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 VFe_3S_4. Finally, we noted at the outset the similarity of the Mo coordination environment in $MoFe_3S_4$ 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 VFe_3S_4 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 $(Me_4N)_2(Et_4N)_2[V_2Fe_6S_8Cl_4(edt)_2]\cdot 2MeCN$ (4 pages); a table of calculated and observed structure factors for $(Me_4N)_2(Et_4N)_2[V_2Fe_6S_8Cl_4(edt)_2]\cdot 2MeCN$ (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 $[VFe_3S_4]^{2+}$ Core

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Received August 6, 1986

The crystal structures of the compounds $(Me_4N)[VFe_3S_4Cl_3(DMF)_3]\cdot 2DMF$ (**1**), $(Me_4N)[VFe_3S_4Cl_3(bpy)(DMF)]\cdot 3DMF$ (**2**, bpy = 2,2′-bipyridyl), and $(n\text{-}Pr_4N)[VFe_3S_4Cl_3(dmpe)(MeCN)]\cdot 3MeCN$ (**3**, dmpe = 1,2-bis(dimethylphosphino)ethane) have been determined. Compound **1** crystallizes in monoclinic space group $P2_1/c$, with $a = 12.479$ (4) Å, $b = 10.638$ (3) Å, $c = 29.422$ (9) Å, $\beta = 92.56$ (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, $\alpha = 78.64$ (2)°, $\beta = 80.18$ (2)°, $\gamma = 88.18$ (2)°, and $Z = 2$. Compound **3** was found in monoclinic space group $C2$, with $a = 35.47$ (1) Å, $b = 9.471$ (3) Å, $c = 12.611$ (4) Å, $\beta = 102.04$ (2)°, and $Z = 4$. All three compounds contain cluster anions with the cubane-type $[VFe_3(\mu_3\text{-}S)_4]^{2+}$ core. They are the initial examples of this structural unit, which is isoelectronic with the $[MFe_3S_4]^{3+}$ 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 C_s 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 Å^3). The FeS_3Cl 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 $[MoFe_3S_4Cl_4(dmpe)]^-$ (**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 ^{57}Fe isomer shifts, certain structural parameters are of utility in an approximate description of (mean) oxidation states and charge distribution in the electronically delocalized $[VFe_3S_4]^{2+}$ core.

Introduction

The first example of a new group of heterometal cubane-type clusters containing the $[VFe_3S_4]^{2+}$ core has been synthesized by reaction 1.[1,2] In this process, the V(V) atom of linear

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

$[VFe_2S_4Cl_4]^{3-}$[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, $VFe_2(\mu_3\text{-}S)(\mu\text{-}S)_3$, which incorporates a Fe(III) atom and binds three DMF molecules at the V site. The product cluster, $[VFe_3S_4Cl_3(DMF)_3]^-$ (**1**), belongs to the family of heterometal cubane clusters of generalized core formulation $MM'_3(\mu_3\text{-}S)_4$. 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 $[VFe_3S_4Cl_3(bpy)(DMF)]^-$ (**2**, bpy = 2,2′-bipyridyl) and $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$ (**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 double[7-15] and

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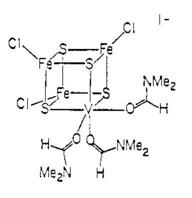
Table I. Crystal Data, Intensity Collections,[a] and Structure Refinement Parameters for $(Me_4N)[VFe_3S_4Cl_3(DMF)_3]\cdot 2DMF$ (**1**), $(Me_4N)[VFe_3S_4Cl_3(bpy)(DMF)]\cdot 3DMF$ (**2**), and $(n\text{-}Pr_4N)[VFe_3S_4Cl_3(dmpe)(MeCN)]\cdot 3MeCN$ (**3**)

	1	2	3
formula	$C_{19}H_{47}Cl_3Fe_3N_6O_5S_4V$	$C_{26}H_{48}Cl_3Fe_3N_7O_4S_4V$	$C_{26}H_{56}Cl_3Fe_3N_5P_2S_4V$
M_r	892.69	975.79	953.77
a, Å	12.479 (4)	10.572 (3)	35.47 (1)
b, Å	10.638 (3)	12.132 (2)	9.471 (3)
c, Å	29.422 (9)	17.412 (4)	12.611 (4)
α, deg		78.64 (2)	
β, deg	92.56 (2)	80.18 (2)	102.04 (2)
γ, deg		88.18 (2)	
cryst syst	monoclinic	triclinic	monoclinic
V, Å^3	3902 (2)	2157 (1)	4149 (2)
Z	4	2	4
d_{calcd} (d_{obsd}),[e] g/cm^3	1.52 (1.53)	1.50 (1.55)	1.53
space group	$P2_1/c$	$P\bar{1}$	$C2$
cryst dimens, mm	0.70 × 0.45 × 0.20	0.65 × 0.40 × 0.20	0.50 × 0.35 × 0.25
abs coeff μ, cm^{-1}	18.1	16.0	17.3
trans factors (max/min)	0.94/0.48	0.88/0.67	0.88/0.68
scan range, deg	2.0–29.3 (ω scan)	3.0–29.3 ($\theta/2\theta$ scan)	3.0–29.3 (ω scan)
scan speed,[b] deg/min	1.4	1.9	1.2
data collcd, deg	5–40 ($+h,+k,\pm l$)	3–47 ($+h,\pm k,\pm l$)	3–50 ($+h,+k,\pm l$)
total no of reflcns	4522	7452	7580
R_{merge},[c] %	2.6	1.1	1.9
no. of unique data ($F_o^2 > 3.0\sigma(F_o^2)$)	2889	5109	2937
no. of variables	319	361	330
R (R_w),[d] %	6.0 (7.9)[f]	5.0 (6.1)[f]	5.3 (6.0)[f]

[a] In all cases: Mo K$\bar{\alpha}$ (λ = 0.71069 Å) radiation; background/scan time ratio = 0.25. [b] Value given is x in $x + (2\theta_{K\alpha_1} - 2\theta_{K\alpha_2})$. [c] $R_{merge} = [\sum N_i \sum_{j=1}^{N_i} (\bar{F}_j - F_j)^2 / \sum (N_i - 1) \sum_{j=1}^{N_i} F_j^2]^{1/2}$, where N_i is the number of reflections in a given set, F_j is one member of the set, and $\bar{F}_j$ is the mean. [d] $R = [\sum ||F_o| - |F_c|| / \sum |F_o|]$; $R_w = [\sum w(|F_o|^2 - |F_c|^2) / \sum w|F_o|^2]^{1/2}$. [e] Determined by flotation in CCl_4/hexane. Accurate density could not be obtained for compound **3** owing to apparent loss of MeCN solvate molecules. [f] Weighting scheme for least-squares refinement: $w = (F_o/P(1))^2$, $F_o \le P(1)$; $w = (P(1)/F_o)^2$, $F_o > P(1)$, where $P(1) = F(\min(|F_o|^2 - |F_c|^2))$. $P(1)$ = 16.0, 36.0, and 25.0 for compounds **1–3** respectively.

single[15-20] cubanes with M = Mo and double cubanes with M = W,[12,21,22] proof of this structure and analysis of comparative metric features is required. This has been accomplished by single-crystal X-ray diffraction studies of clusters **1–3**. Their detailed structures are described herein and, together with accounts of synthesis and reactions[1,2] and electronic properties,[23] constitute our initial report of this new group of heterometal clusters.



