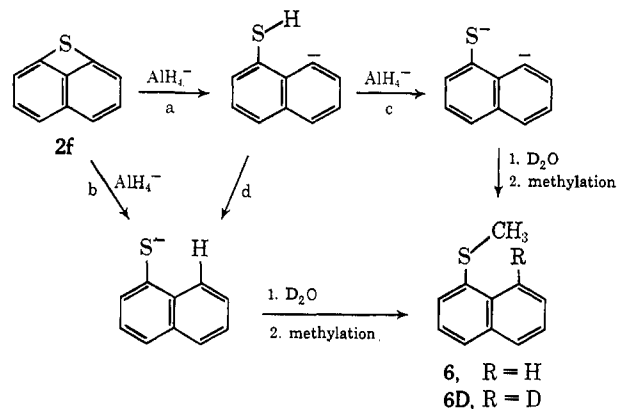


## Scheme III



reaction is attack of hydride at sulfur, followed by deprotonation of the thiol by additional hydride (Scheme III, paths a + c). Undeuterated **6** probably arises *via* paths a + d, although attack at carbon (path b) remains a formal possibility.

The reaction of **2f** with methyllithium provides a further example of facile nucleophilic attack on sulfur.<sup>14</sup> At room temperature, with excess methyllithium in ether, the major product is methyl 1-naphthyl sulfide (**6**); no 8-methyl-1-naphthalenethiol is produced.<sup>15</sup>

Other reactions of these novel heterocyclic compounds, and new synthetic routes to other single-atom peri-bridged naphthalenes, are now being pursued.

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(14) Thietane itself reacts with *n*-butyllithium *via* attack on sulfur to give products derived from 1-lithio-3-thiobutylpropane: F. G. Bordwell, H. M. Andersen, and B. M. Pitt, *J. Amer. Chem. Soc.*, **76**, 1082 (1954).

(15) Also isolated were two minor products, methyl 8-(1-thionaphthyl)-1-naphthyl sulfide (10%) and methyl 8-[8-(1-thionaphthyl)-1-thionaphthyl]-1-naphthyl sulfide (7%), resulting from oligomerization of methyl 8-lithio-1-naphthyl sulfide with **2f** (cf ref. 14).

(16) Fellow, Cornell University Six-Year Ph.D. Program.

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### Spectroscopic and Magnetic Characterization of the High Potential Iron-Sulfur Protein from *Chromatium*

Sir:

Recent work by Holm and coworkers has provided<sup>1,2</sup> excellent synthetic analogs of the  $[Fe_4S_4(S-Cys)_4]$  cluster found<sup>3,4</sup> in certain iron-sulfur proteins. These inorganic complexes  $Fe_4S_4(SR)_4^{2-}$  have been thoroughly

(1) T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S.*, **69**, 2437 (1972).

(2) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 3523 (1973).

(3) C. W. Carter, Jr., J. Kraut, S. T. Freer, R. A. Alden, L. C. Sieker, E. Adman, and L. H. Jensen, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3526 (1972).

(4) E. T. Adman, L. C. Sieker, and L. H. Jensen, *J. Biol. Chem.*, **248**, 3987 (1973).

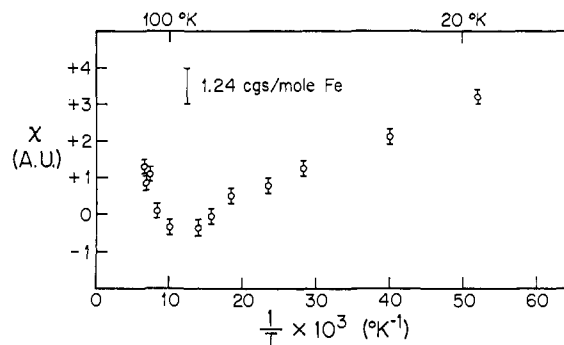


Figure 1. Magnetic susceptibility vs. reciprocal temperature for  $HP_{red}$  between 20 and 150°K.

characterized by a variety of physical measurements.<sup>1,2,5-8</sup> It has been proposed<sup>1,5,6</sup> that the dianionic tetramers, which have been found<sup>7</sup> to contain equivalent Fe sites, correspond electronically to the  $[Fe_4S_4(S-Cys)_4]$  active sites of oxidized ferredoxin and reduced "high potential" ( $HP_{red}$ ) proteins. To put this proposal to a severe test, we have measured the magnetic susceptibility of  $HP_{red}$  from *Chromatium* over a wide temperature range. We have also recorded the electronic absorption spectra of both  $HP_{red}$  and  $HP_{ox}$  at low temperature.

