

Fig. 1
The $[\text{Fe}_4\text{S}_4(\text{S}-\alpha\text{-C})_4]$ 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 $[\text{Fe}_4\text{S}_4]^{3+}$ centers will also be presented.



PS4.3 — TH

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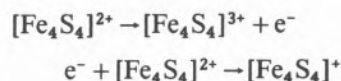
ESR IN SINGLE CRYSTALS OF 4 IRON 4 SULFUR SYNTHETIC CUBANES: A NEW WAY FOR DETAILED SPECTROSCOPIC STUDIES OF THE $[\text{Fe}_4\text{S}_4]^+$ AND $[\text{Fe}_4\text{S}_4]^{3+}$ STATES

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 $[\text{Fe}_4\text{S}_4]^+$ state which corresponds to the reduced ferredoxins and the $[\text{Fe}_4\text{S}_4]^{3+}$ 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 $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_5)_4](\text{NBu}_4)_2$, first synthesized by HOLM *et al.* [1], the two paramagnetic states $[\text{Fe}_4\text{S}_4]^+$ and $[\text{Fe}_4\text{S}_4]^{3+}$. This has been made by inducing by irradiation with gamma rays the following *in situ* reactions in the single crystals:



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 $[\text{Fe}_4\text{S}_4]^{2+}$ 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

thus to deduce the \tilde{g} -tensors. Their principal values are the following:

$$\begin{aligned} \text{A center: } g_1 &= 2.089 & g_2 &= 1.969 \\ &g_3 &= 1.877 \\ \text{B center: } g_1 &= 2.108 & g_2 &= 2.006 \\ &g_3 &= 1.987 \end{aligned}$$

Comparing with known experimental data in proteins, we can assign respectively the A center to the $[\text{Fe}_4\text{S}_4]^+$ of reduced ferredoxins [2] and the B center to the $[\text{Fe}_4\text{S}_4]^{3+}$ of oxidized high potential proteins [3].

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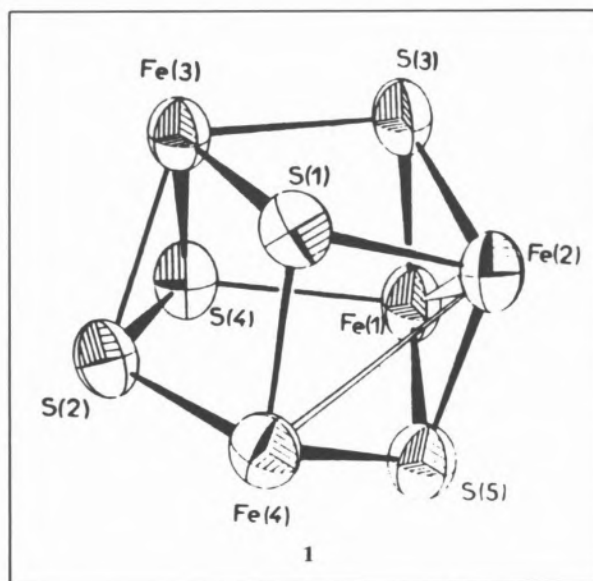
PS4.4 — MO

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A CORRELATION BETWEEN THE STRUCTURAL, ELECTRONIC AND MAGNETIC PROPERTIES OF $[\text{Fe}_4\text{S}_5\text{Cp}_4]^n$ ($n=0,1+,2+$) CORES, PRESENT IN A DISTORTED CUBANE-TYPE CLUSTER WITH ONE PENTA-COORDINATED IRON ATOM

The Fe-S cluster **1** contains an electron-rich disulfide ligand which has the ability to form donor-acceptor complexes, either by S coordination or by S-S reductive cleavage.



Moreover, the X-ray analysis of $\text{Fe}_4\text{S}_5\text{Cp}_4^+$ revealed a new structural Fe-S cluster type, where one Fe atom is five-coordinate, and accounts thus for the distortion from a «conventional» Fe_4S_4 core. It was of interest to assess the spin-density delocalisation and the nature of the interaction between the ligands and the metal sites, and thus to achieve a better knowledge of the chemical reactivity of this entity and its oxidised homologues. Therefore, a detailed structural and bonding comparison of this series has been made, using both X-ray and EXAFS data. This analysis has then been correlated to the Mössbauer, EPR and magnetic susceptibility measurements.

Also, a more detailed Mössbauer study enabled us to predict the iron sites from which the electrons are probably abstracted upon the successive oxidations, and to visualise a spin-state change, at the five-coordinate Fe site, between $\text{Fe}_4\text{S}_5\text{Cp}_4^+$ and $\text{Fe}_4\text{S}_5\text{Cp}_4^{2+}$.

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