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Comparative Electronic Properties of Vanadium-Iron-Sulfur and Molybdenum-Iron-Sulfur Clusters Containing Isoelectronic Cubane-Type $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ Cores

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The electronic properties of the sets of new cubane-type clusters $[\text{VFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Me})_3(\text{DMF})_3]^-$ (1), $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{MeCN})]^-$ (2), and $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ (3) and $[\text{MoFe}_3\text{S}_4(\text{SEt})_4(\text{dmpe})]^-$ (5), $[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{al}_2\text{cat})(\text{THF})]^{2-}$ (6), and $[\text{MoFe}_3\text{S}_4\text{Cl}_4(\text{dmpe})]^-$ (7) as quaternary ammonium salts were investigated in the solid state. The sets allow comparative properties to be assessed for clusters that contain the isoelectronic and essentially isostructural $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ cores. Also included in the comparison is the previously studied cluster $[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_4(\text{al}_2\text{cat})]^{3-}$ (4). Magnetic susceptibility and magnetization determinations for all clusters at 4.2–300 K and H_0/T up to 28 kOe/K, respectively, establish a $S = 3/2$ ground state with $|D| \leq 3 \text{ cm}^{-1}$. The Curie-Weiss law is followed below ca. 100 K with $\mu = 3.86\text{--}3.94 \mu_B$ and small values of the Weiss constant ($-\theta \leq 2 \text{ K}$). Saturation magnetization is approached at large H_0/T values with $\mu = g_e \mu_B S = 3 \mu_B$. The quartet ground state is also maintained in solution. Zero-field Mössbauer spectra were fit with one (C_3v : 1, 3) or two (C_2 : 2, 4–7) quadrupole doublets depending on the idealized cluster symmetry. Isomer shifts of 1–7 indicate that the Fe atoms in the V clusters are slightly more reduced than those in the Mo clusters at parity of Fe terminal ligands. Shifts and structural data imply that the V oxidation state does not exceed 3+ and the Fe mean oxidation state is very near 2.5+. Magnetic Mössbauer spectra of 1–5 and 7 at fields up to 80 kOe revealed two Fe subsites in the ratio 2:1. These are characterized by observed magnetic hyperfine fields of opposite sign, demonstrating that the $S = 3/2$ ground state arises from antiparallel spin coupling. Differences in corresponding properties—spin state, extent of electron delocalization, and magnetic hyperfine fields in antiparallel spin coupling—are minor. Likewise, structures (reported elsewhere) are highly similar in core dimensions. The two isoelectronic cores are electronically and structurally practically interchangeable. Experimental data are compared with a recent SCF-X α theoretical model of the cluster $[\text{MoFe}_3\text{S}_4(\text{SH})_6]^{3-}$; agreement with predicted properties is generally good.

Introduction

Elsewhere we have provided the syntheses and structural definitions of a new group of heterometal cubane-type clusters containing the $[\text{VFe}_3(\mu_3\text{-S})_4]^{2+}$ core.^{2–4} These clusters include 1–3 (dmpe = 1,2-bis(dimethylphosphino)ethane), which are depicted in Table I: $[\text{VFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Me})_3(\text{DMF})_3]^-$ (1), $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{MeCN})]^-$ (2), $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3]^-$ (3). Their cores are isoelectronic and virtually isostructural with the $[\text{MoFe}_3(\mu_3\text{-S})_4]^{3+}$ core found in a variety of single-^{5–12} and double-cubane^{12–14} clusters. All examples of the former have been prepared in this laboratory. Among these are 4–7 ($\text{al}_2\text{cat} = 3,6\text{-diallylcatecholates}(2-)$), which are illustrated in Table II: $[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Cl})_4(\text{al}_2\text{cat})]^{3-}$ (4), $[\text{MoFe}_3\text{S}_4(\text{SEt})_4(\text{dmpe})]^-$ (5), $[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{al}_2\text{cat})(\text{THF})]^{2-}$ (6), $[\text{MoFe}_3\text{S}_4\text{Cl}_4(\text{dmpe})]^-$ (7). (Numerical designations refer to clusters or compounds containing them, as appropriate.) Earlier studies of the mixed-valence Mo-containing clusters have established a spin quartet ground state and Mössbauer spectroscopic properties indicative of delocalized electronic structures with a Fe mean oxidation state near

2.67+.^{9,12,15}

The recent preparation of the V-containing clusters 1–3 and others of this type,³ together with the substantial body of information on the Mo single cubanes¹² and access to new ligated forms,¹¹ provides a rare opportunity to assess comparative properties of isoelectronic heterometal $\text{MM}'_3\text{S}_4$ species with variant M. Here corresponding electronic properties of cluster sets 1–3 and 4–7 are reported and analyzed. Pertinent structural comparisons are also included; structural results are provided in full detail elsewhere.⁴

Experimental Section

Preparation of Compounds. $(\text{Ph}_4\text{P})[\text{VFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Me})_3(\text{DMF})_3]^{4-}$ (1), $(n\text{-Pr}_4\text{N})[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{dmpe})(\text{MeCN})] \cdot 3\text{MeCN}^4$ (2), $(\text{Me}_4\text{N})[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{DMF})_3] \cdot 2\text{DMF}^4$ (3), $(\text{Et}_4\text{N})_3[\text{MoFe}_3\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Me})_4(\text{al}_2\text{cat})]^{7-}$ (4), $(\text{Et}_4\text{N})[\text{MoFe}_3\text{S}_4(\text{SEt})_4(\text{dmpe})]^{11}$ (5), $(\text{Et}_4\text{N})_2[\text{MoFe}_3\text{S}_4\text{Cl}_3(\text{al}_2\text{cat})(\text{THF})]^{1/2} \cdot \text{Me}_2\text{CO}^8$ (6), and $(\text{Et}_4\text{N})[\text{MoFe}_3\text{S}_4\text{Cl}_4(\text{dmpe})]^{11}$ (7) were prepared by published methods. Compound 2 desolvates extremely readily. It was used in the desolvated form after solvate was removed by pumping in vacuo.

