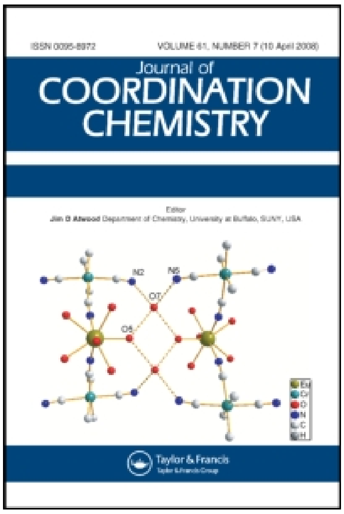

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STRUCTURAL STUDIES AND MÖSSBAUER SPECTRA OF FE_4S_4 CLUSTER SYSTEMS: BIOLOGICAL IMPLICATIONS OF THESE RESULTS

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The structural arrangement of the iron-sulfur centers in the non-heme iron-sulfur proteins has been the subject of extensive physical investigations.[1–4] Particular emphasis has been placed on the "ferredoxins" which have seven or eight iron atoms and eight or more sulfur atoms per protein unit. Several workers[5–7] have proposed that the iron-sulfur cluster compounds of composition $[Fe_4S_4L_4]^{n-}$, where $L = S_2C_2(CF_3)_2$, may be useful model systems for the ferrodoxins. We report here a brief description of the structural parameters for the $Fe_4S_4L_4^{-2}$ cluster and the Mössbauer data for the three derivatives, $n = 0, 1, 2$. The data are compared with that reported for inorganic cluster systems of known structure and with the available data on non-heme iron-sulfur proteins.

The structure of the cluster present in the $n = 2$ derivative is shown in Figure 1. The $C_2(CF_3)_2$

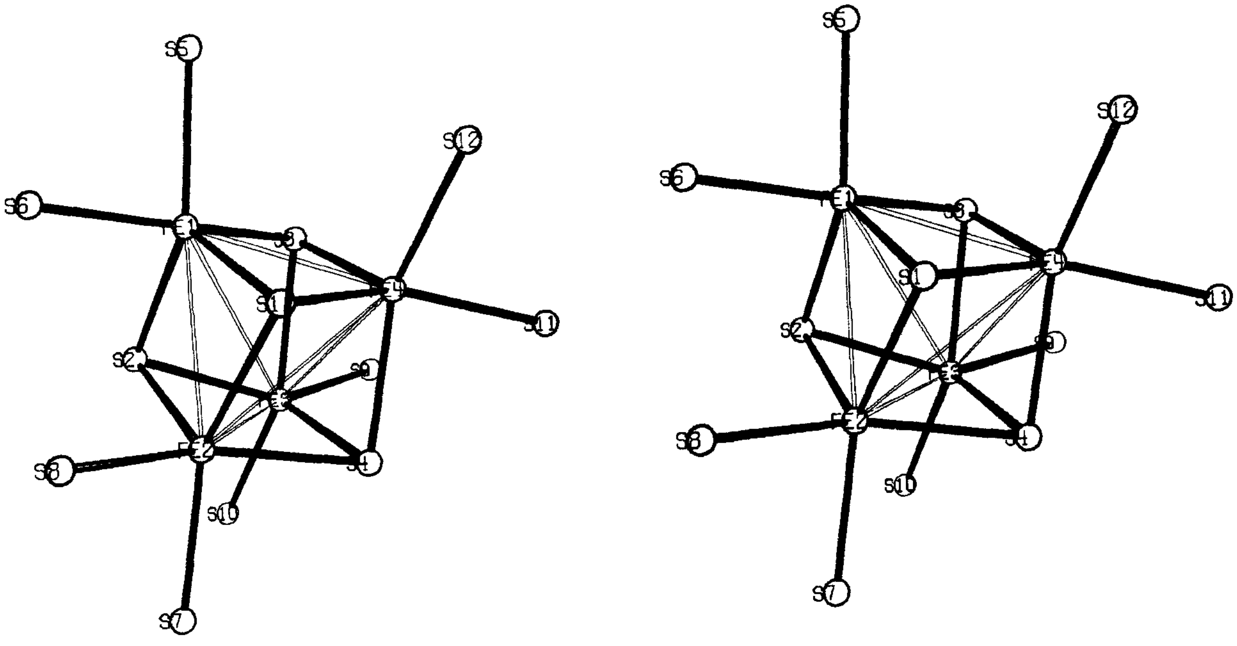

FIGURE 1 The Structure of $[Fe_4S_4\{S_2C_2(CF_3)_2\}_4]^{-2}$ (This figure is a stereo pair which may best be seen with the aid of a hand-held stereo viewer.)