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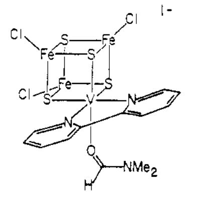

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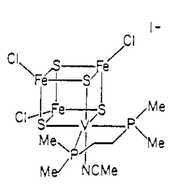

3

Experimental Section

$(Me_4N)[VFe_3S_4Cl_3(DMF)_3]\cdot 2DMF$ (**1**), $(Me_4N)[VFe_3S_4Cl_3(bpy)(DMF)]\cdot 3DMF$ (**2**), and $(n\text{-}Pr_4N)[VFe_3S_4Cl_3(dmpe)(MeCN)]\cdot 3MeCN$ (**3**) were prepared as described.[2] Here and elsewhere, the numerical designations refer to the cluster or the entire compound, as appropriate.

Collection and Reduction of X-ray Data. Black crystals of **1** and **2** were obtained by ether diffusion into DMF solutions, and black crystals of **3** were obtained by ether diffusion into a dilute acetonitrile solution. Crystals were sealed in glass capillaries whose sides were coated with Apiezon-(L) grease. These were flame-sealed under a dinitrogen atmosphere. Diffraction experiments were performed on a Nicolet P3F four-circle automated diffractometer with a Mo X-ray tube equipped with a graphite monochromator. Data collection parameters are summarized in Table I. The final orientation matrices and cell parameters were obtained from least-squares fits of 25 machine-centered reflections having 19° ≤ 2θ ≤ 25° (**1**) and 17° ≤ 2θ ≤ 25° (**2**, **3**). Selected ω scans were symmetrical and exhibited full widths at half-height of 0.31–0.34 (**1**), 0.41–0.55 (**2**), and 0.30–0.50° (**3**). Six standard reflections examined after every 100 reflections (**1**) and three standard reflections examined after every 63 reflections (**2**, **3**) showed no signs of decay over the course of data collection. The data sets were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied by using the programs XTAPE and XEMP of the SHELXTL structure determination package.[24]

For **1** the systematic absences $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$) uniquely define the space group as $P2_1/c$ (No. 14). The space group of **2** was determined to be $P\bar{1}$ by intensity statistics (MULTAN). Subsequent solution and refinement of the structure confirmed this space group. That this compound cannot be described in a higher symmetry space group was indicated by examination of the metric symmetry of the Niggli (reduced cell) matrix by use of the program TRACER.[25] Axial photographs and the systematic absences hkl ($h + k = 2n + 1$), $h0l$ ($h = 2n + 1$), and $0k0$ ($k = 2n + 1$) for **3** are consistent with monoclinic C-centered space groups $C2/m$, Cm, and $C2$; simple E statistics favored the noncentric groups Cm and $C2$. The structure was solved and refined in $C2$ (No. 5). Attempted refinement in Cm was ill-behaved.

Solution and Refinement of Structures. Structures were solved by a combination of direct methods (MULTAN[26]) and Fourier techniques. Atom scattering factors were taken from a standard source.[27] E maps

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Table II. Positional Parameters ($\times 10^4$) for $[VFe_3S_4Cl_3(DMF)_3]^-$

atom	*x/a*	*y/b*	*z/c*
V(1)	7541 (1)[a]	−201 (1)	768.5 (5)
Fe(1)	8724 (1)	1989 (1)	913.6 (5)
Fe(2)	6619 (1)	1922 (1)	1138.3 (5)
Fe(3)	7142 (1)	1956 (1)	261.0 (4)
S(1)	7994 (2)	791 (2)	1459.6 (8)
S(2)	5890 (2)	711 (2)	564.2 (8)
S(3)	7467 (2)	3531 (2)	785.4 (9)
S(4)	8670 (2)	804 (2)	268.8 (8)
Cl(1)	10392 (2)	2738 (3)	1075 (1)
Cl(2)	5388 (2)	2536 (2)	1641.1 (9)
Cl(3)	6599 (2)	2778 (2)	−420.4 (8)
O(1)	8796 (4)	−1505 (5)	955 (2)
C(1)	9371 (5)	−2078 (7)	694 (3)
N(11)	9854 (4)	−3138 (6)	799 (3)
C(4)	10516 (6)	−3770 (8)	478 (4)
C(5)	9738 (6)	−3719 (9)	1238 (4)
O(2)	6635 (4)	−1584 (5)	1108 (2)
C(2)	6866 (6)	−2232 (8)	1450 (3)
N(12)	6341 (5)	−3287 (6)	1544 (2)
C(6)	6637 (7)	−4008 (9)	1946 (4)
C(7)	5482 (7)	−3740 (9)	1246 (3)
O(3)	7316 (5)	−1609 (5)	267 (2)
C(3)	6511 (7)	−2153 (7)	95 (2)
N(13)	6600 (5)	−3200 (5)	−144 (2)
C(8)	5653 (8)	−3801 (7)	−351 (2)
C(9)	7627 (8)	−3771 (7)	−214 (2)

[a] Estimated standard deviation in least significant figures given in parentheses in this and succeeding tables.

with the highest combined figures of merit revealed the positions of some or all of the core metal and sulfur atoms. Other non-hydrogen atoms were located by means of Fourier refinement with intervening cycles of least-squares refinement with use of the program CRYSTALS.[28] Subsequent difference maps revealed the remaining non-hydrogen atoms, usually those of solvate molecules. Refinement details for individual structures are briefly summarized.

(a) Compound 1. Isotropic refinement converged at $R = 13\%$. The asymmetric unit consists of one cation, one anion, and two DMF solvate molecules. The cation and anion were well-ordered and were refined anisotropically by using blocked least-squares refinement. The DMF solvate molecules displayed thermal parameters large enough to indicate disorder. However, no suitable model for the disorder was found. These molecules were isotropically refined and restrained by using the method of additional observational equations.[29] Hydrogen atoms were placed at a fixed C–H distance of 1.05 Å with a thermal parameter of 0.05 $Å^2$ and were allowed to ride on the carbon atom to which they are bound.

(b) Compound 2. Isotropic refinement converged at $R = 17\%$. The asymmetric unit consists of one cation, one anion, and three DMF solvate molecules. The carbon atoms of the cation are disordered over two orientations around the fixed N atom position; refined occupancies of the two orientations were constrained to a sum of unity and converged at 0.75 (9) and 0.25 (9). The three solvate molecules are moderately or severely disordered. Two of these (containing O(20) and O(30)) appeared to be disordered over more than three positions, and the very irregular geometry of one of them could not be corrected by application of constraints to angles and distances. The disorder of the other solvate molecule (containing O(40)) was modeled over two orientations about fixed O and N positions, with refined occupancies converging at 0.60 (2) and 0.40 (2). All three solvate molecules were refined isotropically with use of the method of additional observational equations.[29] The cation was also refined isotropically. The anion was well-behaved and was refined anisotropically by use of blocked least-squares refinement. Hydrogen atoms were placed at a C–H distance of 1.0 Å, with isotropic thermal parameters 1.2 times those of the bonded carbon atoms.

