

of the $W(CO)_4(PPh_3)$ moiety does not pull the sulfur away from the cluster any farther. The geometry about the sulfido ligand approximates very closely that of a square pyramid, but slight differences in the Os-S distances and W-S-Os angles remove a rigorous C_{4v} symmetry.⁹

The question of the orbital hybridization at the pentacoordinate sulfido ligand is one that cannot be answered in detail at this time, but a significant contribution from the sulfur d-orbital set would seem to be very likely.

The existence of the tungsten-sulfur coordinate bond in 2 strongly suggests the existence of a lone pair of electrons on the quadruply bridging sulfido ligand in 1. The pentacoordinate structural form of the sulfido ligand observed in 2 further extends the range of its known coordination forms and further demonstrates its versatility as a ligand.¹ It is believed that these factors can play key roles in the use of sulfido ligands to stabilize cluster complexes and to facilitate their synthesis by serving as sites for metal agglomeration.^{1,13,14}

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Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters, interatomic distances, selected interatomic angles and structure factor amplitudes (53 pages). Ordering information is given on any current masthead page.

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Demonstration of Alternative Spin States in Clusters Containing the Biologically Relevant $[Fe_4S_4]^{1+}$ Core

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The clusters $[Fe_4S_4(SR)_4]^{3-}$,¹⁻⁶ containing the cubane-type odd-electron $[Fe_4S_4]^{1+}$ core, are analogues of reduced clusters in ferredoxins and other Fe-S proteins and enzymes.^{7,8} Standard biological clusters of this type have spin-doublet ground states,

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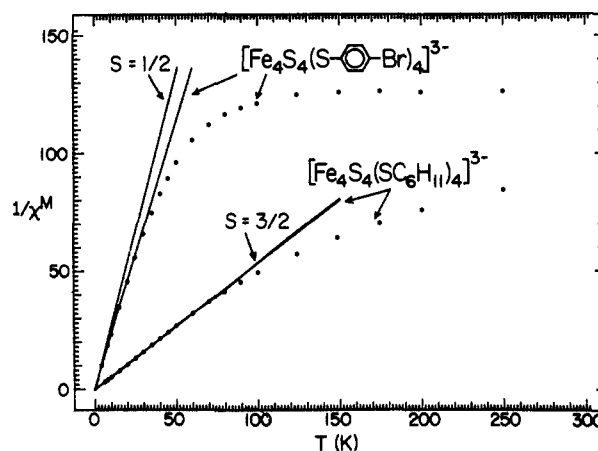
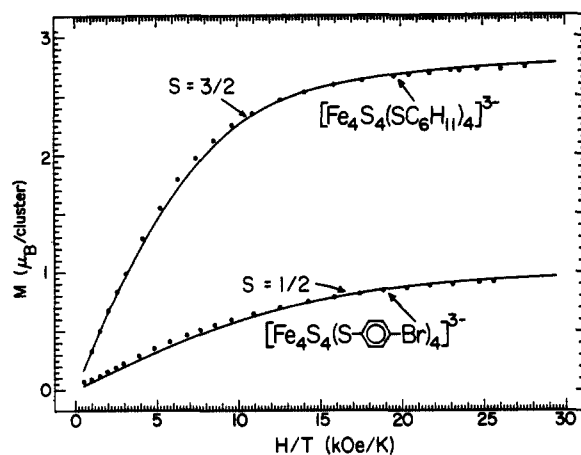


Figure 1. Magnetic properties of $(Et_4N)_3[Fe_4S_4(S-p-C_6H_4Br)_4]^{3-}$ and $(Et_4N)_3[Fe_4S_4(SC_6H_{11})_4]^{3-} \cdot 4MeCN$. Upper: magnetization behavior at $H_0 = 50$ kOe and $T = 1.8-100$ K. Lower: temperature dependence of the reciprocal molar susceptibility at $H_0 = 5$ kOe; the behaviors of $S = 1/2$ and $3/2$ Curie paramagnets are indicated. Solid lines are theoretical fits¹⁶ to the magnetization data.