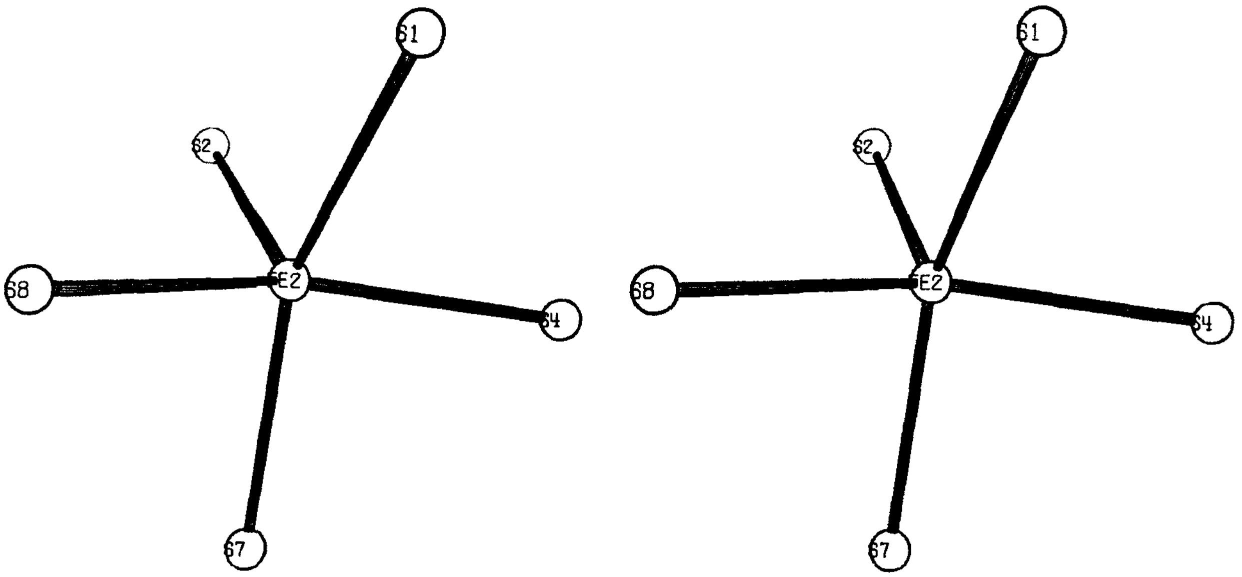

FIGURE 2 Coordination about the Iron Site in $[Fe_4S_4\{S_2C_2(CF_3)_2\}_4]^{-2}$ (This figure is a stereo pair which may best be seen with the aid of a hand-held stereo viewer.)

fragments of the molecule have been omitted from the figure for the sake of clarity. Figure 2 indicates the observed distorted trigonal bipyramid coordination about one of the iron sites (Fe2). Relevant bond lengths and angles for the cluster are listed in Table I. The estimated standard deviations on bond lengths and angles are 0.02 Å and 1°, respectively. The $n = 2$ cluster species differs structurally from the Fe_4S_4 and $Fe_4(CO)_4$ clusters studied by Dahl[8,9] and Fritchie[10] in that the four iron atoms are not arranged in a perfect tetrahedral array and the Fe-Fe contact distances are longer (2.7 Å and 3.2 Å vs. 2.5 Å). The generally accepted[11] electronic description of the dithiolene moiety present in the clusters reported here is that of a (—1) charged species. Thus the neutral cluster is formally isoelectronic with the $(\pi\text{-}C_5H_5)_4Fe_4S_4$ cluster systems of Dahl[8] and Fritchie[10] while the dianion ($n = 2$) cluster contains two additional electrons. Thus it appears that the introduction of these two electrons leads to a deformation of the cluster and an increase in the Fe-Fe contact distances in spite of the fact that the dithiolene ligands are highly delocalized systems capable of accepting electron density from the cluster *via* π bonds between Fe and the ligand sulfurs.[11] In an Fe_4S_4 cluster containing aliphatic systems as the peripheral ligands (i.e. cysteine) removal of electron density from the cluster would not be as likely, thus accounting for the relative instability of the reduction products of the proteins. Even in the clusters reported here, the Fe–Fe contact distances in the dianion species are borderline between very weak metal–metal bonds and no bonds at all. Therefore, by analogy, the introduction of two electrons in the protein would be expected to lead to similar, or even larger, distortions.