All magnetic susceptibility experiments were performed on a superconducting quantum magnetometer.<sup>9</sup> The relative change of the susceptibility was measured on a sample of 70 mg of  $HP_{red}$ <sup>10</sup> in a magnetic field of 150 G from 3 to 150°K (results in the region 20–150°K are presented in Figure 1). Antiferromagnetic behavior is apparent above 100°K.<sup>11</sup> The low temperature (<100°K) paramagnetic component is likely due to residual, high-spin  $Fe^{3+}$  impurities (1.4%  $Fe^{3+}$  ( $S = 5/2$ ) accounts for the observed component).

Data taken in the low temperature range follow Curie-law ( $\chi = C/T$ ) behavior with  $C = (4.1 \pm 0.1) \times 10^{-6}$  emu/g. We have corrected for this paramagnetic component in calculating the temperature dependence of the magnetic moment per iron atom ( $\mu_c$ ) in  $HP_{red}$  (Figure 2).

(5) R. H. Holm, W. D. Phillips, B. A. Averill, J. J. Mayerle, and T. Herskovitz, *J. Amer. Chem. Soc.*, **96**, 2109 (1974).

(6) B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **96**, 4159 (1974).

(7) R. H. Holm, B. A. Averill, T. Herskovitz, R. B. Frankel, H. B. Gray, O. Siiman, and F. J. Grunthaler, *J. Amer. Chem. Soc.*, **96**, 2644 (1974).

(8) L. Que, Jr., M. A. Bobrik, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, **96**, 4168 (1974).

(9) H. E. Hoenig, R.-H. Wang, G. R. Rossman, and J. E. Mercereau, Proceedings of the Applied Superconductivity Conference, Annapolis, Md., May 1-3, 1972, p 570; M. Cerdonio, R.-H. Wang, G. R. Rossman, and J. E. Mercereau, Proceedings of the XIII International Conference on Low Temperature Physics, LT-13, Boulder, Colo., Aug 1972, in press.

(10)  $HP$  was extracted and purified from cells of *Chromatium* by a modification of the Bartsch procedure (R. G. Bartsch, in "Bacterial Photosynthesis," H. Gest, A. San Pietro, and L. P. Vernon, Ed., Antioch Press, Yellow Springs, Ohio, 1963, p 315). A sample of  $HP_{red}$  was prepared for the magnetic susceptibility measurements by reduction with mercaptoethanol, followed by dialysis. After passing the solution through a millipore filter,  $HP_{red}$  was precipitated with ammonium sulfate. Care was taken to protect the sample from metal-containing impurities.

(11) An earlier magnetic susceptibility study of  $HP_{red}$  failed to resolve an antiferromagnetic component up to 200°K [T. H. Moss, D. Petering, and G. Palmer, *J. Biol. Chem.*, **244**, 2275 (1969)]. However, clear evidence of antiferromagnetic behavior at much higher temperatures (5–80°) has been presented [W. D. Phillips, M. Poe, C. C. McDonald, and R. G. Bartsch, *Proc. Nat. Acad. Sci. U.S.*, **67**, 682 (1970)].

Our magnetic susceptibility data on  $\text{HP}_{\text{red}}$  are in strikingly good agreement with the results reported<sup>1</sup> for  $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]$ . Perhaps most impressive is the fact that temperature dependences of  $\mu_e$  in the tetramer<sup>1,12</sup> and the protein are within experimental error in the range 100–150°K. It appears, therefore, that the gross electronic structural features of the  $[\text{Fe}_4\text{S}_4(\text{S-Cys})_4]$  cluster in  $\text{HP}_{\text{red}}$ , including the extent of spin-spin coupling, are reproduced very closely by the dianionic tetramer.

Examination of the low-temperature electronic absorption spectrum of  $\text{HP}_{\text{red}}$  (Figure 3), however, reveals that there must be some differences in the finer details of the electronic structure of the  $\text{Fe}_4\text{S}_4$  core in the protein environment. The relatively weak band at 700 nm in  $\text{HP}_{\text{red}}$  is slightly blue shifted from a similar feature at 780 nm in  $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]$  (thin film, 5°K).<sup>7</sup> More importantly, the spectrum of  $\text{HP}_{\text{red}}$  exhibits a broad, low-energy (1040 nm) band that appears to have no counterpart in the tetramer. One intriguing possibility is that binding to the protein removes the equivalence of the Fe sites in  $[\text{Fe}_4\text{S}_4(\text{S-Cys})_4]$ . The 1040-nm band could then represent either an intracuster transition between inequivalent Fe sites or possibly one or more  $d-d$  excitations at a severely distorted metal center.<sup>13</sup> Interestingly, there is no evidence for a band with  $\lambda_{\text{max}} > 800$  nm in the thin-film spectrum of  $\text{HP}_{\text{ox}}$  at 77°K.

