplementary Material Available: Positional and thermal parameters for $(Me_4N)[VFe_3S_4Cl_3(DMF)_3]\cdot 2DMF$ (3 pages). Ordering information is given on any current masthead page.

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[11] In the series $[Fe_4S_4(SR)_4]^{1-,2-,3-}$, Fe–SR distances clearly increase as the mean oxidation state decreases: (a) Berg, J. M.; Holm, R. H. In "Metal Ions in Biology"; Spiro, T. G., Ed. Interscience: New York, 1982; Vol. 4, Chapter 1. (b) O'Sullivan, T.; Millar, M. *J. Am. Chem. Soc.* **1985**, *107*, 4096. Fe–Cl distances should behave similarly.

[12] Isomer shifts (δ) are referenced to Fe metal at 4.2 K; ΔE_{Q_1} = 1.12 mm/s, ΔE_{Q_2} = 1.36 mm/s.

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[14] An inverse linear relationship between isomer shift and (mean) oxidation state has been established for Fe–S complexes and clusters.[2b]

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Optical Spectroscopic Studies of Heme Proteins at High Pressure

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There has been considerable interest in studying the physical and chemical behavior of small molecules at high static pressure by using diamond-anvil cells.[2] In contrast to the relatively rich chemistry now developing on small molecules at high densities, studies of metalloproteins have largely been limited to relatively low pressures (<7 kbar) using UV–vis absorption,[3,4] magnetic susceptibility,[5] or NMR spectroscopy.[6] Low-pressure studies[3,5] of a variety of oxidized heme proteins have conclusively shown evidence for spin-state changes for the iron site at pressures above 1 kbar. Optical absorption studies of reduced heme proteins, while not conclusive, have also been interpreted in terms of spin-state changes. Other changes within the heme pocket, most notably

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[1] (a) Isotopes and Structural Chemistry, INC-4, Los Alamos National Laboratory. (b) Chemistry Department, University of New Mexico.

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