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Crystal and Molecular Structure of $[(C_5H_5)Fe(SC_2H_5)S]_2$. A Possible Model for Ferredoxin

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The crystal and molecular structure of the title compound has been determined from three-dimensional X-ray data. The structure was solved by the direct method and has been refined by least-squares procedures to a conventional R of 0.022 for 1781 nonzero reflections. The dark green compound crystallizes in space group $P2_1/c$ of the monoclinic system in a cell of dimensions $a = 17.374$ (3) Å, $b = 8.125$ (1) Å, $c = 12.782$ (2) Å, $\beta = 108.37$ (3)°, and $V = 1712.4$ Å^3. There are four dimers per unit cell ($\rho_{\text{exptl}} = 1.63$ g cm^{-3}; $\rho_{\text{calcd}} = 1.661$ g cm^{-3}). The complex contains a planar Fe–S–S–Fe bridge and the two iron atoms are also linked by two bridging mercapto ligands. The structural evidence suggests that the S_2 oxidation state is intermediate between $S_2{}^0$ and $S_2{}^{2-}$. The structure raises the possibility that the ferredoxins with two iron and two labile sulfur atoms might contain a Fe–S–S–Fe bridge.

Introduction

Iron–sulfur proteins are known to participate in a number of biological functions such as photosynthesis (ferredoxins), hydroxylation of steroids (adrenodoxin), and electron transport (iron–sulfur flavoproteins).[1] X-Ray crystal studies have revealed the arrangement of the iron–sulfur core in rubredoxin[2] (1Fe–0S) (S stands for "labile" sulfur[1]), HiPIP[3] (4Fe–4S), and clostridial ferredoxin[4] (8Fe–8S). No X-ray structures are yet available for any of the 2Fe–2S proteins (plant ferredoxins, adrenodoxin, putidaredoxin) but they have been studied extensively by several physical methods.[5] A major difficulty in interpreting the physical properties of the iron–sulfur proteins has been the lack of small molecule models for the iron–sulfur core of these proteins. Knowing the structure and studying the physical properties of such models will provide valuable information in comparison with the proteins. To date the available small molecule analogs to the 2Fe–2S proteins are far from meeting most of the characteristics of a realistic model. We report here the structure of a novel compound with a Fe–S–S–Fe bridge.

Experimental Section

Crystal Data. A sample of the compound was kindly supplied by T. G. Spiro. The dark crystals are stable to air and to X-radiation. The reciprocal lattice symmetry ($2/m$) observed from preliminary precession photographs indicated that the crystals belong to the monoclinic system. Systematic absences, occurring for $h0l$ reflections, when $l = 2n + 1$, and for $0k0$ reflections, when $k = 2n + 1$, are consistent only with space group $P2_1/c$. Lattice constants were calculated by least-squares refinements of the setting angles of 12 reflections centered automatically. (Cu Kα radiation, λ 1.54181 Å, $60° < 2\theta < 75°$). Cell parameters $a = 17.374 \pm 0.003$ Å, $b = 8.125 \pm 0.001$ Å, $c = 12.782 \pm 0.002$ Å, and $\beta = 108.37 \pm 0.03°$ give a unit cell volume of 1712.4 Å^3 and a calculated density of 1.661 g cm^{-3} for $[(C_5H_5)Fe(SC_2H_5)S]_2$ with $Z = 4$. The density measured by flotation in aqueous $ZnBr_2$ is 1.63 ± 0.03 g cm^{-3}. The estimated standard deviations of lattice constants as computed in the least-squares refinement were a factor of 2 better than the errors assigned above and reflect our experience with reproducibility of results. Intensity data were collected from a well-formed crystal which was bounded by the faces $\{100\}$, $\{10\bar{2}\}$, $\{11\bar{1}\}$, $\{011\}$, $\{1\bar{1}\bar{1}\}$, and $\{01\bar{1}\}$ and their centrosymmetric ones, and the distances between these pairs were 0.12, 0.12, 0.16, 0.19, 0.16, and 0.16 mm, respectively.

