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MÖSSBAUER PROPERTIES OF SYNTHETIC ANALOGS OF ACTIVE SITES OF THE IRON-SULFUR PROTEINS

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Résumé. — La spectroscopie Mössbauer des tétramères synthétiques $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ ($\text{R} = \text{alkyle, aryle}$) et les trianions correspondants, obtenus par la réduction d'un électron montre par comparaison avec les données disponibles pour les protéines 4-Fe et 8-Fe fer-soufre, que ces tétramères sont les analogues électroniques des sites actifs des protéines.

Abstract. — Mössbauer spectroscopy of the synthetic tetramers $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ ($\text{R} = \text{alkyl, aryl}$) and the corresponding trianions obtained by one-electron reduction, when compared with available data for 4-Fe and 8-Fe iron-sulfur proteins, shows that these tetramers are electronic analogs of the active sites of the proteins.

1. Introduction. — Iron complexes involved in metabolic processes may be grouped into two rather broad categories [1]: (a) porphyrin complexes, as in the heme-proteins, and (b) non-heme complexes. The latter category can be further divided into complexes in which the iron is bonded to oxygen or nitrogen ligands, as in certain transport and storage proteins such as transferrin and ferritin, and complexes in which the iron is bonded to sulfur ligands, as in the iron-sulfur proteins.

Members of the latter group, the non-heme iron-sulfur proteins, participate in a wide variety of biological processes such as photosynthesis, nitrogen fixation, hydroxylation of steroids and terpenes, and electron transport, in the metabolism of aerobic, anaerobic, and photosynthetic bacteria, green plants, and mammals. The widespread utilization of these complexes is due to the remarkable range of oxidation-reduction potentials apparently available to iron coordinated to sulfur [1, 2].

Aside from those proteins that also contain flavin groups, and those associated with heavy metals such as Mo, the iron-sulfur proteins can be classified into groups containing, respectively, one, two, four and eight iron atoms; zero, two, four and eight atoms of acid-labile or inorganic sulfur (sulfide), and a number of cysteine residues equal to or greater than the number of iron atoms. X-ray structure determinations have been made of the active sites of a one-iron protein (rubredoxin) [3], a four-iron protein (HP) from *Chromatium* [4, 5] and an eight-iron protein (ferredoxin) from *Peptococcus aerogenes* [5, 6]. These studies show that the iron sites have four-coordinate,

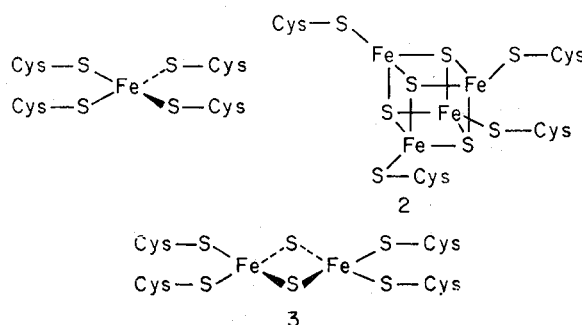


FIG. 1. — Structures of the (1) one, (3) two and (2) four iron proteins.

roughly tetrahedral symmetry (Fig. 1). In the four-iron protein, the Fe-S tetrahedra are packed into a distorted cubic cluster with one sulfide bridging three irons and each iron terminally coordinated by a thiolate sulfur of a cysteine residue. The eight-iron protein consists of two such clusters separated by approximately 12 Å. The structure of a two-Fe protein has not yet been determined, but a variety of physico-chemical techniques point to a dimeric arrangement (Fig. 1) with the sulfides bridging two tetrahedrally coordinated iron atoms [1, 7].

In order to understand the often unique physical properties of the iron-sulfur proteins, it is desirable to have simple coordination complexes whose structure and properties resemble those of the active sites of the proteins themselves. Such model complexes would be especially useful in elucidating the electronic structure of the active sites in the various oxidation states of the

proteins, and in understanding the relationship between redox potential and structure. For example, of the proteins with structurally similar $(\text{Cys-S})_4\text{Fe}_4\text{S}_4$ cores, HP has an oxidation-reduction potential $E_m = +0.35$ V vs. standard hydrogen electrode (SHE), while the 8-Fe ferredoxin (Fd) has $E_m = -0.40$ V vs. SHE. While an epr signal is observed in HP in the oxidized state and not the reduced state, epr is observed in Fd in the reduced state and not the oxidized state. The resolution of this problem has been facilitated by comparisons of the proteins with well defined oxidation states of a synthetic analog.