Physical Measurements. All measurements were performed under anaerobic conditions. Mössbauer spectra were determined with use of a constant acceleration spectrometer equipped with a ⁵⁷Co source in a rhodium matrix. Magnetically perturbed spectra were obtained in longitudinally applied fields up to 80 kOe with the source and absorber at 4.2 K. Zero field measurements were made at temperatures between 4.2 and 280 K with the spectrometer operating in the time mode and the source maintained at room temperature. Sample temperature variation was achieved with a Janis Co. "Super-Vari-temp" Dewar system. The spectrometer was calibrated with Fe foil at room temperature. Polycrystalline samples were well dispersed in boron nitride powder and sealed in plastic sample holders with epoxy resin. Magnetic susceptibility and magnetization measurements at applied fields of 5 kOe and up to 50 kOe, respectively, were carried out on polycrystalline samples with use of a SHE SQUID magnetometer operating between 1.8 and 300 K. Finely ground samples of ca. 20–30 mg were tightly packed and sealed (under a He atmosphere) in precalibrated containers. Duplicate runs on compounds 1 and 2 were reproducible to within 3%; single measurements were made on the remaining compounds. Susceptibilities were corrected for diamagnetism by using literature values.¹⁶ Tabulated susceptibility

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Table I. Electronic and Structural Properties of $[\text{VFe}_3\text{S}_4]^{2+}$ Single Cubanes

property	1 ^a	2 ^f	3
δ , ^a mm/s	0.34	0.41 (1), ^e 0.42 (2)	0.44
ΔE_Q , ^a mm/s	1.08	1.37 (1), 0.93 (2)	1.10
Γ , ^a mm/s	0.64	0.42 (1), 0.50 (2)	0.49
$ D $, cm^{-1} ; $ E/D $	1.8; 0.10	2.7; 0.10	^c
μ , ^b μ_B (T, K)	3.96 (4.02), 3.87 (49.8), 3.92 (99.8), 4.13 (249.9)	3.81 (4.20), 3.89 (49.7), 3.92 (100.0), 4.10 (248.0)	3.59 (8.00), 3.88 (50.0), 3.92 (100.0), 4.13 (299.8)
$\chi^M = C/(T - \Theta)$ range, K	4.2–80	4.2–45	8.0–90
C, emu K/mol	1.905	1.893	1.944
Θ , K; μ_{av} , μ_B	-0.71; 3.90	-0.33; 3.89	-1.73; 3.94
Fe–SR/Cl, Å	^c	2.266 (16) ^d	2.266 (8) ^d
V, Å ³	^c	9.50	9.62

^a 77–80 K; vs. Fe metal at 4.2 K. Add 0.12 mm/s to δ to refer to Fe metal at room temperature. ^b Measured values. ^c Not determined. ^d Reference 4. ^e Relative intensities. ^f Parameters of zero field spectrum at 4.2 K (less intense, more intense subsite): $\delta = 0.41, 0.43$ mm/s; $\Delta E_Q = 1.01, 1.33$ mm/s; $\Gamma = 0.44, 0.48$ mm/s. ^g R = *p*-C₆H₄Me.

Table II. Electronic and Structural Properties of $[\text{MoFe}_3\text{S}_4]^{3+}$ Single Cubanes

property	4 ^{d,k}	5 ⁱ	6	7 ^j
δ , ^a mm/s	0.28 (1), ^c 0.31 (2)	0.31 (1), 0.28 (2)	0.39 (1), 0.40 (2)	0.39 (1), 0.38 (2)
ΔE_Q , ^a mm/s	1.76 (1), 1.14 (2)	1.24 (1), 0.74 (2)	1.02 (1), 0.79 (2)	0.98 (1), 0.59 (2)
Γ , ^a mm/s	0.46	0.46 (1), 0.50 (2)	0.38 (1), 0.44 (2)	0.38 (1), 0.44 (2)
$ D $, cm^{-1} ; $ E/D $	1.3, 0.13	1.8, 0.10	^e	2.0, ~0
μ , ^b μ_B (T, K)	^e	3.74 (4.17), 3.85 (50.0), 3.86 (100.0), 3.95 (249.2)	^e	3.56 (6.10), 3.82 (50.0), 3.84 (100.0), 3.97 (299.7)
$\chi^M = C/(T - \Theta)$ range, K	^e	4.2–80	^e	6.1–100
C, emu K/mol	^e	1.863	^e	1.863
Θ , K; μ_{av} , μ_B	^e	-0.31; 3.86	^e	-1.03; 3.86
Fe–SR/Cl, Å	2.271 (11) ^l	2.254 (10), 2.248 (18) ^{g,h}	2.236 (15) ⁱ	2.204 (5) ^h
V, Å ³	9.56	9.56, 9.57 ^{g,h}	9.37	9.55

^a 77–80 K; vs. Fe metal at 4.2 K. Add 0.12 mm/s to δ to refer to Fe metal at room temperature. ^b Measured values. ^c Relative intensities. ^d Mössbauer data from ref 9. ^e Not determined. ^f Reference 7. ^g Two inequivalent clusters. ^h Reference 11. ⁱ Reference 8. ^j Parameters of zero field spectrum at 4.2 K (less intense, more intense subsite): $\delta = 0.36, 0.41$ mm/s; $\Delta E_Q = 0.74, 1.22$ mm/s; $\Gamma = 0.38, 0.40$ mm/s. ^k R = *p*-C₆H₄Cl. ^l R = Et.

data are available.¹⁷ EPR spectra were recorded at X-band frequencies and ~9 K on a Varian E-109 spectrometer equipped with a Helitran Model LTD-3-110 temperature controller.