(c) Compound 3. Isotropic refinement converged at $R = 11\%$. The asymmetric unit consists of one cation, one anion, and three MeCN solvate molecules. Because of the chiral space group, a polarity factor[30] was refined to determine the correctness of the enantiomorph chosen. Its value of 0.90 ± 0.02 indicated that the choice was correct, as was confirmed by inspection of the Friedel pairs collected. The cation is slightly disordered. Two of the solvate molecules that lie on special positions are moderately disordered, as is the other solvate molecule, which lies in a general position. The disorder was not modeled successfully. The cation and solvate molecules were refined isotropically, and the bond distances and angles were constrained by using the method of additional observational equations.[29] The anion was refined anisotropically as for **2**. The dmpe portion of the chelate ring is disordered over the enantiomerically related half-chair conformations. Hydrogen atoms were included as for **2**.

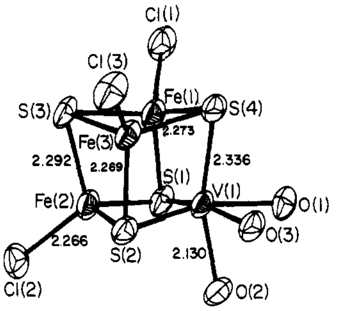

Figure 1. Structure of $[VFe_3S_4Cl_3(DMF)_3]^-$ (**1**), showing 50% probability ellipsoids, atom-labeling scheme, and selected bond distances.

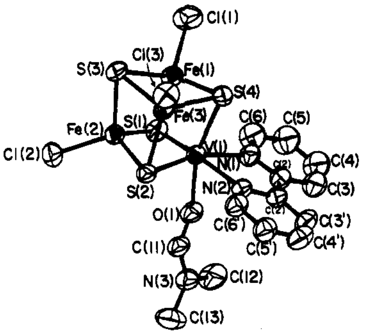

Figure 2. Structure of $[VFe_3S_4Cl_3(bpy)(DMF)]^-$ (**2**), showing 50% probability ellipsoids and atom-labeling scheme.

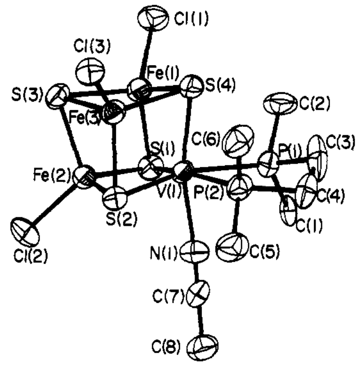

Figure 3. Structure of $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$ (**3**), showing 50% probability ellipsoids and atom-labeling scheme.

Unique data used in the refinements and final *R* values are given in Table I. Positional parameters of the three clusters are listed in Tables II–IV.[31]

Results and Discussion

The crystal structures of compounds **1**–**3** consist of well-separated cations, anions, and solvate molecules. When not complicated by disorder, the dimensions of the cations and solvate molecules are unexceptional[31] and are not considered further. For the clusters $[VFe_3S_4Cl_3(DMF)_3]^-$ (**1**), $[VFe_3S_4Cl_3(bpy)(DMF)]^-$ (**2**), and $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$ (**3**), interatomic distances and angles are collected in Tables V–VII and structures are depicted in Figures 1–3. Because of the large number of inde-

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

Table III. Positional Parameters (×10^4) for $[VFe_3S_4Cl_3(bpy)(DMF)]^-$

atom	*x/a*	*y/b*	*z/c*
V(1)	9825.0 (8)	4050.6 (8)	3065.0 (5)
Fe(3)	11858.4 (7)	2860.5 (7)	3625.4 (5)
Fe(1)	12231.9 (8)	4073.5 (7)	2125.7 (5)
Fe(2)	11900.5 (7)	5144.8 (7)	3389.9 (5)
S(3)	13570 (1)	4016 (1)	3036.7 (9)
S(1)	10986 (1)	5602 (1)	2287.3 (9)
S(2)	10492 (1)	3970 (1)	4288.0 (8)
O(1)	8333 (4)	5171 (3)	3360 (2)
N(3)	6675 (5)	5985 (5)	4025 (3)
C(11)	7762 (5)	5398 (5)	3991 (4)
C(13)	6039 (8)	6316 (9)	4748 (6)
C(12)	6100 (7)	6336 (8)	3313 (5)
Cl(2)	12501 (2)	6620 (1)	3844 (1)
S(4)	10927 (1)	2546 (1)	2607.5 (9)
Cl(1)	13273 (2)	4074 (2)	888 (1)
Cl(3)	12441 (2)	1273 (1)	4401 (1)
N(2)	8230 (4)	2889 (4)	3610 (3)
C(6′)	8058 (6)	2309 (5)	4353 (4)
C(5′)	6983 (7)	1657 (6)	4714 (5)
C(2′)	7280 (5)	2837 (5)	3185 (4)
C(3′)	6195 (6)	2202 (6)	3506 (5)
C(4′)	6049 (6)	1617 (6)	4267 (5)
C(2)	7521 (5)	3494 (5)	2361 (4)
C(3)	6636 (7)	3543 (7)	1845 (5)
N(1)	8632 (4)	4062 (4)	2139 (3)
C(5)	8075 (8)	4667 (8)	852 (4)
C(6)	8907 (7)	4619 (7)	1392 (4)
C(4)	6944 (7)	4175 (8)	1085 (4)

Table IV. Positional Parameters (×10^4) for $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$

atom	*x/a*	*y/b*	*z/c*
V(1)	8571.8 (5)	2210 (6)	1648 (2)
Fe(1)	8410.6 (4)	4643 (6)	2650 (1)
Fe(2)	9098.7 (4)	4307 (6)	1989 (1)
Fe(3)	8412.4 (4)	4684 (6)	534 (1)
S(3)	8729.2 (9)	6265 (7)	1803 (3)
S(2)	8889.8 (8)	3154 (7)	379 (2)
S(4)	7999.2 (8)	3465 (6)	1333 (3)
P(2)	8226.8 (9)	597 (7)	190 (3)
P(1)	8251.9 (9)	522 (7)	2699 (3)
N(1)	9003 (3)	570 (13)	1871 (8)
C(8)	9560 (4)	−1270 (17)	2200 (13)
C(7)	9248 (3)	−242 (14)	2024 (9)
Cl(3)	8110.1 (8)	5794 (6)	−1001 (2)
S(1)	8889.3 (8)	3091 (6)	3319 (2)
Cl(2)	9739.1 (8)	4678 (7)	2361 (3)
Cl(1)	8064.0 (9)	5652 (7)	3787 (2)
C(6)	7843 (6)	1288 (23)	−799 (17)
C(4′)	7857 (7)	−365 (31)	657 (20)
C(6′)	8003 (10)	1528 (41)	−999 (25)
C(5′)	8536 (12)	−634 (33)	−273 (33)
C(5)	8520 (6)	−267 (25)	−609 (16)
C(4)	8026 (6)	−916 (18)	792 (16)
C(3)	7898 (6)	−508 (26)	1787 (18)
C(3′)	7983 (12)	−824 (32)	1845 (24)
C(1)	8535 (5)	−685 (20)	3627 (14)
C(2′)	8651 (9)	−414 (42)	3481 (30)
C(1′)	7996 (11)	1045 (38)	3716 (25)
C(2)	7951 (7)	1403 (23)	3476 (18)

pendent structural parameters, data in these tables are limited to the chemically more interesting angles and distances. Other metric data are tabulated elsewhere.[31] Stereoviews of **2** and **3** are provided in Figure 4. Note the internally consistent atom-labeling schemes of the three clusters.