Collection and Reduction of Experimental Data. The crystal was carefully centered on a Picker FACS-1 four-circle automatic diffractometer and aligned with its c^* axis collinear with the ϕ axis. Ni-filtered Cu Kα radiation was used for the collection of data with a θ–2θ scan technique, employing stationary-crystal, stationary-counter background counts of 40 sec at the beginning and end of each scan range. The data were collected at a takeoff angle of 4.5° and a scan rate of 1°/min. The scan range was 1.7°, applied symmetrically to the calculated 2θ value using Kα_1 for λ. A dispersion factor of $114.6(\Delta\lambda/\lambda)$, where $\Delta\lambda$ is the difference between Kα_1 and Kα_2 and where λ is for K$\bar{\alpha}$ radiation, was added to the high side of 2θ to allow for the separation of the α_1, α_2 doublet. The source-to-crystal distance was 16 cm and the crystal-to-counter distance was 35 cm. Two 1.5-mm collimators were used for the incident and diffracted beams. During the course of the data collection three standard reflections were measured at a period of 30 reflections as a check on crystal and electronic stability. They did not show a variation of more than 2.5% from their respective means nor any trend with time.

A total of 3082 intensity measurements were made in the form $\pm h,+k,+l$ in the region of $2\theta < 105°$ and reduced to a set of 1963 independent reflections after averaging the duplicate ones and taking out the systematically absent ones. The duplicate measurements were within $2\sigma(I)$ of each other and they were averaged, except for 15 reflections which were within $3\sigma(I)$; the ones with the highest net count were accepted. The integrated intensity was calculated as $I(\text{net}) = I(\text{scan}) - 0.5t_{\text{T}}/t_{\text{B}}(B_1 + B_2)$ where $I(\text{scan})$ is the number of counts over the scan range, t_{T} is the scan time, and t_{B} is the time for each background count B_1 and B_2. The standard deviations $\sigma(I)$ were calculated according to the expression $\sigma(I) = [N_{\text{T}} + 0.25(t_{\text{T}}/t_{\text{B}})^2(B_1 + B_2) + (cI)^2 + 0.006^2(I - I_{\text{c}})^2]^{1/2}$, where N_{T} is the total integrated scan count obtained in time t_{T}, c is a factor to account, among other things, for instrumental instability[6] during data collection (for this structure determination c was 0.024), I is the net intensity, and I_{c} is I corrected for absorption. The last term in the brackets is a factor accounting for the errors in the absorption correction.

Only data for which $I > 1.75\sigma(I)$ were used, which left 1781 reflections to be entered into the least-squares refinement.

Absorption correction was applied[7] and the calculated transmission coefficients, based on a linear absorption coefficient of 177.7 cm^{-1} for Cu Kα radiation, ranged from 0.157 to 0.257.

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(1) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, 5, 417 (1970).

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(4) L. S. Sieker, E. Adman, and L. H. Jensen, *Nature (London)*, 235, 40 (1972).

(5) W. R. Dunham, G. Palmer, R. H. Sands, and A. J. Bearden, *Biochim. Biophys. Acta*, 253, 373 (1971).

(6) The factor c has been called by J. A. Ibers the "ignorance factor" and probably includes effects other than instrumental instability. In our case, the value of 0.024 represents the maximum variation of the intensity of the standards from their respective means throughout data collection. The final value of the standard deviation of an observation of unit weight, $[\Sigma w(F_{\text{o}} - F_{\text{c}})^2/(n - m)]^{1/2}$, where n is the number of observations (1963) and m is the number of variables (363), was 1.22 which indicates that a value of $c = 0.03$ would have been preferable.

(7) The computer programs used were locally modified versions of the following: F. R. Ahmed and C. P. Huber, NRC-2 (data reduction); F. R. Ahmed and P. Singh, NRC-3 (absorption correction); C. T. Prewitt, SFLS5 (least-squares refinement); A. Zalkin, FORDAP (Fourier, Patterson maps); R. J. Doedens and J. A. Ibers, NUCLS (least-squares refinement), with block-diagonal option introduced by J. Sygusch and C. K. Johnson, ORTEP (drawings).