Results and Discussion

The electronic properties of clusters 1–7 have been investigated by determination of one or more of the properties of magnetic susceptibility, magnetization, and Mössbauer spectra in zero and applied magnetic fields. This experimental protocol follows closely that employed in our original investigation of the electronic features of MoFe₃S₄ clusters,⁹ which included a thorough study of 4. Data for clusters 1–3 and 4–7 are summarized in Tables I and II, respectively. Note that these clusters contain *isoelectronic* $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ cores.

Magnetic Susceptibilities. Clusters 1–3, 5, and 7 were examined at 4–8 to 300 K. The results for 3 and 7 are reasonably typical and are plotted in Figure 1. Below 90–100 K the two species obey the Curie–Weiss law with quite small Weiss constants ($-\Theta \leq 2$ K). In these intervals the temperature dependence of susceptibility conforms exactly to that required of a $S = 3/2$ ground

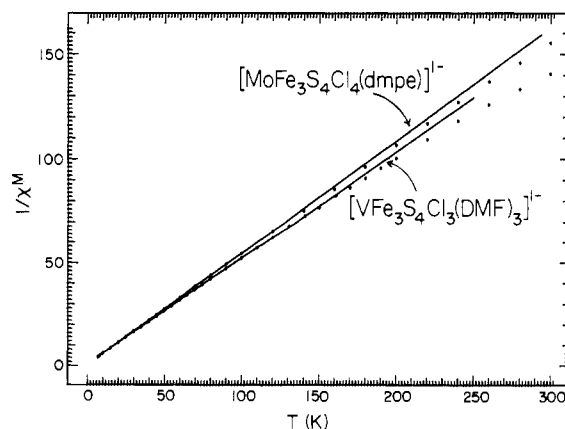


Figure 1. Temperature dependence of the inverse molar susceptibilities in $(\text{emu}/\text{mol})^{-1}$ of compounds 3 (lower line and data points) and 7. Solid lines through the data points are fits to the Curie–Weiss law that use the parameters and apply to the temperature ranges in Tables I and II.

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

state. The same is true of other clusters except that the temperature range of strict Curie–Weiss behavior varies somewhat.

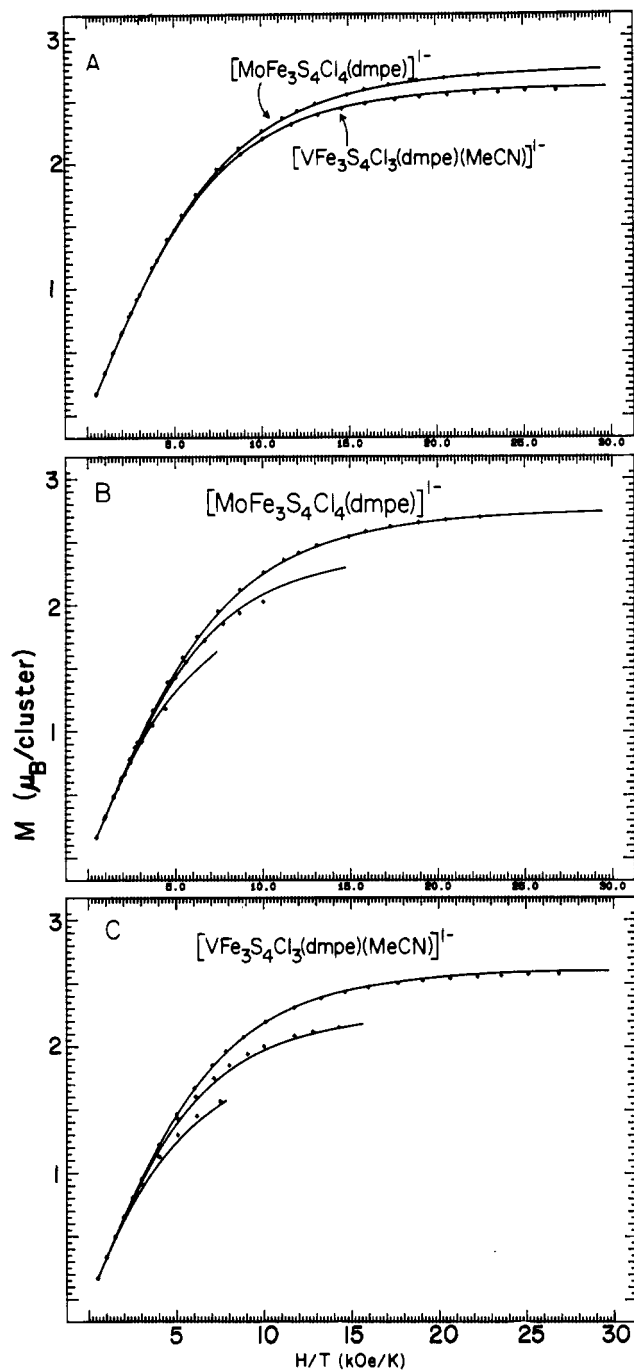


Figure 2. Magnetization ($\mu_B/\text{cluster}$) vs. H_0/T for selected clusters: A, data for compounds **2** and **7** at $H_0 = 50$ kOe and $T = 1.8\text{--}100$ K; B, data for compound **7** at $H_0 = 50, 25,$ and 12.5 kOe and $T = 1.8\text{--}100$ K; C, data for compound **2** under the same conditions as in B. From top to bottom the curves in parts B and C are for decreasing field. Solid lines through data points are theoretical fits for $S = 3/2$ that use eq 1 and the $|D|$ and $|E/D|$ parameters in Tables I and II.