In describing and analyzing the structures of clusters **1**–**3**, core units, terminal Fe ligation, and V sites are considered, followed by a comparison with isoelectronic $MoFe_3S_4$ clusters. Mean values of leading structural parameters of **1**–**3** are compared in Table VIII. Owing to the electronically delocalized nature of the $[VFe_3S_4]^{2+}$ core as sensed by ^{57}Fe Mössbauer spectroscopy,[23] considerable interest attends those structural features that may be reflective of (mean) oxidation states of the Fe and V atoms.

Table V. Selected Interatomic Distances (Å) and Angles (deg) of $[VFe_3S_4Cl_3(DMF)_3]^-$

V(1)···Fe(1)	2.781 (2)	C(1)–N(11)	1.310 (11)
V(1)···Fe(2)	2.778 (2)	C(2)–N(12)	1.335 (11)
V(1)···Fe(3)	2.771 (2)	C(3)–N(13)	1.325 (11)
mean	2.777 (5)[a]	mean	1.323 (13)
V(1)–S(1)	2.338 (3)	Fe(1)–Cl(1)	2.260 (3)
V(1)–S(2)	2.331 (3)	Fe(2)–Cl(2)	2.275 (2)
V(1)–S(4)	2.340 (3)	Fe(3)–Cl(3)	2.263 (3)
mean	2.336 (5)	mean	2.266 (8)
V(1)···S(3)	3.972 (3)	Fe(1)–S(4)	2.276 (3)
Fe(2)···Fe(3)	2.691 (2)	Fe(2)–S(1)	2.267 (2)
Fe(1)···Fe(2)	2.738 (2)	Fe(3)–S(2)	2.263 (3)
Fe(1)···Fe(3)	2.691 (2)	Fe(1)–S(1)	2.272 (3)
mean	2.707 (27)	Fe(2)–S(2)	2.281 (3)
		Fe(3)–S(4)	2.265 (2)
V(1)–O(1)	2.145 (6)	Fe(1)–S(3)	2.289 (3)
V(1)–O(2)	2.132 (6)	Fe(2)–S(3)	2.287 (3)
V(1)–O(3)	2.112 (6)	Fe(3)–S(3)	2.301 (3)
mean	2.130 (17)	mean	2.278 (13)
O(1)–C(1)	1.236 (10)	N–C max	1.454 (12)
O(2)–C(2)	1.242 (10)	N–C min	1.438 (13)
O(3)–C(3)	1.248 (10)	mean of 6	1.445 (5)
mean	1.242 (6)		
O(1)–V–O(2)	80.2 (2)	C–N–C max	121.8 (6)
O(1)–V–O(3)	78.0 (2)	C–N–C min	120.4 (7)
O(2)–V–O(3)	77.4 (2)	mean of 6	121.0 (5)
mean	78.5	V–S–Fe max	74.2 (1)
O(1)–V–S(1)	85.6 (2)	V–S–Fe min	74.0 (1)
O(1)–V–S(4)	90.2 (2)	mean of 6	74.1 (1)
O(2)–V–S(1)	91.0 (2)	Fe–S–Fe max	73.5 (1)
O(2)–V–S(2)	85.8 (2)	Fe–S–Fe min	71.8 (1)
O(3)–V–S(2)	91.6 (2)	mean of 6	72.8 (9)
O(3)–V–S(4)	87.2 (2)		
O(1)–V–S(2)	164.1 (2)	Cl–Fe–S max	116.3 (1)
O(2)–V–S(4)	163.2 (1)	Cl–Fe–S min	110.5 (1)
O(3)–V–S(1)	161.3 (2)	mean of 9	113.5 (19)
S(1)–V–S(2)	102.3 (1)	O(1)–C(1)–N(11)	123.5 (7)
S(1)–V–S(4)	102.2 (1)	O(2)–C(2)–N(12)	122.3 (7)
S(2)–V–S(4)	101.4 (1)	O(3)–C(3)–N(13)	121.3 (7)
mean	102.0 (5)	C(4)–N(11)–C(5)	117.9 (7)
S–Fe–S max	106.3 (1)	C(6)–N(12)–C(7)	118.6 (7)
S–Fe–S min	103.0 (1)	C(8)–N(13)–C(9)	117.7 (6)
mean of 9	105.1 (12)		

[a] In this and succeeding tables the standard deviation of the mean is estimated from $\sigma \approx s = [(\sum x_i^2 - n\bar{x}^2)/(n-1)]^{1/2}$.

Core Units. The three clusters contain isoelectronic and virtually isostructural cubane-type $[VFe_3(\mu_3\text{-}S)_4]^{2+}$ cores formed by interpenetrating, distorted VFe_3 and S_4 tetrahedra. The VFe_3S_4 unit in any oxidation state has not been previously encountered. The six faces of the cores are $VFeS_2$ and Fe_2S_2 nonplanar rhombs with atom displacements of <0.2 Å from unweighted least-squares planes. Atom positional deviations from the six diagonal planes (e.g., VFe(2)S(3,4)) are much smaller (**1**, ≤0.019 Å; **3**, ≤0.051 Å), and in **2** these planes are essentially perfect (≤0.004 Å).

