duced. The experimentally obtained ratios of 0.88 and 1.01 agree quite well with the expected value of 1.0. This indicates that the only major species mediating electron transport between Cr(II)edta and methyl viologen was the Fe-S complex.

The observed change in pH suggests that the Fe-S complex is cotransporting electrons and hydrogen ions by a mechanism of reduction-linked proton binding. Another possible origin for the observed pH changes that should be considered is proton transport by the Fe-S complex driven by separation of charge between toluene and aqueous phases. This can be tested using valinomycin, a ring carrier ionophore which can permit K^+ ion to pass into the hydrophobic toluene phase. If under normal experimental conditions a potential was developed, addition of valinomycin should collapse the potential. Thus the rates of electron transport and the ratio of electron/proton transported would be greatly increased on addition of valinomycin. Because no significant increases were observed, it is concluded that proton transport driven by the separation of charge is not the dominant mechanism.

These results indicate that the Fe-S complex does cotransport protons and electrons. Further, the transport of the proton is not a process driven solely by the separation of charge between the aqueous and toluene phases. The actual site of binding of the hydrogen ion to the reduced Fe-S complex is not yet established. Studies are currently in progress to determine the site or sites of association.

ACKNOWLEDGEMENTS

We wish to thank M.A. Greaney, P. Mandel, and E.I. Stiefel for technical assistance and helpful discussions.

REFERENCES

[1] E.J. Laskowski, R.B. Frankel, W.O. Gillum, G.C. Papaefthymiou, J. Renaud, J.A. Ibers, R.H. Holm, *J. Am. Chem. Soc.*, **100**, 5322 (1978).

[2] a) R.B. Frankel, T. Herskovitz, B.A. Averill, R.H. Holm, P.J. Krusic, W.D. Phillips, *Biochem. Biophys. Res. Commun.*, **58**, 974 (1974);

b) J. Cambray, R.W. Lane, A.G. Wedd, R.W. Johnson, R.H. Holm, *Inorg. Chem.*, **16**, 2565 (1977).

PS4.2 — TU

MICHELLE MILLAR
TIMOTHY O'SULLIVAN
Department of Chemistry
New York University
New York, NY 10003
U.S.A.

SYNTHESIS AND STUDY OF AN ANALOG FOR THE $[Fe_4S_4]^{3+}$ CENTER OF OXIDIZED HIGH POTENTIAL IRON-SULFUR PROTEINS

Although many examples of synthetic analogs for the $[Fe_4S_4]^{n+}$ ($n=1,2$) oxidation levels of iron-sulfur proteins have been prepared and characterized, no previous attempt to synthesize a compound with the $n=3$ oxidation level has been successful. Electrochemical studies have shown that $[Fe_4S_4(S\text{-}2,4,6\text{-}(i\text{-}Pr)_3C_6H_2)_4]$ $[(n\text{-}Bu)_4N]_2$, **(1)** and $[Fe_4S_4(S\text{-}2,3,5,6\text{-}Me_4C_6H)_4]$ $[(n\text{-}Bu)_4N]_2$, **(2)**, can be reversibly oxidized in CH_3CN and CH_2Cl_2 by one electron to the corresponding $[Fe_4S_4(SR)_4]^{1-}$ compounds, **3** and **4**. The -1/-2 and -2/-3 redox couple potentials measured by normal and reverse pulse voltammetry in CH_2Cl_2 *versus* SCE are respectively: -0.12 V and -1.20 V for **1** and -0.05 V and -1.10 V for **2**. The oxidation of **1** with $[(C_5H_5)_2Fe]BF_4$ produces $[Fe_4S_4(S\text{-}2,4,6\text{-}(i\text{-}Pr)_3C_6H_2)_4]$ $[(n\text{-}Bu)_4N]$, **(3)**, in 35% yield. Formulation of **3** as the first example of a synthetic compound containing the $[Fe_4S_4]^{3+}$ core, was confirmed by an X-ray crystal structure. The $[Fe_4S_4\text{-}(S\text{-}\alpha\text{-}C)_4]$ unit of **3** (Fig. 1) has crystallographic C_2 symmetry and approximate D_{2d} symmetry. The average Fe-S (2.26 Å) and Fe-SR (2.21 Å) bond distances are similar to the distances reported for the X-ray structure of the $[Fe_4S_4]^{3+}$ center of the oxidized high potential iron-sulfur protein from *Chromatium vinosum*. Also, the $[Fe_4S_4]$ core of **3** is tetragonally compressed with four short Fe-S bonds and eight long Fe-S bonds. The observed shift to longer wave-