These ranges, Curie constants, and Θ values are given in Tables I and II. The nature of deviation from linear behavior for all clusters is consistent with the occupancy of states with $S > 3/2$ or with a small TIP contribution. Further, the quartet ground state is maintained in solution, as seen from the magnetic moments of **2** ($4.25 \mu_B$, MeCN) and **3** ($4.18 \mu_B$, DMF) at 297 K.³ These are in good agreement with the solid state values of $4.10 \mu_B$ for **2** at 248 K (the highest temperature of measurement) and $4.13 \mu_B$ for **3** at 300 K. We have shown earlier that the iso-electronic Mo clusters also have quartet ground states in solution^{5–8,11} (e.g., for **7** $\mu = 4.12 \mu_B$ in MeCN at 297 K).

Magnetization. This property was determined for V clusters **1** and **2** and Mo clusters **5** and **7**. The behaviors of **2** and **7** at

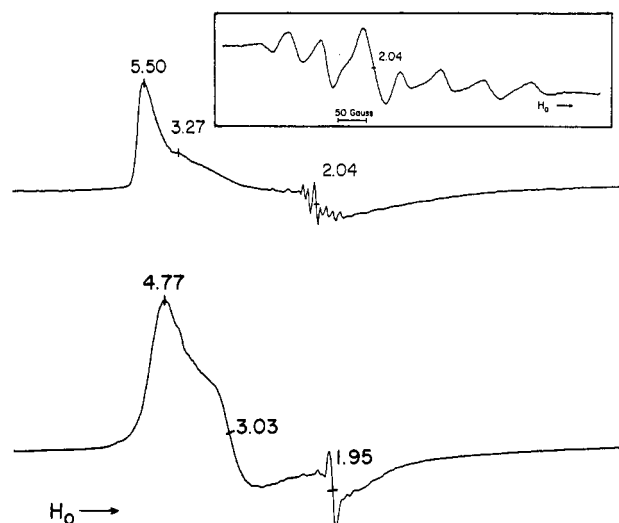


Figure 3. X-Band EPR spectra (~ 10 K) of **1**: (top) ~ 30 mM in DMF; (bottom) polycrystalline solid. Both spectra were recorded at 1-mW microwave power with a 32-G modulation amplitude. Selected g values are indicated. The inset above the solution spectrum is an expansion of the $g = 2$ region showing the detail of the ^{51}V ($I = 7/2$) hyperfine interaction.

1.8–100 K and applied fields H_0 up to 50 kOe are shown graphically in Figure 2. Magnetization results were simulated by calculating the spin projection along the magnetic field direction and using the spin Hamiltonian 1 with $S = 3/2$. Here D and E

$$H_e = D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) + g_e\mu_B\vec{H}\cdot\vec{S} \quad (1)$$

are the zero field axial and rhombic splitting parameters, and the remaining symbols have their usual significance.

For an isotropic $S = 3/2$ system ($D = 0$), the magnetization at a given value of H_0/T would be independent of the applied field. However, when $D \neq 0$ this condition does not necessarily hold and nested magnetization curves as those in Figure 2B,C are obtained at different applied fields. The clusters examined here afforded magnetization behavior that could be well simulated over the entire H_0/T range—from the Curie (small H_0/T) to the saturation region (large H_0/T)—with relatively small D values ($|D| < 3 \text{ cm}^{-1}$). The values of $|D|$ and $|E/D|$ in each case were determined by a least-squares fit of eq 1 to the data. The fitting program used a simplex algorithm and allowed for simultaneous fits of data for three applied fields. The values of $|E/D|$ obtained by this procedure were generally small ($|E/D| \sim 0.1$); however, the magnetization is not very sensitive to $|E/D|$. For cluster **7**, the experimental data were corrected for the molecular exchange field with use of the Weiss constant Θ and equations given elsewhere.¹⁸ This correction was unnecessary for the other compounds. Parameters from the fits are collected in Tables I and II.

All clusters examined show saturation magnetization approaching $\mu = g_e\mu_B S = 3\mu_B$, a behavior previously demonstrated for **4**.⁹ The accurate fit of the data on the assumption of a quartet ground state (Figure 2) further confirms the $S = 3/2$ nature of these clusters. Retention of this ground state in solution, shown above by magnetic susceptibility results, is again confirmed by a magnetization study of **4** in acetonitrile solution (~ 30 mM). The data (not shown) could be satisfactorily fit by using the Hamiltonian (1) with $|D| = 2.3 \text{ cm}^{-1}$ and $|E/D| = 0.10$.