The core of cluster **1** (Figure 1), with three identical terminal ligands at the V site, has idealized C_{3v} symmetry, under which distances divide into the sets 3 V–S, 3 V···Fe, 3 Fe···Fe, 3 + 6 Fe–S, and 3 + 3 S···S. The appropriateness of this description follows from the values of ≤0.008 Å for the standard deviations of the means of symmetry-related bonded distances (excluding Fe···Fe), and the different Fe(1,2,3)–S(3) distances (2.292 (8) Å) compared to the other six Fe–S distances (2.271 (7) Å), none of which overlap with the range of the set of three. As might be expected, the two types of S···S distances, being nonbonded, show larger deviations (S(3)···S(1,2,4), 3.610 (35) Å; others, 3.630 (13) Å). In **2** (Figure 2) and **3** (Figure 3) the presence of chelate rings might be expected to degrade the core symmetry to no higher than C_s (neglecting the nonplanarity of the dmpe ring in **3**). Under this symmetry, distances divide as follows: V–S, Fe···Fe, V···Fe, 2 + 1; Fe-S, 4 × 2 + 1; S···S, 2 × 2 + 2 × 1. Inspection of these

Table VI. Selected Interatomic Distances (Å) and Angles (deg) of $[VFe_3S_4Cl_3(bpy)(DMF)]^-$

V(1)···Fe(1)	2.777 (1)	Fe(1)–S(1)	2.276 (2)
V(1)···Fe(3)	2.760 (1)	Fe(3)–S(2)	2.269 (2)
V(1)···Fe(2)	2.792 (1)	Fe(1)–S(4)	2.279 (2)
mean	2.776 (16)	Fe(3)–S(4)	2.268 (2)
V(1)–S(1)	2.336 (2)	Fe(1)–S(3)	2.290 (2)
V(1)–S(2)	2.338 (2)	Fe(3)–S(3)	2.293 (2)
V(1)–S(4)	2.332 (2)	Fe(2)–S(1)	2.260 (2)
mean	2.335 (3)	Fe(2)–S(2)	2.270 (2)
		Fe(2)–S(3)	2.276 (2)
V(1)···S(3)	3.951 (2)	mean	2.276 (11)
V(1)–N(1)	2.208 (4)	Fe(1)–Cl(1)	2.245 (2)
V(1)–N(2)	2.192 (4)	Fe(2)–Cl(2)	2.243 (2)
V(1)–O(1)	2.112 (4)	Fe(3)–Cl(3)	2.258 (2)
Fe(3)···Fe(1)	2.704 (1)	mean	2.249 (8)
Fe(3)···Fe(2)	2.721 (1)	O(1)–C(11)	1.237 (7)
Fe(1)···Fe(2)	2.738 (1)	N(3)–C(11)	1.332 (7)
mean	2.721 (17)	N(3)–C(12)	1.457 (9)
C(2)–C(2′)	1.481 (9)	N(3)–C(13)	1.446 (9)
N(1)–V–O(1)	78.3 (2)	V–S–Fe max	74.8 (1)
N(2)–V–O(1)	77.3 (2)	V–S–Fe min	73.6 (1)
N(1)–V–N(2)	73.9 (2)	mean of 6	74.1 (5)
O(1)–V–S(2)	90.8 (1)	Fe–S–Fe max	74.3 (1)
O(1)–V–S(1)	87.9 (1)	Fe–S–Fe min	72.4 (1)
N(1)–V–S(1)	90.6 (1)	mean of 6	73.4 (7)
N(2)–V–S(2)	91.9 (1)	Cl–Fe–S max	116.0 (1)
N(1)–V–S(4)	86.8 (1)	Cl–Fe–S min	112.3 (1)
N(2)–V–S(4)	87.8 (2)	mean of 9	113.8 (11)
N(1)–V–S(2)	162.9 (1)	S–Fe–S max	106.6 (1)
N(2)–V–S(1)	161.0 (1)	S–Fe–S min	103.0 (1)
O(1)–V–S(4)	161.2 (1)	mean of 9	104.8 (12)
S(1)–V–S(4)	102.5 (1)		
S(2)–V–S(4)	102.3 (1)		
S(1)–V–S(2)	101.3 (1)		

Table VII. Selected Interatomic Distances (Å) and Angles (deg) of $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$

V(1)···Fe(1)	2.745 (2)	V(1)–N(1)	2.158 (10)
V(1)···Fe(2)	2.699 (2)	N(1)–C(7)	1.145 (14)
V(1)···Fe(3)	2.729 (2)	C(8)–C(7)	1.457 (18)
mean	2.724 (23)	Fe(1)–Cl(1)	2.282 (3)
V(1)–S(1)	2.327 (3)	Fe(3)–Cl(3)	2.266 (3)
V(1)–S(2)	2.321 (4)	Fe(2)–Cl(2)	2.250 (3)
V(1)–S(4)	2.315 (3)	mean	2.266 (16)
mean	2.321 (6)	Fe(1)–S(4)	2.263 (3)
V(1)···S(3)	3.880 (4)	Fe(3)–S(4)	2.261 (3)
Fe(2)···Fe(3)	2.749 (2)	Fe(1)–S(3)	2.298 (4)
Fe(1)···Fe(2)	2.757 (2)	Fe(3)–S(3)	2.306 (3)
Fe(1)···Fe(3)	2.670 (2)	Fe(1)–S(1)	2.271 (3)
mean	2.725 (48)	Fe(3)–S(2)	2.268 (3)
V(1)–P(2)	2.505 (4)	Fe(2)–S(1)	2.282 (3)
V(1)–P(1)	2.496 (4)	Fe(2)–S(2)	2.288 (3)
mean	2.500 (6)	Fe(2)–S(3)	2.255 (4)
		mean	2.277 (18)
		P(1)···P(2)	3.148 (5)
P(1)–V–P(2)	78.0 (1)	V–S–Fe max	73.7 (1)
N(1)–V–P(1)	81.8 (3)	V–S–Fe min	71.7 (1)
N(1)–V–P(2)	83.2 (3)	mean of 6	72.8 (9)
N(1)–V–S(1)	86.8 (3)	Fe–S–Fe max	74.5 (1)
N(1)–V–S(2)	86.2 (3)	Fe–S–Fe min	70.9 (1)
P(1)–V–S(2)	86.3 (1)	mean of 6	73.4 (15)
P(2)–V–S(1)	86.3 (1)	Cl–Fe–S max	119.7 (1)
N(1)–V–S(4)	87.8 (1)	Cl–Fe–S min	108.6 (1)
P(1)–V–S(4)	86.6 (1)	mean of 9	113.8 (32)
P(2)–V–S(4)	84.9 (1)	S–Fe–S max	108.5 (1)
S(1)–V–S(2)	105.9 (1)	S–Fe–S min	101.7 (1)
S(1)–V–S(4)	102.3 (1)	mean of 9	104.9 (25)
S(2)–V–S(4)	102.7 (1)		
P(1)–V–S(2)	162.4 (1)		
N(1)–V–S(4)	164.8 (1)		
P(2)–V–S(1)	162.5 (1)		

distances (Tables VI and VII) reveals for most a tendency to separate into these sets. This is especially clear for Fe–S and S···S separations. For example, in **3** the distances Fe(1,2,3)–S(3) and S(3)···S(1,2,4), equivalent in trigonal symmetry, separate as 2.298 (4)/2.306 (4) + 2.255 Å and 3.543 (4)/3.558 (4) + 3.668 (4) Å, respectively. In **1** the ranges of these parameters are much less, *viz.*, 2.287 (3)–2.301 (3) and 3.570 (4)–3.631 (4) Å. Cluster **2** is an intermediate case, with distortions toward C_s not as pronounced. Any designation of core symmetry is clearly idealized inasmuch as not all distance types in each cluster adhere to it. The symmetries C_{3v} for **1** and C_s for **2** and **3** are meaningful, albeit approximate, descriptions of core structure. The effective mirror symmetry of **3** is manifested in a 2:1 ratio of Fe sites in its Mössbauer spectrum.[23] Lastly, differences in structural parameter types notwithstanding, the core volumes of clusters **1**–**3**, calculated from atom coordinates, are practically identical (Table VIII).