Table I. Positional and Thermal Parameters of the Nonhydrogen Atoms in $[(C_5H_5)Fe(SC_2H_5)S]_2$ [a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe1	68,033 (2)	59,592 (5)	34,667 (3)	344 (2)	430 (2)	459 (2)	−0 (1)	48 (1)	1 (1)
Fe2	82,902 (2)	32,285 (5)	41,344 (3)	424 (2)	303 (2)	359 (2)	−6 (1)	61 (1)	2 (0)
S1	77,858 (4)	51,000 (8)	27,656 (5)	436 (4)	345 (4)	310 (3)	−6 (1)	49 (1)	−3 (1)
S2	69,294 (4)	32,144 (9)	38,888 (6)	428 (4)	431 (4)	480 (4)	−52 (1)	63 (1)	6 (1)
S3	85,548 (4)	50,244 (9)	54,119 (5)	422 (4)	429 (4)	329 (3)	−19 (1)	43 (1)	−8 (1)
S4	76,351 (4)	66,725 (9)	50,131 (6)	464 (4)	436 (4)	423 (4)	−3 (1)	85 (1)	−43 (1)
C1	55,289 (21)	59,681 (54)	29,060 (41)	364 (20)	817 (28)	1185 (35)	−2 (10)	19 (11)	43 (13)
C2	58,243 (25)	60,628 (57)	20,120 (36)	696 (27)	849 (30)	753 (27)	105 (12)	−77 (11)	−56 (11)
C3	62,834 (22)	75,252 (57)	21,253 (33)	618 (23)	842 (28)	749 (26)	151 (12)	66 (10)	161 (11)
C4	62,609 (21)	82,854 (46)	30,871 (37)	483 (21)	498 (22)	1091 (32)	63 (9)	45 (11)	34 (11)
C5	57,973 (21)	73,214 (60)	35,613 (35)	490 (22)	936 (30)	874 (28)	133 (11)	117 (10)	26 (12)
C6	91,721 (22)	15,725 (43)	50,336 (29)	663 (23)	482 (20)	554 (20)	78 (9)	58 (9)	30 (8)
C7	94,575 (20)	23,442 (46)	42,423 (33)	494 (19)	458 (19)	946 (28)	47 (9)	134 (10)	−11 (9)
C8	89,192 (25)	19,524 (47)	32,080 (30)	856 (27)	608 (23)	630 (22)	127 (10)	182 (10)	−3 (9)
C9	83,089 (24)	9,818 (43)	33,384 (31)	790 (25)	420 (19)	637 (22)	56 (9)	28 (10)	−73 (8)
C10	84,605 (23)	7,264 (40)	44,708 (34)	703 (24)	311 (18)	875 (26)	24 (9)	108 (10)	74 (9)
C11	84,898 (19)	67,962 (38)	28,914 (23)	531 (19)	398 (17)	367 (16)	−11 (7)	78 (7)	15 (7)
C12	92,054 (21)	63,786 (47)	25,291 (30)	544 (21)	681 (24)	638 (22)	−15 (9)	128 (9)	27 (9)
C13	68,203 (22)	28,206 (51)	52,431 (30)	645 (23)	780 (27)	645 (22)	68 (10)	148 (9)	102 (10)
C14	59,816 (28)	30,968 (71)	52,925 (40)	757 (27)	1315 (43)	1013 (34)	−70 (15)	262 (13)	50 (16)

[a] The coordinates are in fractions of unit cell edges ×10^5. The thermal parameters are given ×10^4. The standard deviations refer to the least significant digits. The temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \cdots + 2U_{23}klb^*c^*)]$.