EPR Spectra. EPR spectra were obtained on polycrystalline solid and ~ 30 mM DMF solution samples of V clusters **1–3** and Mo clusters **5** and **7** at ~ 10 K. The solution- and solid-state spectra of **1** are representative and are shown in Figure 3. The spectra are consistent with a $S = 3/2$ ground state; however, there are differences in the degree of rhombicity between solution and solid states. Magnetic hyperfine structure due to 99.8% abundant

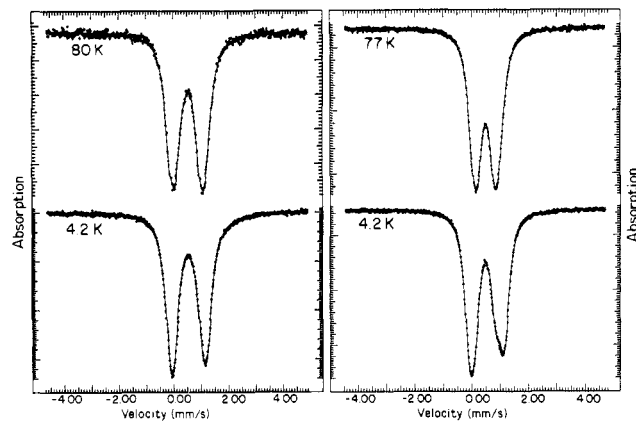


Figure 4. Zero field Mössbauer spectra of compounds **2** (left) and **7** (right) in the solid state at 4.2 and 77 or 80 K. Solid lines through data points are least-squares fits to the spectra based on the parameters in Tables I and II.

^{51}V ($I = 7/2$) is apparent in the $g = 2$ region of the solution spectrum but less apparent in the polycrystalline sample. The ^{51}V hyperfine structure implies that a significant portion of the cluster 3d electron density is localized at the V site. The diminished hyperfine structure in the polycrystalline sample may be due to intercluster exchange interactions or other perturbations in the solid state.

Mössbauer Spectra. The Mössbauer spectroscopic properties of V clusters **1–3** and Mo clusters **5–7** were investigated at 4.2–280 K in zero applied field and in longitudinal magnetic fields up to 80 kOe at 4.2 K. Magnetically perturbed spectra of **6** were not determined.

Zero Field Spectra. The zero field spectra of **2** and **7** at 77–80 K are representative and are shown in Figure 4 together with spectra at 4.2 K. At about 80 K and above, all clusters exhibit a broadened, symmetric quadrupole doublet, which becomes increasingly asymmetric as the temperature is decreased below 80 K. At 80 K, least-squares fits to the spectra of **2** and **7**, which contain V-dmpe and Mo-dmpe chelate rings, respectively, were investigated with no parameter constraints. Best fits gave a ~2:1 site ratio, consistent with effective C_s symmetry, which is also evident in the crystal structure of **2** at ambient temperature.⁴ The spectra of **5** and **6**, also chelated clusters, were treated with this same site ratio. Mirror symmetry in **6** is crystallographically imposed.⁸ Trigonal symmetry was assumed for **1** and **3** and is closely approached by the latter cluster in the crystalline state at room temperature.⁴ All spectra were fit with the electric field gradient (efg) parameter $\eta = 0$. At 4.2 K the spectra of **2** and **7** were fit without parameter constraints. Again best fits gave a 2:1 site ratio. Other clusters showed substantial line broadening at this temperature, presumably a consequence of intermediate spin relaxation. Because of this effect, spectra of the entire set of clusters are best compared at 77–80 K. Isomer shifts (δ), quadrupole splittings (ΔE_Q), and linewidths (Γ) derived from spectral fits are listed in Tables I and II.

In the present context, the property of primary interest in the zero field spectra is the isomer shift. Since this property depends on s-electron densities at the Fe nuclei, significant dependencies on cluster composition and structure must be considered. Structural differences within and between the $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ core units in the various clusters are small and unsystematic⁴ (other than those affording a distinction between idealized C_{3v} and C_s symmetry) and are not readily interpreted in terms of their effects on isomer shifts or quadrupole splittings. The cores are nearly isostructural, a matter reflected by core volumes calculated from atomic coordinates (Tables I and II). These are practically constant in **1–3**, and in **4–7** the smallest volume (**6**) is only 2.1% smaller than the largest volumes. The effect of thiolate vs. chloride coordination in the V clusters can be assessed by the comparison **1/3**, and by comparisons **4/6** and **5/7** in the Mo set. The relationship between isoelectronic V and Mo clusters is best investigated by the comparison **2/7**, whose

clusters differ only in one terminal ligand at the heterometal site. No precisely analogous clusters differing only in the heterometal have yet been prepared.

Substitution of chloride for thiolate always increases the isomer shift, with the changes being 0.10–0.11 mm/s. This is somewhat larger than the average increase of 0.05 (1) mm/s in the pairs $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}/[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-}$ at 4.2 or 77 K.¹⁹ Similar results have been obtained by others.²⁰ This isomer shift difference is larger than that produced by variation in the heterometal, as in $\delta(7) - \delta(2) = 0.02$ and 0.04 mm/s for the two sites in these clusters. Evidently, chloride withdraws more 4s electron density from the Fe atoms than does the more highly polarizable thiolate, resulting in increased isomer shifts.