The Mössbauer parameters for the three cluster systems are given in Table II and representative spectra are shown in Figure 3. Note that the isomer shift, quadrupole splitting, and linewidth values are essentially temperature independent.[15] Also, there is no line broadening at low temperatures which implies that the iron nuclei are held close enough together to interact. This is obviously consistent with the structure shown in Figures 1 and 2. A single narrow-lined doublet is observed for all three cluster compounds indicating that all iron sites in a given cluster are equivalent (or nearly so) with respect to their electronic environment. This is somewhat surprising in view of the different Fe–Fe and Fe–S distances given in Table I.

The isomer shift values for the clusters fall in the range observed for a large number of high-spin iron(III) species although the metal oxidation state is probably not very meaningful in these systems where extensive electron delocalization over the total cluster occurs. Evidence for this delocalization is implicit in the fact that the reduction of the neutral cluster by one or two electrons, causes a very small change in the isomer shift value. This

TABLE I

Table of Interatomic Distances and Angles[a]

For the $Fe_4S_4L_4$ = Dianion (See Figures 1 and 2)

Fe1	Fe2		2.80	Fe2	Fe1		2.80
	Fe3		3.26		Fe4		3.19
	Fe4		2.78		Fe3		2.58
	S1		2.21		S1		2.39
	S2		2.23		S2		2.12
	S3		2.31		S4		2.24
	S5		2.22		S7		2.14
	S6		2.12		S8		2.36
S5	Fe1	S6	83	S7	Fe2	S8	85
		S1	110			S2	115
		S2	146			S1	144
		S3	96			S4	90
S1	Fe1	S2	104	S2	Fe2	S1	101
		S3	102			S4	105
		S6	100			S8	106
S2	Fe1	S3	75	S1	Fe2	S4	80
		S6	92			S8	85
S3	Fe1	S6	156	S4	Fe2	S8	147
Fe2	Fe1	Fe3	50	Fe1	Fe2	Fe4	55
		Fe4	70			Fe3	75
Fe3	Fe1	Fe4	54	Fe3	Fe2	Fe4	56
Fe3	Fe2		2.58	Fe4	Fe1		2.78
	Fe1		3.26		Fe2		3.19
	Fe4		2.75		Fe3		2.75
Fe3	S2		2.17	Fe4	S1		2.29
	S3		2.22		S3		2.16
	S4		2.14		S4		2.21
	S9		2.22		S11		2.27
	S10		2.10		S12		2.23
S10	Fe3	S9	88	S12	Fe4	S11	88
		S4	109			S3	108
		S3	149			S4	151
		S2	94			S1	87
S4	Fe3	S2	107	S3	Fe4	S1	104
		S3	102	S3	Fe4	S4	102
		S9	109			S11	109
S3	Fe3	S2	78	S4	Fe4	S1	83
		S9	81			S11	85
S2	Fe3	S9	142	S1	Fe4	S11	147
Fe1	Fe3	Fe4	54	Fe2	Fe4	Fe3	51
Fe2	Fe3	Fe4	73	Fe1	Fe4	Fe3	72
Fe1	Fe3	Fe2	56	Fe1	Fe4	Fe3	55

[a] At this stage of refinement the estimated standard deviations are 0.02Å in the bond lengths and 1.0° in the bond angles.

small increase of the isomer shift with increasing reduction means that the s-electron density about the iron centers is decreasing slightly; thus the d-electron shielding is increasing as the electrons (partially) are added to the metal d-orbitals. This effect is similar to that exhibited by the HPI Chromatium as recorded in Table II. Note that a two electron reduction in our clusters increases the isomer shift value by about 0.06 mm/sec. The change in the HPI for a one electron reduction is about 0.03. The two electron change in the dimer species, $[Fe\{S_2C_2(CF_3)_2\}_2]_2^{n-}$, results in an increase in δ of 0.08 which is again indicative of extensive electron delocalization.

The values of the isomer shifts for these clusters are somewhat lower than those for all of the comparable compounds in Table II. This probably reflects the difference in character of the outer ligands, those not in the cluster. This would explain the different values found for the $[(\pi\text{-}C_5H_5)FeCO]_4^{n+}$ clusters. The fact that δ does