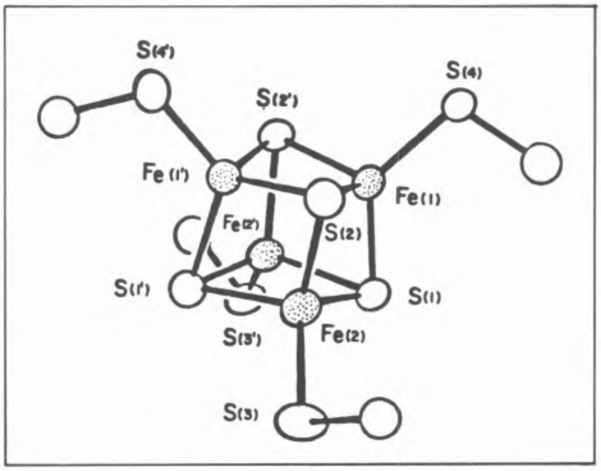

Fig. 1
The $[Fe_4S_4(S\text{-}\alpha\text{-}C)_4]$ *unit of 3*

length of the lowest energy band in the electronic spectrum of **1** and **2** upon oxidation to **3** and **4** parallels the behavior of the high potential protein. Further spectroscopic and synthetic studies of $[Fe_4S_4]^{3+}$ centers will also be presented.

PS4.3 — TH

J. GLOUX*
P. GLOUX**
B. LAMOTTE
G. RIUS
Centre d'Etudes Nucleaires de Grenoble
Département de Recherche Fondamentale
Service de Physique
85 X - 38041 Grenoble, Cedex
France

ESR IN SINGLE CRYSTALS OF 4 IRON 4 SULFUR SYNTHETIC CUBANES: A NEW WAY FOR DETAILED SPECTROSCOPIC STUDIES OF THE $[Fe_4S_4]^+$ AND $[Fe_4S_4]^{3+}$ STATES

Electron Spin Resonance (ESR) represents certainly one of the best methods in order to identify and study the redox states of iron-sulfur cores in proteins as well as in synthetic models. For the 4 Iron 4 Sulfur cubanes, the two paramagnetic states are the $[Fe_4S_4]^+$ state which corresponds to the reduced ferredoxins and the $[Fe_4S_4]^{3+}$ state which corresponds to the oxidized high potential iron-sulfur proteins.

These ESR studies have always been made in non-oriented systems, *i.e.* frozen solutions or polycrystalline powders. Thus, it is the comparison between only the principal values of the $\tilde{g}$-tensors of the proteins and of their synthetic models which is used to check the similarity between the active sites of these proteins and their synthetic analogs. But from such an approach it is not possible to deduce precise data concerning the electronic and magnetic cubane structures which are only poorly understood till now. A better knowledge would require first the acquisition of more spectroscopic informations, *i.e.* the complete $\tilde{g}$-tensors, by ESR studies in single crystals.

We want to report here that we have succeeded to create in single crystals of the compound $[Fe_4S_4(SC_6H_5)_4](NBu_4)_2$, first synthesized by HOLM *et al.* [1], the two paramagnetic states $[Fe_4S_4]^+$ and $[Fe_4S_4]^{3+}$. This has been made by inducing by irradiation with gamma rays the following *in situ* reactions in the single crystals:

$$[Fe_4S_4]^{2+} \rightarrow [Fe_4S_4]^{3+} + e^-$$

$$e^- + [Fe_4S_4]^{2+} \rightarrow [Fe_4S_4]^+$$

Moreover, these paramagnetic species are then created in the best conditions permitting detailed ESR studies since they are diluted at low concentration in the crystal built on $[Fe_4S_4]^{2+}$ cores which are diamagnetic at low temperature.

The ESR spectra show anisotropic lines spreading over about 500 Gauss and centered around $g=2$. We have been able to obtain the complete angular variations of the two main sets of lines in the three perpendicular planes ab, bc* and c*a defined with respect to the monoclinic unit cell and

---

* USM-G
** CNRS