In addition to inorganic systems with Fe tetrahedrally bonded to four sulfur atoms such as CuFeS_2 , KFeS_2 and Fe in ZnS, model complexes have been prepared which correspond structurally to the two-Fe proteins [8] and the four-Fe proteins. The latter include $[(\text{h}^5\text{-C}_5\text{H}_5)_4\text{Fe}_4\text{S}_4]^{n+}$ ($n = 0, 1, 2$) [9] and the structurally similar complex $[(\text{h}^5\text{-C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_4]^{n+}$ ($n = 0, 1$) [10] and $[((\text{CF}_3)_2\text{C}_2\text{S}_2)_4\text{Fe}_4\text{S}_4]^{n-}$ ($n = 0, 1, 2$) [11]. However, these complexes, although interesting in their own right, are not ideal protein analogs because among other reasons, the first two contain the non-physiological cyclopentadienyl group as a terminal ligand, while in the latter, the iron sites have five sulfur coordination with two of the sulfur atoms part of a dithiolene π -electron system.

More recently, a series of complexes of the type $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ have been synthesized, where SR is a simple alkyl or aryl mercaptide, by the reaction of ferric chloride in methanol with 3 equivalents of sodium mercaptide, followed by 1 equivalent of a methanolic solution of sodium hydrosulfide. These complexes have been shown by a variety of physical techniques to be close structural and electronic representatives of the active sites of oxidized 4-Fe and 8-Fe bacterial ferredoxin (Fd_{ox}) and reduced high potential non-proteins (HP_{red}) [12-15]. In this paper we will review some of the electronic and structural properties of these complexes, and compare the Mössbauer spectral parameters with available data from the proteins. In Section 2 below we review the properties of the tetramer dianions, and the changes that occur on reduction to the trianion, and in Section III we compare these results with data from the proteins.

2. Mössbauer spectroscopy. — 2.1 $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$.

— The crystal structure of $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]$ consists of discrete anions and cations arranged in layers. The Fe_4S_4^* tetramer core (S* refers to labile sulfur) is a distorted cube of D_{2d} symmetry with Fe and S atoms at alternate vertices (see Fig. 1). The mean Fe-Fe bond length is 2.746 Å, the mean Fe-S* length is 2.239 Å, and the mean Fe-S (terminal) length is 2.251 Å. Although the dianion consists formally of 2 Fe(II) + 2 Fe(III) there are no significant differences in the structural parameters of the various Fe sites. Moreover, no differences in the iron sites could be

detected by a variety of physical techniques such as optical spectroscopy, nmr, ESCA, and Mössbauer spectroscopy [16] (see below).

Magnetic susceptibility measurements [12] as a function of temperature for the benzyl dianion yield a magnetic moment per iron atom of 1.04 μB at room temperature which decreases with decreasing T to ~ 0.3 μB per iron at 77 K, characteristic of antiferromagnetic exchange between the iron atoms. Below 60 K the susceptibility increases, presumably due to high-spin iron (III) impurities.

The apparent equivalence of all the Fe sites is reflected in the Mössbauer spectrum which in zero external magnetic field consists of a single quadrupole doublet (Fig. 2) from 1.5 K to room temperature

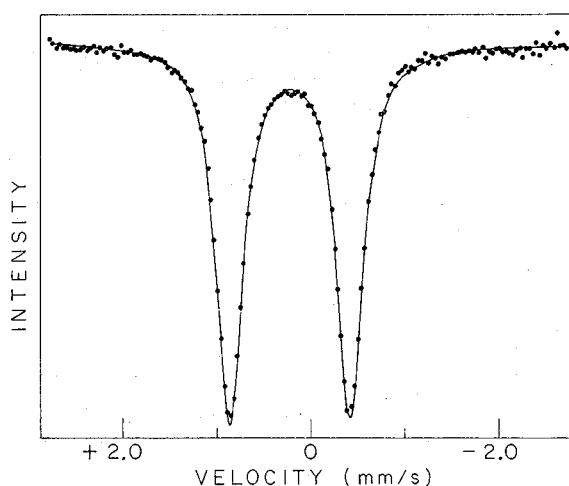


Fig. 2. — Mössbauer spectrum of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ with $\text{R} = \text{CH}_2(\text{C}_6\text{H}_5)$ at 4.2 K.