characteristic EPR spectra centered around $g \sim 1.94$ which integrate to ca. one spin per cluster, and consistent Mössbauer spectral features. Evidence is accumulating that one or more varieties of nonstandard clusters exist, whose unconventional nature is evidenced in EPR and Mössbauer spectral properties and sometimes in redox potentials. Examples include "P-clusters" of the FeMo protein of nitrogenase⁹ and the clusters in *B. subtilis* glutamine phosphoribosylpyrophosphate amidotransferase,¹⁰ Se-reconstituted clostridial ferredoxin,¹¹ and the Fe protein of nitrogenase.^{9,12,13} Indeed, in the crystalline state, analogue clusters $[Fe_4S_4(SR)_4]^{3-}$ do not possess uniform core structures^{1,5,6} or electronic properties,^{3,4} suggesting possibly similar behavior by biological clusters. One particularly arresting aspect of certain analogues is their magnetic behavior, which indicates population of low-lying states of a spin manifold with $S > 1/2$,¹⁴ a matter reexamined here.¹⁵

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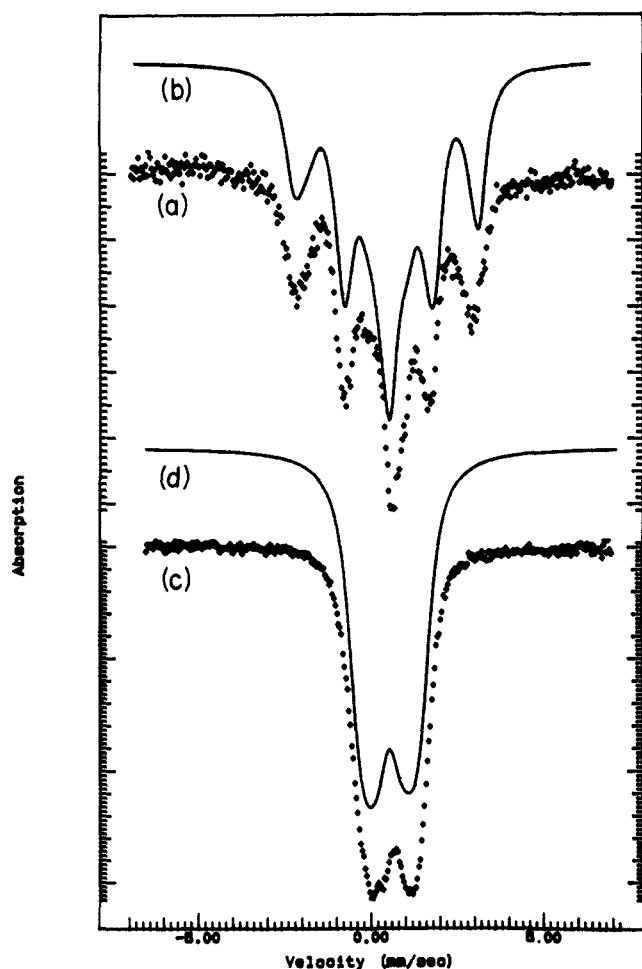


Figure 2. Mössbauer spectra of polycrystalline $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Br})_4]$ (a) and $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_{11})_4]\cdot 4\text{MeCN}$ (c) at 4.2 K and $H_0 = 60$ kOe. (b) Simulation of spectrum (a) with $\delta_1 = 0.43$ mm/s, $\Delta E_{Q1} = 0.94$ mm/s, $\Gamma_1 = 0.58$ mm/s, $H_{n(1)} = -52$ kOe, $\delta_2 = 0.48$ mm/s, $\Delta E_{Q2} = -2.07$ mm/s, $\Gamma_2 = 0.58$ mm/s, and $H_{n(2)} = 102$ kOe (1:1 ratio of sites 1 and 2). (d) Simulation of spectrum (b) with $\delta_{1,2} = 0.42$ mm/s, $\Delta E_{Q1,2} = 1.10$ mm/s, $\Gamma_{1,2} = 0.62$ mm/s, $|H_{n(1)}| = 15$ kOe, and $|H_{n(2)}| = 30$ kOe (1:1 ratio of sites 1 and 2). Experimental and simulated spectra are offset from each other. Isomer shifts are quoted with respect to Fe metal at 4.2 K (add 0.12 mm/s to refer to Fe metal at room temperature).