Terminal Fe Ligation. In each cluster trigonally distorted tetrahedral coordination at the Fe sites is completed by terminal binding of chloride. We have observed on several previous occasions that terminal Fe–Cl/SR bond lengths should convey information about Fe mean oxidation states in electronically delocalized cubane-type clusters. This point is based on the Shannon tetrahedral radius difference r[Fe(II)–Fe(III)] = 0.14 Å,[32] as manifested in bond length differences in the mononuclear complexes $[FeCl_4]^{2-,-}$ (0.10–0.11 Å[33]) and $[Fe(SPh)_4]^{2-,-}$ (0.06 Å[34]). The smaller difference in the latter pair of complexes is due to the more electron-rich nature of thiolate, which tends to decrease actual Fe atom charge differences and thus bond length differences in the two oxidation states. Among cubane-type clusters, the bond length/oxidation state trend is clear in the series $[Fe_4S_4(SPh)_4]^{3-}$ (2.295 (4) Å), $[Fe_4S_4(SPh)_4]^{2-}$ (2.263 (7) Å), $[Fe_4S_4(S\text{-}2,4,6\text{-}i\text{-}Pr_3C_6H_2)_4]^-$ (2.206 (3) Å).[35] Here the mean oxidation state increases from $Fe^{2.25+}$ to $Fe^{2.75+}$; mean Fe–S terminal bond lengths are indicated. A similar trend appears to exist in the double cubanes $[Mo_2Fe_6S_8(SPh)_9]^{5-,3-}$,[11,36] but the large standard deviations in bond lengths of the 3– cluster render comparisons inexact.

Table VIII. Comparative Structural Parameters[a] of $[VFe_3S_4Cl_3(DMF)_3]^-$ (**1**), $[VFe_3S_4Cl_3(bpy)(DMF)]^-$ (**2**), $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$ (**3**), and $[MoFe_3S_4Cl_4(dmpe)]^-$ (**4**)

	1	**2**	**3**	**4**[c]
M···Fe,[b] Å	2.777 (5)	2.776 (16)	2.724 (23)	2.714 (15)
Fe···Fe, Å	2.707 (27)	2.721 (17)	2.725 (48)	2.746 (22)
M–S, Å	2.336 (5)	2.335 (3)	2.321 (6)	2.352 (9)
Fe–S, Å	2.278 (13)	2.276 (11)	2.277 (18)	2.272 (13)
V–O, Å	2.130 (17)	2.112 (4)		
V–N, Å		2.200 (11)	2.158 (10)	
M–P, Å			2.500 (6)	2.554 (8)
Fe–Cl, Å	2.266 (8)	2.249 (8)	2.266 (16)	2.204 (5)
$V(MFe_3S_4)$, Å^3	9.62	9.64	9.50	9.55

[a] Mean values given where possible. [b] M = V or Mo. [c] Data from ref 20.

In the present set of clusters Fe–Cl bond lengths span the range 2.243 (2)–2.282 (3) Å; mean values are given in Table VIII. When compared with the Fe–Cl bond distances in $[Fe_4S_4Cl_4]^{2-}$[37]

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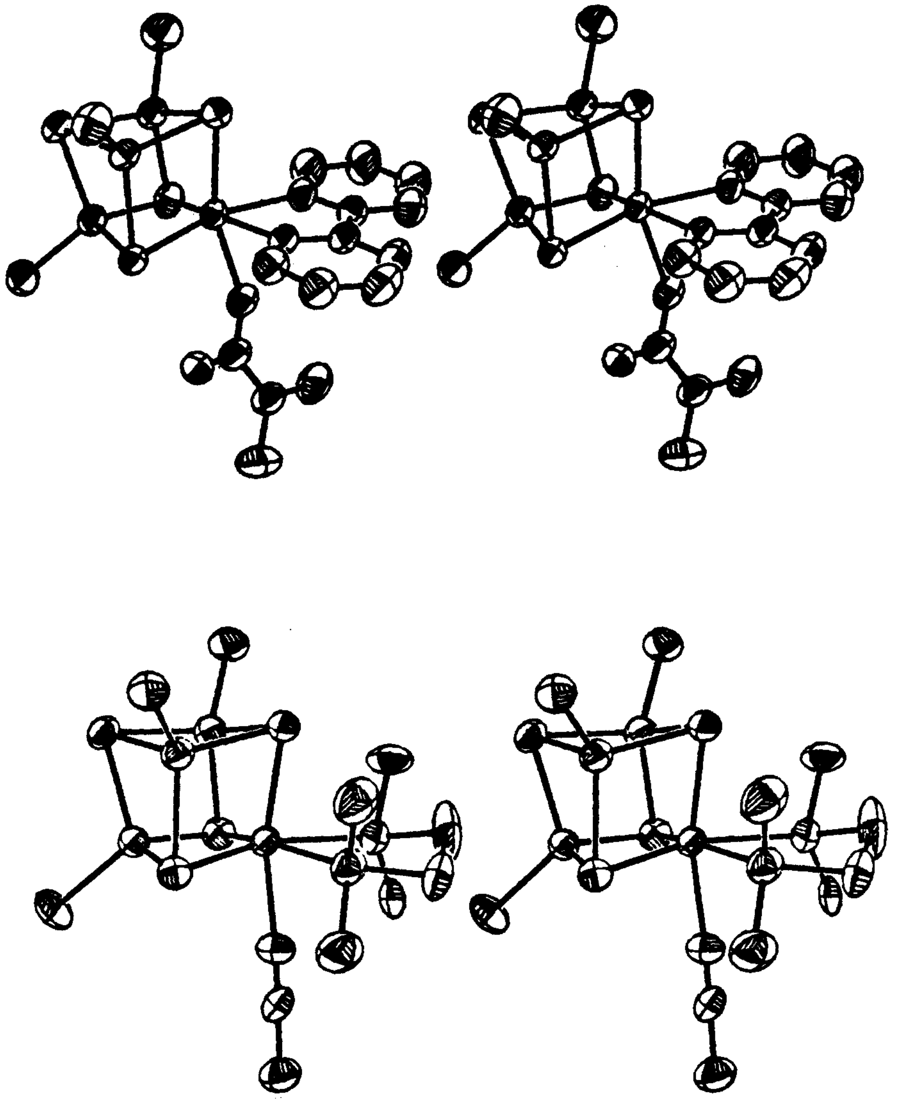
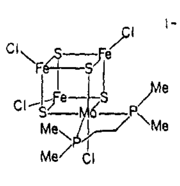


Figure 4. Stereoviews of the structures of $[VFe_3S_4Cl_3(bpy)(DMF)]^-$ (**2**, upper) and $[VFe_3S_4Cl_3(dmpe)(MeCN)]^-$ (**3**, lower).