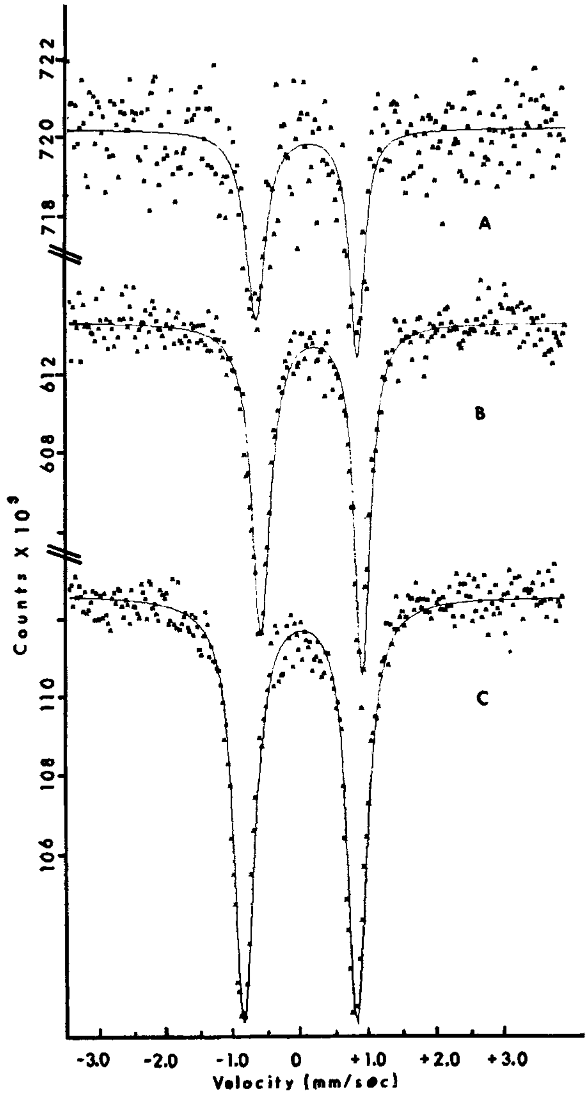

FIGURE 3 The Mössbauer Spectra of the $[Fe_4S_4\{S_2C_2(CF_3)_2\}_4]$ Cluster at Various Temperatures. A, 296°K; B, 77°K: C. 4.2°K.

not change significantly when the cyclopentadienyl cluster is oxidized probably means that the electrons are being withdrawn primarily from the π-C_5H_5 ring system with a negligible change in the iron electron environment.

The quadrupole splitting parameters for these sulfur clusters are of the same order of magnitude as those reported for the $[(\pi\text{-}C_5H_5)FeCO]_4^{n+}$ series and the HPI Chromatium compound. This indicates a similar electronic configuration in each. This is in contrast to the larger Δ values reported for the dimer species[12] which are assumed to have square pyramidal configuration about the iron centers and would be expected to exhibit larger Δ values than the trigonal bipyramidal configuration for the clusters shown in Figures 1 and 2.

The results reported for the Euglena and spinach ferredoxin indicate that they are a different type of molecular species. These materials are reported to have only two iron atoms per protein and the Mössbauer results indicate that the reducing electron goes to one of the iron centers without significantly changing the other.

A recent article on the structure of the Fe—S complex in a bacterial ferredoxin[16] indicates that an Fe_4S_4, cubic cluster model is consistent with the X-ray structural data. The similarity of this preliminary structure and the Mössbauer data of the

TABLE II

Mössbauer Data for the Iron-Sulfur Cluster Compounds and Other Comparable Systems

Compound	T(°K)	δ(mm/sec)[a]	Δ(mm/sec)	Γ(mm/sec)	Ref.
$Fe_4S_4[S_2C_2(CF_3)_2]_4$	296	0.06	1.67	0.35 0.31	*b*
	78[c]	0.13	1.67	0.35 0.32	*b*
	4.2	0.03	1.68	0.36 0.33	*b*
$[Ph_4As]\{Fe_4S_4[S_2C_2(CF_3)_2]_4\}$	296	0.10	1.60	0.26 0.27	*b*
	78[c]	0.17	1.62	0.31 0.30	*b*
	4.2	0.06	1.63	0.31 0.30	*b*
$[Ph_4As]_2\{Fe_4S_4[S_2C_2(CF_3)_2]_4\}$	296	0.14	1.62	0.37 0.38	*b*
	78[c]	0.19	1.66	0.27 0.33	*b*
	4.2	0.09	1.65	0.35 0.32	*b*
$[Fe\{S_2C_2(CF_3)_2\}_2]$	77	0.25	2.39	—	12
$[Et_4N]_2[Fe\{S_2C_2(CF_3)_2\}_2]_2$	295	0.23	2.50	—	12
	77	0.33	2.50	—	12
$[\pi\text{-}C_5H_5FeCO]_4$	77	0.40	1.76	—	13
$[\pi\text{-}C_5H_5FeCO]_4Cl$	77	0.41	1.38	—	13
$[\pi\text{-}C_5H_5FeCO]_4Br_3$	77	0.41	1.40	—	13
oxidized Ferredoxin of *Euglena*	77	0.22	0.65	—	14
reduced Ferredoxin of *Euglena*	77	0.25 0.70	0.70 3.00	—	14
HPI Chromatium (oxidized)	77	0.32	0.82	—	4
HPI Chromatium (reduced)	77	0.35	1.18	—	4
Spinach Ferredoxin (oxidized)	77	0.25	0.60	—	4
Spinach Ferredoxin (reduced)	77	1.39	3.18	—	4