Of the many $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$ salts scrutinized in this and prior work,³⁻⁵ two are of immediate significance: $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{S}-p\text{-C}_6\text{H}_4\text{Br})_4]$ ⁵ (cluster 1) and $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_{11})_4]\cdot 4\text{MeCN}$ (cluster 2; $\lambda_{\text{max}}(\epsilon_M)$ 275 (sh, 24 000), 364 (15 000) nm; $^1\text{H NMR}$ (CD_3CN) 27.2 (SCH), 4.43 (SCH(CH_2)₂) ppm). The latter was obtained by the single-step synthesis of reduced clusters⁵ as black, easily desolvated crystals (61%). Magnetic properties (Figure 1) are strikingly different. Susceptibilities accurately follow the Curie-Weiss law $\chi^M = C/(T - \theta) = 0.438/(T + 0.291)$ (1, 4.2–15 K, $\mu_{\text{av}} = 1.87\mu_B$) and $1.860/(T - 0.438)$ (2, 4.2–70 K, $\mu_{\text{av}} = 3.86\mu_B$); Curie constants are close to theoretical values for $S = 1/2$ (0.375) and $3/2$ (1.876 emu K/G) states. The magnetization of 1 follows a Brillouin function of $S = 1/2$,^{16a} and that of 2 was simulated by calculating the spin projection along the magnetic field direction by use of a spin Hamiltonian with $S = 3/2$.^{16b} Best

results were obtained with $|D| = 1.6 \text{ cm}^{-1}$ and $|E/D| = 1/3$. The latter value is consistent with the solid-state EPR spectrum (vide infra). Both clusters approach saturation magnetizations at high H/T . Deviations of χ^M from Curie behavior at higher temperatures imply population of excited states of higher spin.

The zero-field Mössbauer spectrum of 1 contains two overlapping quadrupole doublets,⁵ and that of 2 consists of a broadened doublet indicative of (at least) two overlapping subspectra. Results at $H_0 = 60$ kOe (Figure 2) show that the spectrum of 1 contains two subspectra in 1:1 intensity ratio and magnetic hyperfine fields $\bar{H}_{\text{hf}} = \bar{H}_n - \bar{H}_0$ ^{16c} that increase and decrease with increasing H_0 in a manner characteristic of antiparallel spin coupling to produce the $S = 1/2$ ground state.¹⁸ From $\bar{H}_{\text{hf}} = H_{\text{hf}}^0 \langle S_z \rangle / S$ we obtain the saturation magnetic hyperfine fields $H_{\text{hf}}^0 = +57$ and -150 kOe for the two magnetic subsites.¹⁹ The behavior of 2 is entirely different: spectral splitting is only $\sim 1/4$ as large, and spectral components are not resolved. The 60 kOe spectrum can be simulated assuming two subspectra with magnetic fields at the nucleus $|\bar{H}_n| = 15$ and 30 kOe. The spectra are consistent with both hyperfine fields being negative. Proceeding similarly, we obtain $H_{\text{hf}}^0 = -34$ and -52 kOe for the subsites. The very different magnetic hyperfine fields in the two clusters are a consequence of the coupling of local spins to produce the total spin of the cluster. Previously we had shown, using a simple isotropic Heisenberg exchange Hamiltonian,^{16d} that ground-state spins $S = 1/2$, $3/2$, and higher are possible, depending on the relative magnitudes of two exchange integrals J_{ij} coupling Fe atoms i and j .¹⁴