Earlier we had shown that the isomer shifts of a series of Fe complexes and clusters containing well-defined Fe (mean) oxidation states s in tetrahedral FeS_4 sites follow the empirical linear relationship of eq 2.¹⁵ It is immediately evident that V cluster

$$\delta = 1.44 - 0.43s \quad (2)$$

1 is electronically delocalized inasmuch as its isomer shifts (0.34 mm/s) is an intermediate between the approximate limiting values for Fe(II) (0.60 mm/s) and Fe(III) (0.15 mm/s). The same property obviously applies to **2** and **3** given the ~0.1 mm/s difference in their isomer shifts owing to the presence of chloride. Interpolation of the isomer shifts of $[\text{MoFe}_3\text{S}_4]^{3+}$ single and double cubanes indicated the oxidation state description $\text{Fe}^{2.67+}$ ($2\text{Fe}^{3+} + \text{Fe}^{2+}$) + Mo^{3+} , with the last obtained by difference. The approach is simple and formalistic, and has been appropriately qualified.^{9,15} When applied to **4** and **5**, the same description emerges. The physical meaning is that the Fe atoms in these clusters are slightly more oxidized than those in $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-19}$ (mean $\text{Fe}^{2.5+}$) and certainly more oxidized and reduced than those in $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-21}$ ($\text{Fe}^{2.25+}$) and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-22}$ ($\text{Fe}^{2.75+}$), respectively. A corresponding relationship between chloride-ligated clusters **6** and **7** and $[\text{Fe}_4\text{S}_4\text{Cl}_4]^{2-19}$ (also $\text{Fe}^{2.5+}$) cannot be affirmed from isomer shifts, which are indistinguishable among the three clusters.

Somewhat more direct is a comparison between the isoelectronic V and Mo clusters at parity of Fe terminal ligands. Clusters **1–3** exhibit a small bias toward larger isomer shifts, with the specific comparison **2/7** affording the shift differences noted above. From eq 2, $s = 2.6$ for **1**. We have also utilized structural features of $[\text{VFe}_3\text{S}_4]^{2+}$ clusters to infer oxidation states, although such an approach cannot be notably precise owing to the small differences involved. The following are the principal conclusions from that investigation:⁴ (i) M–S distances in the pair **2/7** are compatible with any combination of effective oxidation states $\text{M} = \text{V}^{3+,4+}/\text{Mo}^{3+,4+}$; (ii) V–O bond distances in **3** indicate that the V oxidation state does not exceed 3+; (iii) mean Fe–Cl distances are consistent with a mean oxidation state no higher than $\text{Fe}^{2.5+}$. These conclusions are drawn solely from structural data and serve to narrow oxidation state possibilities, especially at the heterometal site, which is not observable by Mössbauer spectroscopy. They are subject to some refinement with inclusion of isomer shift data. Thus the V^{4+} state allowed in point i but unlikely on the basis of point ii can be discounted for it would require 3Fe^{2+} , contrary to the observed isomer shifts. The distances in point iii are included in Table I; in addition, the mean Fe–Cl distance in $[\text{VFe}_3\text{S}_4\text{Cl}_3(\text{bpy})(\text{DMF})]^-$ is 2.266 (16) Å.⁴ These bond lengths are longer than those in **6** and **7** (Table II), consistent with

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Table III. Parameters for Magnetic Mössbauer Spectra^a (4.2 K)

compd	subsite ^b	δ , ^c mm/s	ΔE_Q , mm/s	Γ , mm/s	η	A_x , ^d mm/s (H_x) ^e	A_y , mm/s (H_y) ^e	A_z , mm/s (H_z) ^e
1	1	0.29	1.13	0.50	0.46	-0.782 (163)	-0.907 (193)	-0.643 (119)
	2	0.35	-1.35	0.50	0.89	0.991 (-207)	0.969 (-207)	1.297 (-240)
5	1	0.23	1.07	0.57	0.13	-0.828 (173)	-0.687 (146)	-0.635 (118)
	2	0.31	-1.34	0.57	1.00	1.007 (-210)	0.752 (-160)	1.305 (-242)

^a From least-squares-fitting procedure of the spin Hamiltonian 1 to the data with $D = 1.8 \text{ cm}^{-1}$ and $E/D = 0.10$ for both compounds. ^b Subsite number refers to relative intensity. ^c Vs. Fe metal at 4.2 K; to refer to 300 K, add 0.12 mm/s. ^d Magnetic hyperfine parameters for the 14.4-keV excited state of ⁵⁷Fe. ^e Magnetic hyperfine fields in kOe. Negative hyperfine fields oppose the applied field.

somewhat more pronounced Fe(II) character.

We conclude from the collective evidence of Mössbauer and structural data that the Fe atoms in the isoelectronic cores $[\text{VFe}_3\text{S}_4]^{2+}$ and $[\text{MoFe}_3\text{S}_4]^{3+}$ are in very nearly the same state of oxidation. Apparently the Fe atoms in the V clusters are marginally more reduced, on the basis of isomer shifts and Fe-Cl bond lengths. Thus in the comparison **2**(2.250 (3)-2.282 (3) Å)/**7**(2.198 (4)-2.208 (4) Å), the Fe-Cl distances occur in the indicated distinct ranges and, as the isomer shifts, are consistent with a greater degree of reduction of the Fe atoms in **2**. We prefer these qualitative statements to a specification of oxidation states for the V clusters. Owing to the lack of suitable compounds, a relationship analogous to eq 2 for FeS_3Cl sites is unknown, with the result that Fe oxidation states in these clusters and in **6** and **7** cannot be approximated by similar means.

