

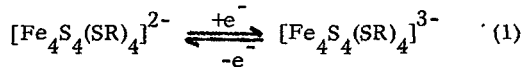
MAGNETIC PROPERTIES OF  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$  CLUSTERS

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



which serves as a representation of the protein site electronic and structural changes in a  $\text{Fd}_{\text{ox}}/\text{Fd}_{\text{red}}$  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  $\text{Fe}_4\text{S}_4$  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  $\text{Fe}_4\text{S}_4$  core structure to terminal ligand variations and crystal packing effects.

In the dianion, with formal electronic configuration  $2\text{Fe}^{2+} + 2\text{Fe}^{3+}$ , various experimental measurements [1] show that the electrons are highly delocalized resulting in four equivalent iron ions of intermediate valence  $\text{Fe}^{2.5+}$ . The iron spins are strongly exchange coupled producing a singlet ground state. Furthermore, the electronic properties of the  $\text{Fe}_4\text{S}_4$  core are relatively insensitive to terminal ligand substitution and crystal packing effects.

In the trianion with formal electronic configuration  $3\text{Fe}^{2+} + 1\text{Fe}^{3+}$ , 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*-isopropylphenyl) [2,5] as indicated by magnetization measurements obtained at  $T = 1.45$  and  $T = 4.2\text{K}$ . Representative data are shown in Fig. 1.

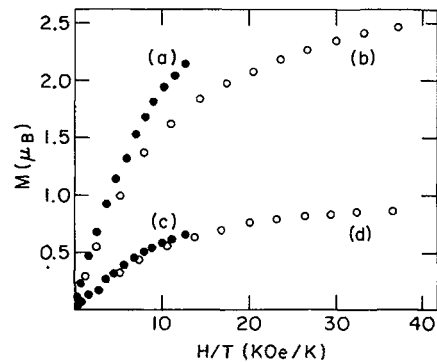


Fig. 1. Magnetization vs.  $H/T$  for  $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SR})_4]$  crystals (a) R = benzyl,  $T = 4.2\text{K}$ , (b) R = benzyl,  $T = 1.4\text{K}$ , (c) R = phenyl,  $T = 4.2\text{K}$ , (d) R = phenyl,  $T = 1.4\text{K}$ .

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

$$\chi = g\mu_B \vec{H} \cdot \sum_{i=1}^4 \vec{S}_i - 2 \sum_{i < j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

in the limit of the applied field  $\vec{H}$  approaching zero. Here  $g = 1.97$ , the electronic spin g-factor observed in epr experiments,  $\mu_B$  is the Bohr magneton,  $S_i$  is

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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  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$  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  $-2J$  or  $\Delta_1 \sim 460 \text{ cm}^{-1}$  above the ground state. For  $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$  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,  $\Delta_i$ , and the degeneracy of the spin states are indicated. When  $kT \ll \Delta_1$  only the ground state will be populated and the observed epr signal results from transitions within the  $S = 1/2$

	Energy	Spin
(18)	-80J	17/2
(48)	-63J	15/2
(84)	-48J	13/2
(120)	-35J	11/2
(150)	-24J	9/2
(144)	-15J	7/2
(108)	-8J	5/2
(6C)	-3J	3/2
(18)	0	1/2

Fig. 2

Fig. 2. Energy level diagram of an exchange coupled spin system of  $S_1 = 5/2, S_2 = 2, S_3 = 2$  and  $S_4 = 2$ . The numbers in parenthesis give the degeneracy of each spin state.

Fig. 3. Plot of  $\log[(I_0 T_0 - IT)/(IT)]$  vs.  $1/T$ . The solid line is a least-squares fit to the data points.

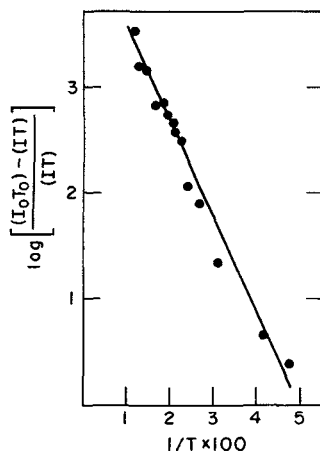


Fig. 3

manifolds. 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 [8]

$$I(T)T = I(T_0)T_0 [1 + \text{mexp}(-\Delta_1/kT)]^{-1} \quad (4)$$

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

ature  $T$ ,  $T_0$  is the lowest temperature of observation and  $m$  is the ratio of the degeneracy of the first excited state to that of the ground state. Measurements of a glassed acetonitrile solution of  $(\text{Et}_4\text{N})_3[\text{Fe}_4\text{S}_4(\text{SPh})_4]$  structure (I) were made with the spectrometer described in [2]. Data were collected from 18 to 83K at 3 mw power since in this region no power saturation effects are present [2]. Integration of the spectra was done by hand. A plot of  $\ln[(I(T_0)T_0 - I(T)T)/(I(T)T)]$  vs.  $1/T$  gives  $\Delta_1 \sim 22 \text{ cm}^{-1}$  and  $m \sim 4.5$  (Fig. 3).

These results show that the overall exchange coupling in the trianions is more than one order of magnitude lower than in the dianions with approximately 60 states lying within  $30 \text{ cm}^{-1}$  of the ground state. With this constraint, efforts are being made to find a unique set of  $J_{ij}$ 's that will provide theoretical simulations of the magnetization and  $\chi(T)$  data using Eq. (2).

The spin-only Hamiltonian in Eq. (2) operating on the system of spin states in Eq. (3) alone does not lead to a 3/2 ground state as is observed in structure (II). However, crystal field interactions in the lower symmetry structure (II)[2] may result in a substantial zero field splitting and mix higher spin character into the ground state yielding the observed results.

The observation that the  $\text{Fe}_4\text{S}_4$  core structure in the trianion is sensitive to crystal packing effects suggest an important role of the crystalline electric fields and may have implications relating to possible constraints imposed by the protein moiety such as to stabilize different oxidation states of the core. This may explain the fact that seemingly identical  $\text{Fe}_4\text{S}_4$  active sites occurring in ferredoxins and in high potential iron-sulfur proteins [1] can exist in different oxidation states with very different oxidation reduction potentials.

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