[a] Relative to metallic iron (99.99%). δ and Δ are precise to better than ± 0.03 mm/sec for those values determined in this work.

[b] This work.

[c] Source at room temperature and absorber at 77°. At 296° and 4.2° source and absorber were maintained at the same temperature.

HPI chromatium protein systems with the structural and Mössbauer results reported here for the iron-sulfur dithiolene clusters, indicates the possible significance of these clusters as model compounds for certain ferredoxins. Further characterization of these clusters is presently underway.

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REFERENCES

1. Blomstrom, D. C., Knight, E., Jr., Phillips, W. D., and Weiher, J. F., *Proc. U.S. Nat. Acad. Sci.* **51,** 1085 (1964).
2. Bearden, A. J. and Dunham, W. R., *Structure and Bonding* **8,** 1 (1971).
3. Moss, T. H., Bearden, A. J., Bartsch, R. G., and Cusanovich, M. A., *Biochem.* **7,** 1583 (1968).
4. Moss, T. H., Bearden, A. J., Bartsch, R. G., Cusanovich, M.A., and San Pietro, A., *Biochem.* **7,** 1591 (1968).
5. Poe, M., Phillips, W. D., McDonald, C. C., and Lovenberg, W., *Proc. U.S. Nat. Acad. Sci.* **65,** 797 (1970).
6. Phillips, W. D., Poe, M., McDonald, C. C., and Bartsch, R. G., *Proc. U.S. Nat. Acad. Sci.* **67,** 682 (1970).
7. Carter, C. W., Freer, S. T., Xuong, Ng H., Alden, R. A., and Kraut, J., *Cold Spring Harbor Symp. Quant. Biol.* **36** (in press).
8. Wei, C. H., Wilkes, G. R., Treichel, P. M. and Dahl, L. F., *Inorg. Chem.* **5,** 900 (1966).
9. Dahl, L. F., Private communication. The preliminary crystal structures of $[Cp_4Fe_4(CO)_4]^x$ (where Cp is the *cyclopentadienyl ion and* $x = 0, \pm 1$) *indicate that* essentially identical tetrahedra of iron atoms are observed for both clusters. In both cases, short Fe-Fe distances (from 2.48 Å for the cation to 2.52 Å for the neutral species) were determined. The cation species is slightly deformed from T_d to approximately D_{2h} symmetry. However, this effect is minor compared to the distortions observed in the Fe_4S_4 cluster described in this paper.
10. Schunn, R. A., Fritchie, C. J., Jr., and Prew tt, C. T., *Inorg. Chem.* **5,** 892 (1966). The structure of the same compound as reported in ref. 8 was done. However, these authors studied a sample which crystallized in the orthorhombic system while Dahl and co-workers had studied the monoclinic species. There were no significant structural differences between the two forms.
11. Schnauzer, G. N., Accounts, *Chem. Res.* **2,** 72 (1969) and in Transition Metal Chem., **4,** 299 (1968).
12. Birchall, T., and Greenwood, N. N., *J. Chem. Soc.* (A) 286 (1969).
13. Greatrex, R. and Greenwood, N. N., *Discuss. Faraday Soc.*, **47,** 126 (1969).
14. Johnson, C. E., Elstner, E., Gibson, J. F., Benfield, G., Evans, M. C. W., and Hall, D. O., *Nature* **220,** 1291 (1968).
15. The small difference in isomer shift at 77°K is caused by the fact that the absorber and source are not at the same temperature as they are for the measurements made at 296° and 4.2°K. Shifts of a similar order of magnitude have been observed in previous studies where the temperature differential between source and absorber has been a factor. See: R. A. Prados and M. L. Good, *J. Inorg. Nucl. Chem.* **33,** 3733 (1971).
16. Sieker, L. C., Adman, E., and Jensen, L. H., *Nature* **235,** 40 (1972).