(Table I). For $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$ the splitting $\Delta E_Q = 1.25$ mm/s with isomer shift $\delta = +0.34$ mm/s (relative to iron metal) from 1.5 K to above 77 K, and ΔE_Q is 10 % lower at room temperature. The line width at all temperatures is relatively narrow ($\Gamma \sim 0.25$ mm/s at 77 K) and the f factor decreases considerably between 77 K and 300 K.

Spectra have been obtained for the various substituents R and some parameters are listed in Table I. As can be seen, the substituent R has a relatively small effect on the low temperature quadrupole splitting and on the isomer shift, although the redox potential is apparently dependent on the electronegativity of the terminal ligands [15].

Mössbauer spectra obtained in longitudinal magnetic fields H_0 up to 80 kOe at 4.2 K (Fig. 3) can be understood as the superposition of an effective field at the nucleus H_n on the axial electric field gradient tensor with principal axis of positive sign in the randomly oriented powder. Moreover, $H_n = H_0$ for all H_0 , i. e., there is no hyperfine field. This observation that the ground state is a non-magnetic singlet state implies an intramolecular exchange constant of negative sign,

TABLE I
Mössbauer Data

	T K	ΔE_Q (°)	δ (°)	Ref.
$(Et_4N)_2[Fe_4S_4(SCH_2Ph)_4]$	296	1.15	0.34	This work
	77	1.26	0.34	—
	4.2	1.26	0.34	—
$(n-Bu_4N)_2[Fe_4S_4(SPh)_4]$	296	0.54	0.34	—
	4.2	1.10	0.35	—
$(Me_4N)_2[Fe_4S_4(S-t-Bu)_4]$	296	0.71	0.34	—
	4.2	1.10	0.35	—
$(Ph_4As)_2[Fe_4S_4(SET)_4]$	296	1.10	0.34	—
	4.2	1.17	0.34	—
$[((CF_3)_2C_2S_2)_4Fe_4S_4]$	77	1.67	0.13	[11]
$(Ph_4As)[((CF_3)_2C_2S_2)_4Fe_4S_4]$	77	1.62	0.17	[11]
$(Ph_4As)_2[((CF_3)_2C_2S_2)_4Fe_4S_4]$	77	1.66	0.19	[11]
$[\pi-C_5H_5FeCO]_4$	77	1.76	0.40	[32]
$[\pi-C_5H_5FeCO]_4Cl$	77	1.38	0.41	[32]
<i>Chromatium</i> HP _{ox}	77	0.80	0.31	[24]
<i>Chromatium</i> HP _{red}	77	1.13	0.42	[24]
<i>Clostridium pasteurianum</i> Fd _{ox}	77	0.91	0.43	[23]
	4.2	1.08	0.44	[23]
	4.2	{ 1.34 0.72	{ 0.33 0.31 (°)	[21]
<i>Clostridium pasteurianum</i> Fd _{red}	77	1.25	0.57	[23]
	4.2	1.54	0.58	[23]
	4.2	1.54	0.45 (°)	[21]
$[Fe_4S_4(SCH_2Ph)_4]^{3-}$	77	1.15	0.46	[17]
$[Fe_4S_4(SPh)_4]^{3-}$	77	1.08	0.45	This work

(°) Quadrupole splitting in mm/s.

(^b) Isomer shift relative to iron metal in mm/s.

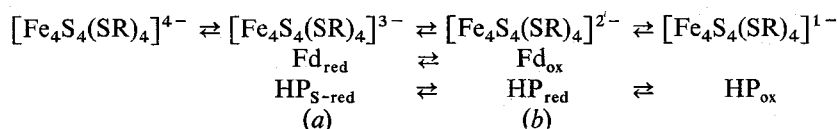
(^c) Values obtained by adding 0.226 mm/s to values quoted for Co⁵⁷ in Cu.

large compared to μH_0 and kT . This is consistent with the decreasing magnetic susceptibility as a function of temperature and shows that the low temperature tail in the magnetic susceptibility measurements must be due to paramagnetic impurities.

