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_{4n} 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.

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 $(Et_4N)_3[Fe_4S_4(S-p-C_6H_4Br)_4]$ and $(Et_4N)_3[Fe_4S_4(SC_6H_{11})_4]$ -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 = $\frac{1}{2}$ and $\frac{3}{2}$ 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 Sereconstituted 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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Meorption



Of the many $[Fe_4S_4(SR)_4]^{3-}$ salts scrutinized in this and prior work,³⁻⁵ two are of immediate significance: (Et₄N)₃[Fe₄S₄(S-p- $C_6H_4Br)_4]^5$ (cluster 1) and $(Et_4N)_3[Fe_4S_4(SC_6H_{11})_4]\cdot 4MeCN$ (cluster 2; λ_{max} (ϵ_M) 275 (sh, 24000), 364 (15000) nm; ¹H NMR (CD_3CN) 27.2 (SCH), 4.43 (SCH $(CH_2)_2$) ppm). The latter was obtained by the single-step synthesis of reduced clusters⁶ 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, $\mu_{av} = 1.87\mu_{B}$) and 1.860/(T-0.438) (2, 4.2–70 K, $\mu_{av} =$ 3.86 $\mu_{\rm B}$); 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 $S = \frac{3}{2}$.^{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 $\chi^{\rm M}$ 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 $\vec{H}_{\rm hf} = \vec{H}_{\rm n} - \vec{H}_{\rm 0}^{16c}$ that increase and decrease with increasing $H_{\rm 0}$ in a manner characteristic of antiparallel spin coupling to produce the S = 1/2 ground state.¹⁸ From $\vec{H}_{hf} = H^0_{hf} \langle \vec{S}_z \rangle / S$ we obtain the saturation magnetic hyperfine fields $H^0_{hf} = +57$ and -150kOe 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 $|\vec{H}_n| = 15$ and 30 kOe. The spectra are consistent with both hyperfine fields being negative. Proceeding similarly, we obtain $H_{\rm hf}^0 = -34$ 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 $g \simeq$ 1.89, 1.93, and 2.06 and no other signals. The spectrum of solid 2 resembles that of $(Et_4N)_3[Fe_4S_4(SCH_2-p-C_6H_4OMe)_4]^4$ 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, $[Fe_4S_4(SR)_4]^{3-}$ 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 $[Fe_4S_4]^{1+}$ 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 $S = \frac{1}{2}$ and $\frac{3}{2}$ 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 $[Fe_4S_4]^{1+}$ 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., $(Et_4N)_3[Fe_4S_4(SCH_2Ph)_4]$) with saturation magnetization between 1 and 3 $\mu_{\rm B}$ /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 $S = \frac{1}{2} + \frac{3}{2}$ 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 acceleration spectrometer in zero retu and in our units to 50 kOe by using an fields; magnetic measurements were made in fields up to 50 kOe by using an SHE SQUID magnetometer (results corrected for diamagnetism); EPR

SHE SQUID magnetometer (results corrected for diamagnetism); EPR spectra were measured at X-band frequencies and ~8 K. (16) (a) $M = g\mu_{\rm B}SB_{1/2}(g\mu_{\rm B}SH_0/kT)$, where the applied field H_0 was corrected for the molecular exchange field.¹⁷ (b) $H = g\mu_{\rm B}\dot{\rm H}\cdot\dot{\rm S} + D[S_z^2 - 1/_3S(S + 1)] + E(S_x^2 - S_y^2)$; the angle between H and z was averaged for a polycrystalline sample. (c) For 1: at 4.2 K and 60 kOe; $\dot{H}_n = +102$ and -52 kOe; $\langle S_z \rangle = 0.37$; (d) $H_{\rm ex} = -\sum_i p_i J_i S_i \cdot S_j$. (17) Ginsberg, A. P. Inorg. Chim. Acta Rev. 1971, 5, 45.

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ground states perhaps produced by significant contributions of nonisotropic exchange coupling.¹⁷ Last, the existence of pure spin-quartet clusters is not an isolated phenomenon. We have also demonstrated this state in, e.g., $(Me_4N)_3[Fe_4Se_4(SPh)_4]$.

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Crossed-Beam Studies of Energy and Angular Distributions of Organometallic Reactions: Decarbonylation of Acetaldehyde by Fe⁺ and Cr⁺

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The energetics and dynamics of the reactions of gas-phase transition-metal ions with organic molecules are topics of active research and speculation at present.^{3,4} In the present work, we report the first crossed-beam studies of gas-phase transition-metal ion chemistry, demonstrating that product kinetic energy and angular distributions probe the potential energy surface topology of simple carbon-carbon bond cleavage reactions. The studies yield information on the lifetimes and stabilities of key intermediates and assess the partitioning of energy in these species. We present results on the direct decarbonylation of acetaldehyde by Fe⁺ and Cr⁺.⁵

$$Fe^+ + CH_3CHO \rightarrow FeCO^+ + CH_3$$

 $\Delta H = -24 \text{ kcal mol}^{-1}$

 $Cr^+ + CH_3CHO \rightarrow CrCO^+ + CH_4$

 $\Delta H = -27 \text{ kcal mol}^{-1}$

Gas-phase decarbonylations of aldehydes and ketones by cyclopentadienyl nickel cation, CpNi⁺, as well as the bare Fe⁺ and Co⁺ cations have been demonstrated in ICR experiments by Beauchamp^{6,7} and Freiser,⁸ as well as ion beam experiments by Beauchamp and collaborators,⁹ and Scheme I represents the mechanism which has been proposed for these systems.^{9,10}

Our experiments address the nature of the intermediates along the Scheme I reaction coordinate by measuring product fluxes which contain dynamical information on the timescale of a ro-

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Figure 1. Product angular and kinetic energy distributions for FeCO⁺ and CrCO⁺ production. The dashed portion of the FeCO⁺ angular distribution in the top panel corresponds to forward scattered products inaccessible to our detector, and therefore the curve is extrapolated.



Figure 2. Schematic reaction coordinates for decarbonylation of acetaldehyde by Cr⁺ and Fe⁺ according to Scheme I as described in the text. The horizontal dashed lines correspond to the collision energies of these experiments. The ground (⁶S) and several excited energy levels are shown for Cr⁺, with a concomitant increase in the total energy available to reaction products. The presence of excited states with \geq 50 kcal mol⁻¹ excitation energies raises the total energy significantly relative to the Fe⁺ system.

Scheme I



tational period of the transient intermediates. We employ the crossed-beam technique,¹¹ in which collimated beams of transition-metal ions, produced by impact of 100-eV electrons¹² on the

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