(2.216 (2) Å), $[Fe_4S_4(SPh)_2Cl_2]^{2-}$ [38] (2.210 (3) Å), and $[Fe_4S_4(OPh)_2Cl_2]^{2-}$ [38] (2.203 (3) Å), no single distance of **1**–**3** is within $\sim 10\sigma$ of an individual bond length in the Fe–S clusters. Mean values (indicated) are different by at least 0.033 Å, or $\sim 2\sigma$ of the average value of cluster **3**. The same is not true in relation to $[Fe_4S_4Cl_2(S_2CNEt_2)_2]^{2-}$ (2.249 (2) Å) and $[Fe_4S_4Cl_3(S_2CNEt_2)]^{2-}$ (2.231 (10) Å).[39] The two identical Fe–Cl distances of the first cluster and one of the three distances of the second just overlap with the low end of the range of **1**–**3**. However, owing to bidentate coordination by dithiocarbamate, these clusters have rather irregularly shaped cores that may disturb normal terminal ligand bond lengths at other sites. The clusters $[MoFe_3S_4Cl_4(dmpe)]^-$ [20] (**4**) and $[MoFe_3S_4Cl_3(al_2cat)(THF)]^{2-}$ [18] (**5**, al_2cat = 3,6-diallylcatecholate(2–)) have none (2.198 (4)–2.208 (4) Å) and one (2.245 (2) Å) Fe–Cl bond lengths in the range of **1**–**3**. They contain the $[MoFe_3S_4]^{3+}$ core, isoelectronic with $[VFe_3S_4]^{2+}$, and provide the only comparisons available with Mo clusters.[5] Taking the foregoing comparisons into consideration, we conclude that the mean oxidation state in **1**–**3** is no higher than $Fe^{2.5+}$, the value in the Fe–S clusters, and perhaps slightly lower. This also applies to the double cubane $[V_2Fe_6S_8Cl_4(edt)_2]^{4-}$ (**6**, edt = ethane-1,2-dithiolate), whose structure is described separately.[2] Elsewhere we have argued from ^{57}Fe isomer shifts that the mean oxidation state in $[MoFe_3S_4]^{3+}$ clusters may be somewhat higher than $Fe^{2.5+}$, perhaps near $Fe^{2.67+}$.[36]



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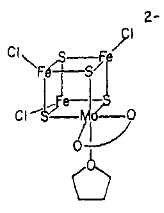
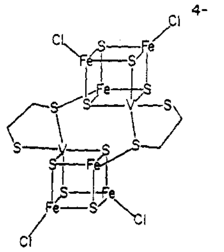


5



6

Vanadium Sites. The V atoms in **1**–**3** exhibit distorted octahedral coordination involving one or three solvent molecules. In **1** the VS_3O_3 coordination unit approaches a trigonally distorted octahedron with the C_3 axis coincident with body diagonal V–S(3). The form of the distortion is evident from the three S–V–S, O–V–O, and S–V–O angles near 102, 78, and 163°, respectively. The S–V–O angles involving cis atoms occur in the 85–92° range, nearer the octahedral value of 90°. The S–V–S angles are set by the core structure inasmuch as they vary only slightly in the three clusters.

The mean V–O bond length in **1** is 2.130 (17) Å. The only appropriate comparisons are with neutral O-donor ligands in six-coordinate species. In $[VO(Me_2SO)_5]^{2+}$ [40] the four V(IV)–O

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bond lengths cis to the oxo ligand average to 2.015 (24) Å. The two V(III)–O distances in *mer*-$VCl_3(THF)_3$[41] are 2.061 (8) Å for the trans bonds and 2.102 (3) Å for the bond trans to a chloride. In two salts of *trans*-$[VCl_2(H_2O)_4]^+$,[42a,b] the V(III)–O distances are 1.96–2.02 Å, and in one salt of $[V(H_2O)_6]^{3+}$, these distances average to 1.995 (4) Å.[42c] Bond lengths in *trans*-$[VCl_2(H_2O)_2(THF)_2]^+$[42d] are 2.013 (3) and 2.034 (3) Å for V(III)–O(THF) and V(III)–O(H_2O), respectively. In the dimer $[V_2(\mu\text{-}Cl)_3(THF)_6]^+$[41,43] and $[V(H_2O)_6]^{2+}$[43b] the mean V(II)–O distances are 2.147 (7) and 2.131 (11) Å, respectively. This information suggests that the V oxidation state in **1** does not exceed V^{3+}, and may be marginally lower. There are no comparison values of lengths of V–O bonds cis or trans to an anionic sulfur ligand.

In cluster **2** coordination at the V atom is completed by a chelating bpy and a DMF solvent molecule. The VS_3N_2O geometry is irregular, as marked by, e.g., the S–V–O/N angles of 161–163° and the (normal) bpy bite angle of 73.9 (2)°. The bpy ligand itself is nearly planar, the dihedral angle of twist about the C(2)–C(2′) bond being 2.3°, and it is roughly coplanar with the core face VFe(2)S(1,2) (dihedral angle 12.8°). The length of this bond (1.481 (9) Å) is indistinguishable from that in the free ligand (1.490 (3) Å[44]), indicating that any V → bpy back-donation is not structurally detectable. This bond is observably shortened (by as much as 0.08 Å) when bpy is bound to a strong π-donor.[44,45]

The V–N distances in **2** are 0.04–0.08 Å longer than those cis to the multiply bound ligand in the V(V) complexes V(NCl)(bpy)Cl_3[46] (2.130 (6) Å) and $[VO(O_2)_2(bpy)]^-$[47] (2.151 (2) Å). The results indicate an oxidation state below V^{5+}, a matter emphasized by the V–O(1) bond length of 2.112 (4) Å, which is close to those in **1**.

Cluster **3** contains a chelating dmpe ligand and has a VS_3P_2N coordination unit that is distorted from octahedral geometry in much the same way as is the unit in **2**. The dmpe bite distance of 3.148 (5) Å is close to that in the Mo cluster **4** and is otherwise normal. The bite angle of 78.0 (1)° falls in the established range of 74–86° for dmpe complexes and is the same as that in **4**. The mean V–P distance of 2.500 (6) Å is at the short end of the 2.51–2.55 Å range of V(II,III)–P bond lengths in five- or six-coordination.[48] Like one form of **4**,[20] the V–dmpe chelate ring adopts the "asymmetric" skew (near-half-chair) conformation[49] that is disordered over the two enantiomeric forms. In conformation 1 the C atom deviations from the VP_2 plane are +0.193 and –0.419 Å with a PCCP torsional dihedral angle of +47.7°; these values in conformation 2 are +0.574 and –0.138 Å and –40.9°. Conformation 1 is shown in the stereoview of Figure 4. Conformational disorder of the sort encountered here is not at all uncommon in dmpe complexes.[50] Methyl groups above the VP_2 plane are within van der Waals contact (≤3.51 Å) of core atom S(4).