Our combined magnetic and spectroscopic results confirm the close structural and electronic relationship between  $\text{Fe}_4\text{S}_4(\text{SR})_4^{2-}$  complexes and the  $[\text{Fe}_4\text{S}_4(\text{S-Cys})_4]$  unit in  $\text{HP}_{\text{red}}$  but at the same time demonstrate that there are some key differences that remain to be elucidated fully. Detailed X-ray photoelectron spectroscopic experiments are in progress in our laboratory on  $\text{HP}_{\text{red}}$  and  $\text{HP}_{\text{ox}}$ , in an effort to provide additional information relating to the electronic structures of the Fe centers in the protein environment.

(12) R. H. Holm, private communication.

(13) Attempts to locate a band attributable<sup>7</sup> to tetrahedral  $\text{Fe}^{\text{II}}\text{S}_4$  yielded inconclusive results, as the spectrum of  $\text{HP}_{\text{red}}$  in the 1500–2500-nm region is dominated by vibrational overtones. A difference spectrum ( $\text{HP}_{\text{red}} - \text{HP}_{\text{ox}}$ ) in this region failed to reveal any absorptions with  $\epsilon > 200$ , but a  $d-d$  band of moderate intensity could have been masked. It should be noted, however, that the Mössbauer spectral data for  $\text{HP}_{\text{red}}$  rule against the presence of localized  $\text{Fe}^{\text{II}}\text{S}_4$ : T. H. Moss, A. J. Bearden, R. G. Bartsch, M. A. Cusanovich, and A. San Pietro, *Biochemistry*, **7**, 1591 (1968); M. C. W. Evans, D. O. Hall, and C. E. Johnson, *Biochem. J.*, **119**, 289 (1970); D. P. E. Dickson, C. E. Johnson, R. Cammack, M. C. W. Evans, D. O. Hall, and K. K. Rao, *ibid.*, **139**, 105 (1974).

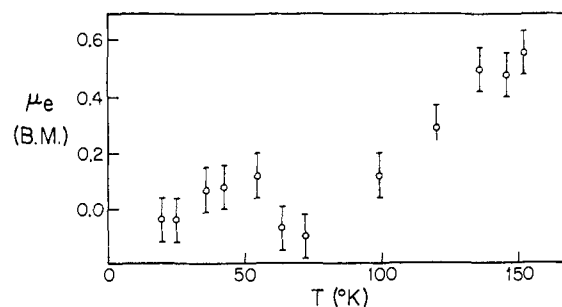


Figure 2. Corrected magnetic moment per iron ( $\mu_e$ ) vs.  $T$  for  $\text{HP}_{\text{red}}$  in the region 20–150°K. Values for  $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]$  are<sup>12</sup> ( $T$ , °K;  $\mu$ , B.M.): 100, 0.33; 110, 0.37; 120, 0.41; 130, 0.46; 140, 0.50; 150, 0.55; 160, 0.59.

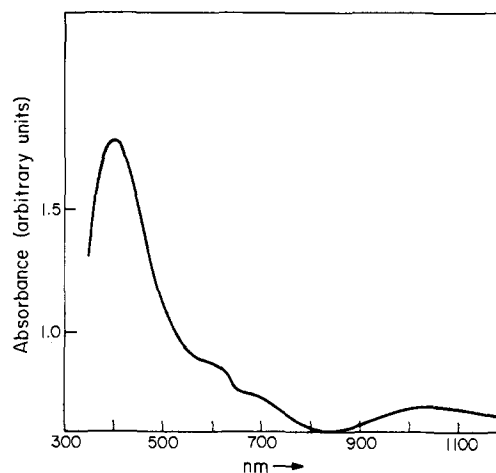


Figure 3. Electronic absorption spectrum of a thin film of  $\text{HP}_{\text{red}}$  at 77°K. A spectrum measured in 1:1 ethylene glycol- $\text{D}_2\text{O}$  at 77°K showed the same bands.

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