2.2 $[Fe_4S_4(SR)_4]^{3-}$. — Benzyl and phenyl dianions in dimethyl formamide were reduced by several methods including the addition of a ten-fold excess of the acenaphthalene radical anion in tetrahydrofuran. In addition to characteristic changes in the optical spectrum, an axial epr signal was observed at 4.2 K with $g_{av} \sim 1.96$ [17]. Mössbauer spectra were obtained in frozen solutions of both the dianion and the corresponding trianion. The frozen dianion solutions gave spectra which were virtually identical to those obtained with the solid. The spectra of the trianions at 77 K consist of quadrupole doublets (Fig. 4) with splitting $\Delta E_Q = 1.15$ mm/s and isomer shift $\delta = 0.46$ mm/s for

benzyl and $\Delta E_Q = 1.05$ mm/s, $\delta = 0.45$ mm/s for phenyl. The linewidths ($\Gamma \sim 0.45$ mm/s) were also greater than in the dianion spectrum. At 4.2 K, the trianion spectrum consists of a very broad, asymmetric line, indicative of magnetic hyperfine interaction due to slow paramagnetic relaxation. Application of a small, longitudinal magnetic field sharpens the spectrum and, in addition, reveals the presence of some unreduced dianion in the trianion sample. Application of magnetic fields up to 80 kOe results in a decrease of the splitting (Fig. 5) and indicates that the magnetic hyperfine field is of the order of -100 kOe.

3. Discussion. — In addition to the dianion and trianion, electrochemistry in non-aqueous media shows the existence of a monoanion and a tetra-anion. Evidence has been presented [15, 17] to support the following correspondences in total oxidation level between the proteins and the synthetic analogs :



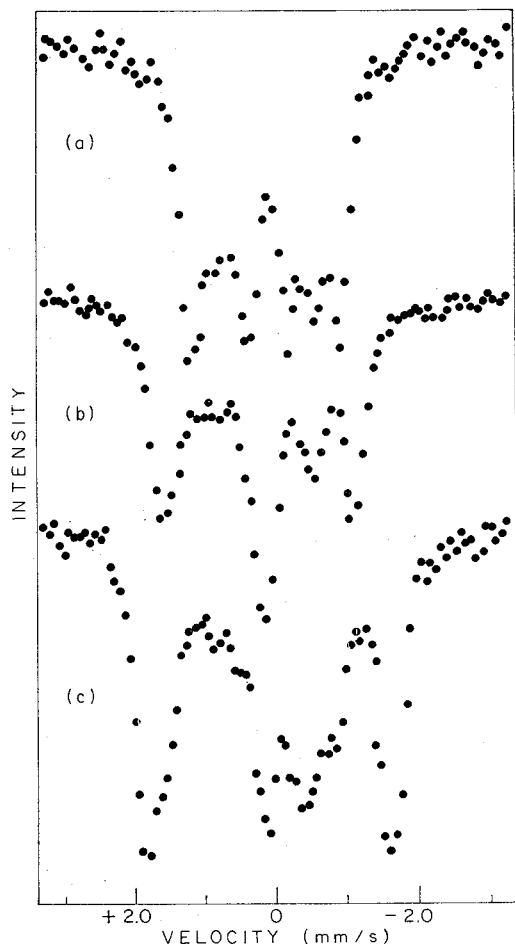


FIG. 3. — Mössbauer spectra of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ at 4.2 K and in longitudinal magnetic fields: a) $H_0 = 30$ kOe; b) $H_0 = 50$ kOe; c) $H_0 = 80$ kOe.

According to this scheme, Fd_{ox} and HP_{red} correspond to the dianion and consist formally of 2 Fe (II) and 2 Fe (III).

Mössbauer measurements have been reported [18-24] for the oxidized and reduced forms of both HP and Fd. The spectra of HP_{red} and Fd_{ox} consist of apparent quadrupole doublets characterized by similar parameters which fall in the ranges $\delta \sim 0.32 - 0.46$ mm/s (rel. to iron metal) and $\Delta E_Q \sim 1.1-1.3$ mm/s at 4.2 K. The parameters for the dianions quoted in Table I are within those intervals. Moreover, magnetic field experiments at low temperature show no induced magnetic hyperfine interaction in either Fd_{ox} or HP_{red} [20, 21, 23, 24], i. e., the ground states are singlet, as in the dianion. These and other measurements [12-15] allow us to correlate the electronic state of the dianion with Fd_{ox} and HP_{red} .