Coordination is completed by an acetonitrile molecule bound in an end-on, slightly nonlinear fashion with V–N(1) = 2.158 (10) Å and V–N(1)–C(7) = 176 (1)°. Precise V–NCMe bond distances are in short supply. The distance in **3** appears to be longer than that in $VOCl_3(MeCN)$[51] (2.098 (2) Å, cis to oxo) but is not readily distinguished from that in distorted octahedral $[V(MeCN)_6]^{2+}$[52] (range 2.08(1)–2.14(1) Å).

In summary, the configurations of the V coordination units in **1**–**3** follow from the near invariance of core structure and the angular restrictions of the chelating ligands. Attempts to utilize terminal bond lengths as a rough index of V oxidation state, and therewith core charge distribution, are perhaps meaningful only with the V–O bonds of **1** and **2**, where comparative results indicate a value of, or somewhat below, V^{3+}. We have previously observed that in some Mo clusters (**4**,[20] $[MoFe_3S_4(SEt)_4(dmpe)]^-$,[20] $[MoFe_3S_4(S\text{-}p\text{-}C_6H_4Cl)_4(al_2cat)]^{3-}$[19]) terminal bond lengths to unidentate ligands are rather long compared to conventional measures in noncluster species with well-defined Mo oxidation states. To the extent that this effect is present in **1**–**3**, bond distances overestimate the extent of V atom reduction. However, the collective information excludes V^{5+}, which is otherwise unlikely because it would require a charge distribution leading to a Fe mean oxidation state less than 2+, in disagreement with isomer shifts. The matter of charge distribution in the $[VFe_3S_4]^{2+}$ core is considered more fully elsewhere in relation to these structural results and to Mössbauer spectroscopic properties.[23]

Isoelectronic Mo Clusters. Some 15 clusters containing the $[MoFe_3S_4]^{3+}$ core have been structurally characterized.[7-20] While core dimensions do not vary largely, the most meaningful comparison with V clusters **1**–**3** involve single cubanes. Of these, **3** and **4** have nearly identical terminal ligation and therefore represent the closest comparison. Selected structural parameters are set out in Table VIII. Among core dimensions, the data show substantial differences only in metal–metal separations, and these are of no obvious chemical significance. Similar comments apply to angles (not listed). Particularly noteworthy is the near invariance of M–S distances in **1**–**4**. These span a range of 0.031 Å. In terms of individual distances, the range is only 2.315 (3)–2.340 (3) Å for **1**–**3** and 2.342 (3)–2.359 (3) Å for **4**.[20] Taking Shannon six-coordinate radii[53] as a basis, the difference in mean values *d*(Mo–S, **4**) – *d*(V–S, **3**) = 0.031 Å must be considered compatible with any combination of the effective oxidation states $Mo^{3+,4+}/V^{3+,4+}$. Of these, the two involving V^{4+} are perhaps less likely since they suggest bond length differences as large as 0.07–0.09 Å. It should be noted that bond length differences in electron-rich environments may be less than predicted from radii, as is the case for the M = Mo^{4+}/V^{4+} pair $[M(mnt)_3]^{2-}$[55] (~0.01 Å, mnt = maleonitriledithiolate(2–)). With the M = Mo^{3+}/V^{3+} pair $M(S_2P(OR)_2)_3$,[56] containing uninegative ligands, the difference is the predicted value (0.05 Å).[57] It would further appear

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that the limiting V^{2+} oxidation state is improbable. Its large radius would predict longer V–S than Mo–S bonds (by 0.10–0.15 Å), contrary to the properties of the clusters in Table VIII and all other isoelectronic Mo clusters.[5]

Summary. The results presented here provide the initial structural characterization of VFe_3S_4 cubane-type clusters. Together with data for **6**,[2] detailed structural information is now available for the $[VFe_3S_4]^{2+}$ core in four ligating environments at the V site. Given this information and that for a larger body of clusters containing the isoelectronic $[MoFe_3S_4]^{3+}$ core, the following results and conclusions are offered.

(1) The core of **1** has idealized C_{3v} symmetry, and those of **2** and **3** approach idealized C_s symmetry arising from the existence of chelate rings at the V sites. Small, unsystematic differences in corresponding structural parameter types occur in **1**–**3** but their core volumes are nearly constant (9.50–9.64 Å^3).

(2) Fe–Cl bond lengths at the trigonally distorted tetrahedral Fe sites suggest a mean oxidation state no higher than $Fe^{2.5+}$ in the electronically delocalized $[VFe_3S_4]^{2+}$ cores, and a marginally lower oxidation state than in $[MoFe_3S_4]^{3+}$ clusters **4** and **5**.

(3) The V site can accommodate three external ligands, including bpy and dmpe, whose chelate dimensions are unexceptional. V–O(DMF) distances are suggestive of the V^{3+} oxidation state. When compared to the Mo–S bond lengths in **4**, the most closely comparable $[MoFe_3S_4]^{3+}$ cluster, and considered in terms of Shannon radii, V–S bond distances in **3** admit the oxidation state possibilities $M^{3+,4+}$ for the isoelectronic cores. The limiting V^{2+} description is unlikely to apply.

The small bond length differences involved in conclusions 2 and 3 are acknowledged, but with attention to the point that the conclusions are consistent with the structures of four V clusters, **1**–**3** and **6**. In dealing with the problem of an approximate description of oxidation states and charge distribution in these clusters, we have chosen to make use of all information available, viz. structural and ^{57}Fe isomer shift results. Metric data at heterometal sites are of value inasmuch as V and Mo are not directly observable by Mössbauer spectroscopy. A more detailed consideration of this problem is provided elsewhere.[23] Lastly, the formation of the heterometal cubane core MFe_3S_4 is likely to be more widespread than with M = V, Mo, and W. Strong evidence has been presented for the existence of a $CoFe_3S_4$ cluster bound in a protein matrix.[61] Considerable interest attends the synthesis of such species and their structural characterization in relation to current heterometal clusters. With the exception of one Mo double cubane,[36] comparative structural chemistry of the latter clusters is confined to isoelectronic and nearly isostructural species.

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

Registry No. **1**, 99688-10-5; **2**, 106589-93-9; **3**, 106589-62-2.

Supplementary Material Available: Tables of X-ray structural data for compounds **1**–**3** giving positional and thermal parameters, calculated hydrogen atom positions, and dimensions of cations and solvate molecules (19 pages); tables of calculated and observed structure factors for **1**–**3** (90 pages). Ordering information is given on any current masthead page.

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(57) The only other comparison between analogous Mo and V complexes with mainly or exclusively anionic sulfur coordination and M–S bond lengths sufficiently precise for the argument involves $Mo(S_2C_6H_4)_3$[58a] (2.367 (6) Å) and $V(S_2C_2Ph_2)_3$[58b] (2.337 (6) Å). In these electronically ambiguous complexes metal oxidation states are not well defined. Bond distance differences predicted from Shannon radii generally become more pronounced with less polarizable ligands. Examples include $[MoCl_4(THF)_2]^-/VCl_3(THF)_3$[41,59] and $M(acac)_3$,[60] for which $d(Mo–O) - d(V–O) = 0.09$ Å.

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