

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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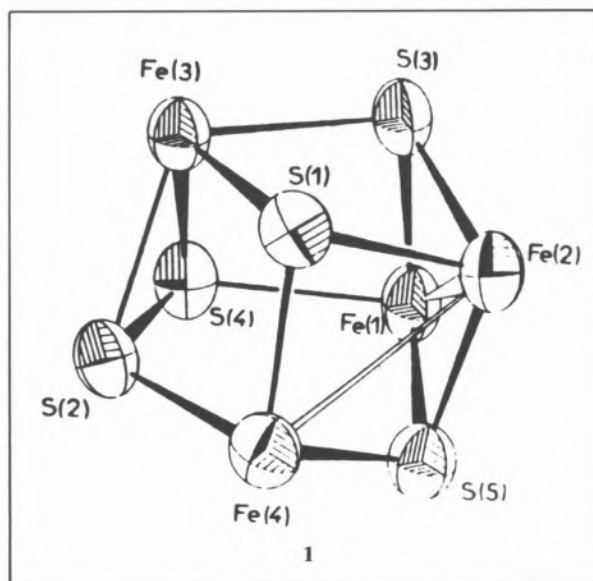
PS4.4 — MO

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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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PS4.5 — TU

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CHELATION EFFECT OF A Cys-X-Y-Cys TETRAPEPTIDE SEQUENCE FOR THE 4Fe-4S CLUSTER

Physical and chemical properties of the 4Fe-4S cluster in simple alkane- or arylthiolato model complexes have been established by HOLM's group [1,2]. The differences between native ferredoxin and the model complexes have been discussed in terms of redox potential, electron transfer rate, and redox stability. These differences are caused by a peptide chain of native ferredoxin. For example, invariant amino acid residues in the protein sequence of *P. aerogenes* ferredoxin play a crucial role in the construction of an unusual 4Fe-4S core environment. Previously we reported the importance of a Cys-Gly-Ala fragment of $[\text{Fe}_4\text{S}_4(\text{Z-cys-Gly-Ala-OMe})_4]^{2-}$ (Z = benzyloxy-carbonyl) with NH---S hydrogen bonding which is supported in a nonpolar solvent [3]. This paper presents a study on the chelation effect of an invariant Cys-X-Y-Cys sequence to a 4Fe-4S cluster and the effect of two amino acid residues placed between two Cys residues. A simple 4Fe-4S model complex with Cys-Gly-Gly-Cys ligands has already been synthesized by QUE *et al.* [4].

$[\text{Fe}_4\text{S}_4(\text{Z-cys-Gly-Ala-cys-OMe})_2]^{2-}$, **1**, and $[\text{Fe}_4\text{S}_4(\text{Z-cys-Ile-Ala-cys-OMe})_2]^{2-}$, **2**, having a conservative sequence of *P. aerogenes* ferredoxin were synthesized from the ligand exchange reaction of $[\text{Fe}_4\text{S}_4(\text{S-}t\text{-Bu})_4]^{2-}$ and the corresponding tetrapeptides. The $^1\text{H-NMR}$ spectrum of **1** in $\text{Me}_2\text{SO-d}_6$ exhibits two $\beta\text{-CH}$ signals of Cys resi-

dues at 11.0 and 12.3 ppm which are observed separately, with different contact shifts from the 4Fe-4S core to the $\beta\text{-CH}$ groups of two Cys thiolato ligands. The redox potential of **1** was -0.95 V (SCE) with a positive shift (0.04 V) from that (-1.00 V , SCE) of $[\text{Fe}_4\text{S}_4(\text{Z-cys-Gly-Ala-OMe})_4]^{2-}$ in *N,N*-dimethylformamide (DMF) and -0.91 V (SCE) in dichloromethane. These values may be compared with that (-0.98 V , SCE) of $[\text{Fe}_4\text{S}_4(\text{Z-cys-Gly-Ala-OMe})_4]^{2-}$ at room temperature. This positive shift in DMF is ascribed to a chelation effect by Cys-X-Y-Cys to the 4Fe-4S cluster. A decrease in the temperature for **1** in dichloromethane results in a positive shift of the redox potential; it attains -0.85 V (SCE) at 243 K, which is similar to the redox potential of $[\text{Fe}_4\text{S}_4(\text{Z-cys-Gly-Ala-OMe})_4]^{2-}$ at 233 K, indicating a preferable conformation for the NH---S hydrogen bonding, frozen at low temperature (233 K). In the case of **2**, the Cys-Ile-Ala-Cys sequence was found to chelate to the 4Fe-4S core in spite of the disadvantageous hairpin turn structure of the Cys-Ile-Ala sequence [5].

Redox behaviors of **1** and **2** in aqueous micellar solutions will be discussed as a model for a metalloprotein which acts as an electron transfer mediator.

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