For Fd_{red} , there is less consistency among the available data. The most recent work [20, 21, 23] indicates that at 77 K the spectrum consists of an apparent quadrupole doublet with $\delta \sim 0.45-0.6$ mm/s and $\Delta E_Q = 1.1-1.4$ mm/s. At 4.2 K, magnetic hyperfine interactions are induced by applied magnetic fields.

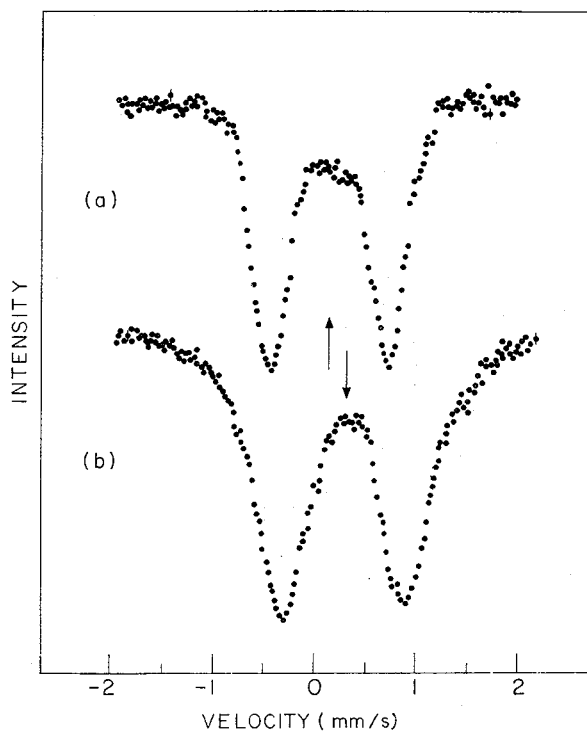


FIG. 4. — Spectrum of frozen solutions of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{n-}$ with $\text{R} = \text{C}_6\text{H}_5$ at 77 K; a) $n = 2$; b) $n = 3$.

Thus, the Mössbauer parameters and the qualitative magnetic field behavior of the trianions are comparable to Fd_{red} . Recently, a super-reduced form of HP has been reported [25] but no Mössbauer data are presently available. From the three state scheme we would predict that the oxidation level of $\text{HP}_{\text{S-red}}$ corresponds to that of the trianions and Fd_{red} .

The near invariance of quadrupole splitting in the dianion and trianion implies that no major structural changes in the environment of the iron atoms occur upon reduction. The observed increase of isomer shift upon reduction suggests that the electron is added to an orbital of substantial d-character centered on the iron atoms. The interpenetration of the 3d and 3s, 4s orbitals is such that an increase in electron density in the former actually shields the nucleus from electrons in the latter, resulting in a net decrease in electron density at the nucleus. The trianion formally consists of 3 Fe (II) + Fe (III) and its isomer shift may be compared with $\delta = 0.54$ mm/s (195 K) found for $\text{Ba}_6\text{Fe}_8\text{S}_{15}$, which contains tetrahedral Fe-S₄ units with an average iron oxidation state of 2.25 [26]. The magnetic hyperfine structure in the trianion spectrum, as well as the epr spectra, show that the electronic ground state is paramagnetic and that the electron spin relaxation time is of the order of the ^{57}Fe nuclear Larmor precession time. This result is expected from the addition of the electron to the ground state of the dianion which is singlet (non-magnetic) [12]. The observed line broadening in the trianion may reflect structural or electronic differences among iron atoms