The existence of heterometal MFe_3S_4 clusters apparently extends beyond those with $\text{M} = \text{V}^{2-4}$ and Mo and W.¹² Recently, strong evidence has been presented for a CoFe_3S_4 cluster bound in a protein environment,²³ although its detailed structure is not known. The oxidized form of this cluster appears to be $[\text{CoFe}_3\text{S}_4]^{2+}$, which is isoelectronic with the well-known core $[\text{Fe}_4\text{S}_4]^+$. Isomer shifts and the EPR spectrum indicate an electronically delocalized structure and suggest the approximate oxidation state description $3\text{Fe}^{2.67+} + \text{Co}^{2+}$.

Magnetically Perturbed Spectra. The magnetic spectra of V clusters **1-3** and Mo clusters **5** and **7** were determined in fields up to 80 kOe at 4.2 K. Those of **1** and **5** are typical and are depicted in Figure 5. Two inequivalent subsites with a 2:1 intensity ratio are resolved at $H_0 = 60$ and 80 kOe. The splitting of the more intense and less intense subsite decreases and increases, respectively, with increasing applied field. This indicates antiparallel spin coupling in the clusters to produce the $S = 3/2$ ground state, in which the magnetic moments of the Fe atoms of the more and less intense subsites are parallel and antiparallel, respectively, to H_0 . This is the same spin-coupling arrangement found earlier for **4**.⁹

The magnetic spectra of **1** and **5** were least-squares fitted by using the spin Hamiltonian 1 with D and $|E/D|$ determined by fits to the magnetization data. The Mössbauer fitting program was a modified version of the Lang-Dale minimizer.²⁴ The fits were performed in the limit of fast relaxation with the assumption of a 2:1 subsite ratio and a powder sample with random crystallite orientation. Thus each subsite had magnetic hyperfine fields proportional to the thermal average of the spin expectation value with the applied field in a given direction. The quantization axis system was taken to be that of the EFG assumed parallel at the two subsites. For each site the variable parameters in the calculation were the magnetic hyperfine coupling constants A_i ($i = x, y, z$), the EFG asymmetry parameter η , and the sign of V_{zz} . The magnitudes of the quadrupole splittings and isomer shifts were fixed by the zero field spectra. The fits to the spectra of **1** and **5** are shown in Figure 5, and the fitted parameters are collected in Table III. The regions of the spectrum where deviations from the theoretical line are observed may arise from intermediate relaxation phenomena²² or partial packing effects in the polycrystalline sample. The magnetic spectra of the other clusters are very similar to those in Figure 5 and were not treated in detail.

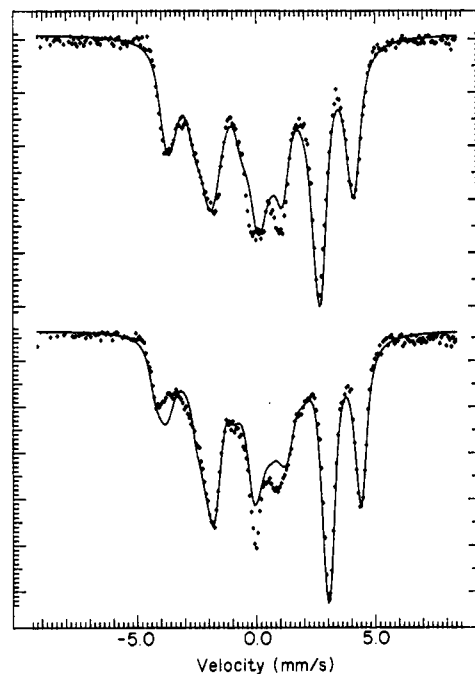


Figure 5. Magnetically perturbed Mössbauer spectra at $H_0 = 80$ kOe and 4.2 K: top, compound **5**; bottom, compound **1**. The solid lines are least-squares fits to the data with use of the parameters in Table III.

Both subsites in the V clusters have slightly larger observed magnetic hyperfine fields than the corresponding subsites in Mo clusters for both chloride and thiolate terminal ligands. This may be due to somewhat different configurations of local spins that are coupled to form the total spin of the cluster, a matter consistent with the isomer shift differences noted above. In any event, the spectra and fits show that the clusters examined (and by inference all V and Mo clusters with isoelectronic cores) have antiparallel-coupled Fe atoms with similar magnetic hyperfine coupling constants A_i .

The experimental results may be compared with the theoretical SCF- $X\alpha$ calculations by Cook and Karplus²⁵ on $[\text{MoFe}_3\text{S}_4(\text{SH})_6]^{3-}$. The calculated ground state under C_3 symmetry has $S = 3/2$, in agreement with experiment. The majority Fe atoms (α -Fe in their nomenclature) have positive spin density and the minority Fe atom (β -Fe) has negative spin density. The calculations further predict similar charge and spin densities at the Fe atoms, each with a local spin of ~ 1.5 . This indicates that all Fe atoms have about equal core polarization contributions to their internal hyperfine fields and that the differences observed must reflect the spin coupling schemes in these species and possibly differences in orbital and dipolar contributions. Although spin-coupling models have been utilized effectively to calculate local spin densities in localized valence clusters such as those containing the $[\text{Fe}_2\text{S}_2]^{2+}$ and $[\text{Fe}_3\text{S}_4]^{26-28}$ cores, they have been less suc-

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successful when applied to delocalized mixed-valence systems such as $[\text{Fe}_4\text{S}_4]^+$ clusters.²⁹ Other calculated quantities including the magnitudes of quadrupole splitting constants, asymmetry parameters, and isomer shifts are in good agreement with experiment. The theoretical indication that α -Fe atoms are "more reduced" than β -Fe atoms is upheld by parameter-unrestricted fits of the 4.2 K spectra of clusters **2** and **7** and by inspection of the magnetically perturbed spectra. At higher temperatures, this pattern does not always hold. The calculated energy level scheme also suggests that reduction of the Mo clusters to the $[\text{MoFe}_3\text{S}_4]^{2+}$ level will produce a $S = 2$ state, in agreement with experiment.^{9,15} Irreversible reduction of the V clusters³ has thus far prevented determination of the spin state of the $[\text{VFe}_3\text{S}_4]^+$ unit.