Polycrystalline 1 exhibits a rhombic EPR spectrum with $g \approx 1.89$, 1.93, and 2.06 and no other signals. The spectrum of solid 2 resembles that of $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{-}p\text{-C}_6\text{H}_4\text{OME})_4]$ ⁴ and contains an intense feature at $g \approx 5.25$. Thus a resonance in the low-field region around $g = 5$ is associated with the $S = 3/2$ state. Previously we had shown that, regardless of solid-state electronic features, $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$ clusters in solution exhibited virtually identical axial EPR spectra,⁴ as exemplified by 1 in DMF ($g = 1.92$, 2.04). With alkyl thiolate clusters such as 2 ($g = 1.92$, 2.01, 5.2 (br) in DMF), the solution spectra indicate a mixture of $S = 1/2$ and $3/2$ clusters, the latter being securely identified from the solid-state spectrum.

The present results, obtained with fully identified compounds, unequivocally demonstrate that *different spin ground states of the $[\text{Fe}_4\text{S}_4]^{1+}$ core can be realized*, here $S = 1/2$ (1) and $S = 3/2$ (2), and that a quartet cluster in the solid state can be transformed to a mixture of quartet and doublet clusters in solution. These results fully support interpretation of the EPR and Mössbauer spectra of properties of the reduced Fe protein of nitrogenase as a $S = 1/2$ and $3/2$ mixture of clusters.^{12,13} For example, the EPR spectrum of 2 is strikingly similar to that of this protein in the presence of denaturants.¹² It is now clear that the $[\text{Fe}_4\text{S}_4]^{1+}$ cores of reduced synthetic analogues and proteins are subject to facile and unpredictable structural, and hence electronic, variations by factors external to the clusters themselves, viz., crystalline packing forces acting on thiolate substituents and protein conformation. Thus the core of 1 has C_2 symmetry,⁵ and three other arrangements of long and short Fe-S core bonds are known.^{1,3,6} Future reports will describe the structure of the *pure* spin-quartet cluster 2 and examine more fully than heretofore structure-property relationships of reduced clusters. There are a number of clusters (e.g., $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]$) with saturation magnetization between 1 and $3 \mu_B$ /cluster and magnetic hyperfine constants quite different from those of 1 and 2. In these cases magnetic properties in the solid state cannot be interpreted in terms of $S = 1/2 + 3/2$ mixtures (unlike the nitrogenase Fe protein¹²), implying mixed-spin

(15) Experimental: Mössbauer spectra were obtained with a constant acceleration spectrometer in zero field and in 60- and 80-kOe longitudinal fields; magnetic measurements were made in fields up to 50 kOe by using an SHE SQUID magnetometer (results corrected for diamagnetism); EPR spectra were measured at X-band frequencies and ~ 8 K.

(16) (a) $M = g\mu_B S B_{1/2}(g\mu_B S H_0 / kT)$, where the applied field H_0 was corrected for the molecular exchange field.¹⁷ (b) $H = g\mu_B \bar{H} \cdot \bar{S} + D(S_z^2 - 1/3 S(S+1)) + E(S_x^2 - S_y^2)$; the angle between \bar{H} and \bar{S} was averaged for a polycrystalline sample. (c) For 1: at 4.2 K and 60 kOe; $\bar{H}_n = +102$ and -52 kOe; $\langle S_z \rangle = 0.37$; (d) $H_{\text{ex}} = -\sum_{i,j} J_{ij} \bar{S}_i \bar{S}_j$.

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(19) These magnetic hyperfine fields are based on an effective field model best simulation of the experimental spectrum with the minimum number of parameters; i.e., assuming an isotropic magnetic hyperfine interaction and electric quadrupole asymmetry parameter $\eta = 0$. The spectrum can also be simulated with an anisotropic magnetic hyperfine field and $\eta \approx 0.5$, as in, e.g., ref 11a and 12. Under this condition estimates of H_{hf}^0 are increased to ca. +70 and -130 kOe for the two subsites.

