MAGNETIC PROPERTIES OF $\left[Fe_4S_4(SR)_4\right]^{3-}$ CLUSTERS

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Synthetic analogues of the active sites of bacterial ferredoxins [1] under suitable conditions undergo the oxidation-reduction process

$$\left[Fe_4S_4(SR)_4\right]^{2-} + e^- \leftrightarrow \left[Fe_4S_4(SR)_4\right]^{3-} \quad (1)$$

which serves as a representation of the protein site electronic and structural changes in a Fe$^{2+}$/Fe$^{3+}$ electron transfer couple in the absence of extrinsic constraints such as might be imposed by protein structural features [2,3]. Mössbauer, epr, magnetization and x-ray crystallographic measurements on analogues in both oxidation states have been used to characterize the properties of the Fe$_4$S$_4$ core [1-5]. In the present paper we compare the results previously obtained in the two oxidation states and present additional experimental data on the trianion analogue in order to gain insight into the relative strengths of exchange interactions between the iron ions and the sensitivity of the Fe$_4$S$_4$ core structure to terminal ligand variations and crystal packing effects.

In the dianion, with formal electronic configuration $3Fe^{2+} + 1Fe^{3+}$, observed isomer shifts and quadrupole splittings indicate a high degree of electron delocalization resulting in four equivalent iron ions of intermediate valence Fe$^{2.5+}$. The iron spins are strongly exchange coupled producing a singlet ground state. Furthermore, the electronic properties of the Fe$_4$S$_4$ core are relatively insensitive to terminal ligand substitution and crystal packing effects.

In the trianion with formal electronic configuration $3Fe^{2+} + 1Fe^{3+}$, observed isomer shifts and quadrupole splittings indicate a high degree of electron delocalization [2,3,5]. However, in contrast to the dianion, the trianion is sensitive to changes in the nature of both the terminal ligand and quaternary ammonium counterion when studied in crystalline form. Mössbauer and magnetization studies show that the trianions with different R groups assume one of two possible structures (I, II) resulting in different ground state configurations [2,3]. Furthermore, the iron ions are exchange coupled resulting in a ground state of $S = 1/2$ for structure (I) (R = phenyl, o-tolyl) and approaching $S = 3/2$ for structure (II) (R = benzyl, m-tolyl, p-tolyl, p-methoxybenzyl and p-isopropyl-phenyl) [2,5] as indicated by magnetization measurements obtained at $T = 1.45$ K and $T = 4.2$ K. Representative data are shown in Fig. 1.

![Graph](image)

**Fig. 1.** Magnetization vs. $H/T$ for $(Et_4N)_3[Fe_4S_4(SR)_4]$ crystals (a) $R = benzyl$, $T = 4.2$ K, (b) $R = benzyl$, $T = 1.4$ K, (c) $R = phenyl$, $T = 4.2$ K, (d) $R = phenyl$, $T = 1.4$ K.

The moment for the $R = phenyl$ cluster approaches $1 \mu_B$, the expected value for spin 1/2, whereas the moment for $R = benzyl$ approaches 3 $\mu_B$, the value for an $S = 3/2$ ground state. In both cases, the moment is still increasing at the highest applied field, reflecting low lying excited states. Moreover, the moment in both cases is not a simple function of $H/T$ but increases with increasing temperature (see Fig. 1) reflecting higher spin multiplicity of the excited states.

A measure of the strength of the exchange coupling in the two oxidation states can be observed in the spectrum of low energy electronic levels. Calculation of the magnetic susceptibility vs. temperature behavior, $\chi(T)$, was made using an exchange interaction model of the form

$$\chi = g_B \mu_B \frac{4}{3} \sum_{i \neq 1} S_i \cdot S_1 - 2 \sum_{i < j} \frac{1}{\epsilon_{ij}} J_{ij} S_i \cdot S_j$$

in the limit of the applied field $H$ approaching zero.

Here $g = 1.97$, the electronic spin $g$-factor observed in epr experiments, $\mu_B$ is the Bohr magneton, $S_i$ is
the iron spin and $J_{ij}$ couples iron ions $i,j$ with spins $S_i, S_j$ corresponding to the formal values 5/2 and 2. For $[\text{Fe}_4\text{S}_4(SR)_4]^{2-}$ the simulated $\chi(T)$ behavior with all $J_{ij}$'s equal gives a best fit to the data for $J = -232 \text{ cm}^{-1}$ [2,7]. This places the first excited ($S = 1$) state at $-2\delta_1 \approx -460 \text{ cm}^{-1}$ above the ground state. For $[\text{Fe}_4\text{S}_4(SR)_4]^{2-}$ the ground state is at least a doublet. Calculations of the susceptibility vs. temperature behavior for structure (I), corresponding to an $S = 1/2$ ground state using the above exchange interaction model in which all $J_{ij}$'s are equal, does not yield satisfactory fits to the data. Simulations using inequivalent $J_{ij}$'s are better, but give similar fits with non-unique sets of $J_{ij}$'s.

To restrict the parameter space in which possible combinations of values for the exchange interactions could range, the temperature dependence of the epr signal has been studied. In Fig. 2 the energy level diagram for the states of a spin

$$S_1 = 5/2, S_2 = 2, S_3 = 2, S_4 = 2 \quad (3)$$

system resulting when all $J_{ij}$'s are equal is given. The energy level spacings, $\Delta \Omega$, and the degeneracy of the spin states are indicated. When $kT \ll \Delta \Omega$ only this ground state will be populated and the observed epr signal results from transitions within the $S = 1/2$ manifold. Assuming that population of the excited states follows a Boltzmann distribution and states with $S > 3/2$ are well separated in energy from the $S = 1/2$ and $S = 3/2$ states, the intensity of the epr signal as a function of temperature follows the relationship

$$I(T)T = I(0)T [1 + \exp(-\Delta \Omega/kT)]^{-1}. \quad (4)$$

Here $I(T)$ is the intensity of the epr signal at temper-