This research has afforded a reasonably detailed description of the electronic properties of a new set of clusters containing the $[\text{VFe}_3\text{S}_4]^{2+}$ core, as well as providing additional data for clusters with the isoelectronic $[\text{MoFe}_3\text{S}_4]^{3+}$ core. As this is a comparative study, we have tended to examine the results for differences between cluster sets **1-3** and **4-7**. However, in terms of the chemically most significant properties—spin state, existence and extent of electron delocalization, parallel vs. antiparallel spin

coupling and magnetic hyperfine coupling constants, as well as geometric structures⁴—the similarities far outweigh the differences. The two core units are electronically and structurally practically interchangeable.

The interchangeability of Mo and V in these complexes takes on added significance with the recent finding of a V-nitrogenase system.³⁰ It will be interesting to see if the similarities that exist between Mo single cubanes and the Mo cofactor of nitrogenase—namely heterometal coordination environment and overall spin state—are also found between the V single-cubane clusters and the V-containing nitrogenase.

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Supplementary Material Available: Tabulated magnetic susceptibility data for compounds **1-3**, **5**, and **7** (6 pages). Ordering information is given on any current masthead page.

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Comparison of the Molecular and Electronic Structures of $(\mu\text{-Oxo})\text{bis}[(5,10,15,20\text{-tetraphenylporphyrinato})\text{iron(III)}]$ and $(\mu\text{-Oxo})\text{bis}[(7,8\text{-dihydro-}5,10,15,20\text{-tetraphenylporphyrinato})\text{iron(III)}]$

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The molecular and electronic structures of $(\mu\text{-oxo})\text{bis}[(5,10,15,20\text{-tetraphenylporphyrinato})\text{iron(III)}]$, $[\text{Fe}(\text{TPP})_2]\text{O}$, and $(\mu\text{-oxo})\text{bis}[(7,8\text{-dihydro-}5,10,15,20\text{-tetraphenylporphyrinato})\text{iron(III)}]$, $[\text{Fe}(\text{TPC})_2]\text{O}$, show many similarities and one significant difference. The compound $[\text{Fe}(\text{TPC})_2]\text{O}\cdot 4\text{CHCl}_3$ crystallizes in space group $D_{2h}^2\text{-Pnna}$ ($Z = 4$) with unit cell dimensions $a = 15.467$ (4) Å, $b = 16.196$ (4) Å, $c = 32.889$ (8) Å, and $V = 8239$ (2) Å³. The structure has been refined to an R index on F_o^2 of 0.0726 on the basis of 4741 reflections (142 K) and 472 variables. The chlorin complex has a crystallographically imposed twofold axis passing through both iron atoms and the $\mu\text{-oxo}$ bridge, requiring each chlorin macrocycle to be at least twofold disordered. The chlorin macrocycles have larger cores and are more ruffled than the porphyrin macrocycles of the literature compound $[\text{Fe}(\text{TPP})_2]\text{O}$, but other structural features such as Fe-O-Fe angles, Fe-O distances, and Fe out-of-plane displacements are virtually the same for the two compounds. The gross magnetic behavior and Mössbauer spectra are nearly identical for the two compounds: $-2J$, δ , and ΔE_Q are 265 cm⁻¹, 0.40 mm/s, and 0.70 mm/s for $[\text{Fe}(\text{TPC})_2]\text{O}$ and 258 cm⁻¹, 0.41 mm/s, and 0.67 mm/s for $[\text{Fe}(\text{TPP})_2]\text{O}$, respectively. Despite all of these similarities, ¹H NMR spectra indicate that unpaired spin density may be distributed differently in the two compounds.

Introduction

Our interest in the chemical,²⁻⁵ structural,^{4,6} and magnetic^{2,6-8} properties of iron hydrophorphyrins⁹ (chlorins and isobacterio-

chlorins) stems from their occurrence in a wide variety of heme proteins and enzymes.¹⁰⁻¹² Magnetic properties are of funda-

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- (9) (a) The fully unsaturated porphyrin macrocycle contains 11 conjugated double bonds. A variety of compounds are known in which the macrocycle porphyrin skeleton is retained while one or more double bonds are removed. These compounds are formally derived from porphyrins by hydrogenation and are, therefore, commonly called hydrophorphyrins. Note that the generic term hydrophorphyrin refers to compounds in which the substituent(s) added across the double bond(s) are hydrogen atoms, alkyl or substituted alkyl groups, alkylidene groups, or oxygen or sulfur atoms: Scheer, H. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1978; Vol. II, pp 1-44. Scheer, H.; Inhoffen, H. H. *Ibid.*, pp 45-90. (b) Chlorins, which contain 10 conjugated double bonds, are porphyrins that have interrupted conjugation at vicinal C₂ atoms of a single pyrrole ring. The affected ring is called a pyrrole ring. Isobacteriochlorins, which contain nine conjugated double bonds, are porphyrins that contain two adjacent pyrrole rings.
- (10) See ref 6 and references therein.