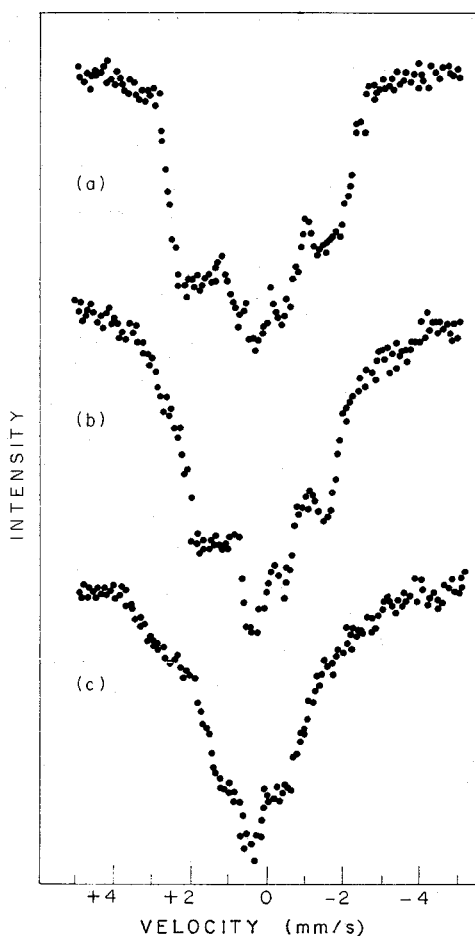


FIG. 5. — Spectra of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-}$ with $\text{R} = \text{CH}_2(\text{C}_6\text{H}_5)$ in external magnetic fields; a) $H_0 = 20$ kOe; b) $H_0 = 40$ kOe; c) $H_0 = 80$ kOe.

in the Fe_4S_4 core. However, such differences, if any, are small. The unpaired electron is concluded to interact with all four atoms; localization on one or two metal sites is ruled out.

The interaction of the unpaired spin with iron atoms in the *core* distinguishes these complexes from some of the others mentioned above which might be regarded as synthetic analogs. The series $(\text{h-C}_5\text{H}_5\text{FeCO})_4^{n+}$ with $n = 0$ and 1 has recently been examined [27] in magnetic fields at low temperature, and a magnetic hyperfine interaction of less than 10 kOe was observed to be induced in the paramagnetic ($n = 1$) complex. Similarly, the series of dithiolene complexes $[((\text{CF}_3)_2\text{C}_2\text{S}_2)_4\text{Fe}_4\text{S}_4]^{n-}$ with $n = 0, 1, 2$ show identical spectra [28] at 4.2 K in external magnetic fields, even though the $n = 1$ complex is paramagnetic. This suggests that the oxidation and reduction takes place primarily in the dithiolene ligands.

A rationalization of the physical properties of the various clusters cannot be made in terms of localized or trapped valence oxidation states. Most recently, Gall *et al.* [29] have discussed the clusters in terms of a qualitative M. O. scheme, in which the twenty 3d orbitals of the four iron atoms considered as a cluster are split by the ligand field and by direct metal-metal interactions into configurations which transform under T_d symmetry as $(a_1 + e + t_2)$ (bonding), $(e + t_1 + t_2)$ (non-bonding) and $(t_1 + t_2)$ (antibonding). When this scheme is applied to $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$, the twenty-two core electrons produce a ground state $(a_1 + e + t_2)^{12}(e + t_1 + t_2)^{10}(t_1 + t_2)^0$ [13, 29]. Upon reduction, the additional electron goes into the tetrametal $(e + t_1 + t_2)$ orbitals so that a strong interaction of the unpaired spin with the iron nuclei is expected. Because of the non-bonding nature of the orbitals, no essential structural changes are expected, as implied by the Mössbauer data.

The suggestion that the highest filled (and unfilled) orbitals are essentially tetrametal in character is supported by SCF-X α cluster calculations [30] which show that the core electrons partially occupy a 3d-like band. A small gap of the order of 300 K in the band at the «fermi surface» accounts for the magnetic behavior in terms of spin unpairing corresponding to excitations across the gap. Upon reduction, the additional electron goes into a 3d band state above the gap and hence interacts strongly with the nuclei.

In conclusion, we have shown that study of the complexes $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{n-}$ has been valuable in elucidating the comparative electronic structure of certain of the iron-sulfur proteins. Further work will involve the question of the strict equivalence of the iron atoms in the trianion, and the structural factors that affect the electron distribution in the presumably less symmetric clusters of the proteins. This latter work will be facilitated by the discovery [31] of facile ligand exchange of the terminal mercaptides which allows the *construction* of clusters with side chains which approach those of the proteins in complexity [33].

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Note added in proof: Recent Mössbauer spectroscopy [34] of $\text{HP}_{\text{S-red}}$ indicates an iron valence state similar to that in FD_{red} and the trianion.

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