Table II. Positional and Thermal Parameters of the Hydrogen Atoms[a]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
HC1	5248 (21)	5183 (56)	3054 (37)	43 (25)	104 (33)	137 (38)	1 (12)	−14 (12)	17 (15)
HC2	5788 (23)	5414 (51)	1475 (31)	86 (29)	93 (32)	71 (27)	25 (13)	−6 (11)	1 (12)
HC3	6549 (25)	7949 (62)	1609 (34)	110 (35)	124 (43)	84 (31)	16 (16)	7 (14)	9 (15)
HC4	6516 (19)	9318 (46)	3364 (33)	30 (20)	73 (27)	124 (34)	3 (9)	−3 (11)	18 (13)
HC5	5700 (21)	7568 (51)	4307 (33)	69 (24)	73 (27)	119 (32)	7 (12)	29 (12)	5 (12)
HC6	9407 (18)	1690 (37)	5801 (25)	53 (20)	46 (21)	58 (21)	11 (8)	7 (9)	10 (8)
HC7	9908 (20)	2960 (43)	4391 (28)	67 (24)	70 (26)	64 (23)	12 (11)	2 (10)	1 (10)
HC8	8936 (22)	2387 (53)	2502 (31)	99 (28)	92 (30)	84 (28)	19 (13)	28 (12)	3 (12)
HC9	7844 (21)	614 (40)	2723 (32)	83 (27)	26 (20)	112 (32)	−0 (9)	13 (12)	−8 (10)
HC10	8143 (20)	124 (39)	4779 (26)	79 (25)	42 (21)	53 (21)	1 (9)	6 (10)	−1 (8)
H1C11	8656 (15)	7160 (34)	3648 (19)	40 (16)	38 (18)	15 (14)	−6 (7)	4 (6)	0 (6)
H2C11	8174 (17)	7596 (38)	2414 (24)	65 (21)	40 (19)	48 (20)	−12 (9)	16 (9)	−4 (8)
H1C12	9553 (23)	7360 (59)	2542 (31)	105 (31)	135 (37)	75 (26)	−6 (16)	33 (12)	11 (13)
H2C12	9039 (26)	5856 (54)	1800 (33)	114 (34)	118 (37)	89 (30)	−18 (15)	30 (13)	−21 (13)
H3C12	9519 (19)	5573 (41)	3011 (27)	51 (21)	78 (24)	66 (23)	11 (10)	15 (9)	19 (10)
H1C13	6922 (27)	1642 (53)	5393 (34)	132 (36)	88 (32)	95 (32)	−5 (14)	30 (15)	0 (13)
H2C13	7206 (24)	3522 (62)	5759 (30)	93 (31)	159 (44)	67 (27)	−15 (15)	19 (12)	−5 (14)
H1C14	5948 (23)	2832 (56)	5984 (34)	76 (26)	119 (35)	107 (31)	−13 (14)	−23 (12)	−2 (14)
H2C14	5813 (29)	4152 (63)	5101 (40)	149 (46)	127 (44)	124 (39)	5 (18)	34 (18)	24 (17)
H3C14	5677 (25)	2289 (64)	4773 (31)	122 (34)	139 (41)	75 (28)	−42 (16)	24 (13)	−31 (14)

[a] The coordinates are in fractions of unit cell edges ×10^4. The thermal parameters are given ×10^3. The standard deviations refer to the least significant digits. The temperature factor is of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + \cdots + 2U_{23}klb^*c^*)]$.

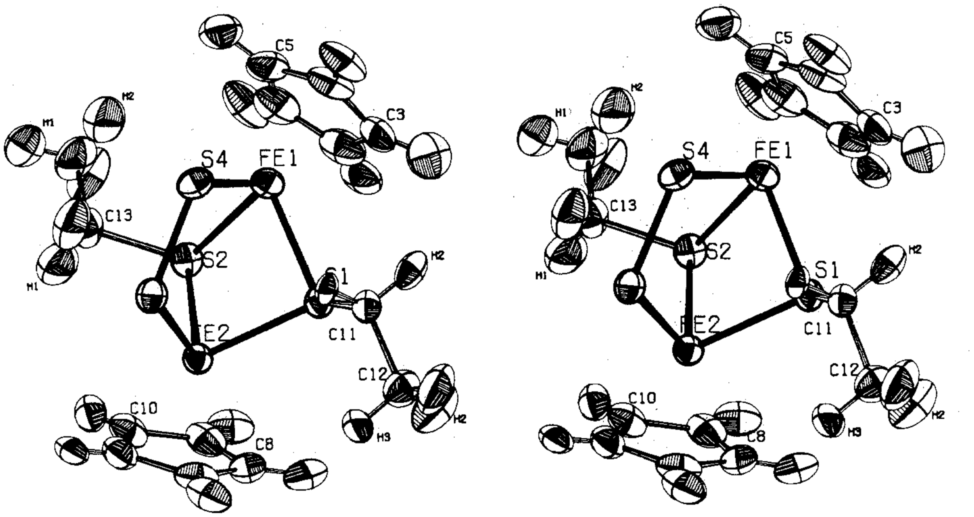

Figure 1. Stereoscopic illustration of the molecular structure of $[(C_5H_5)Fe(SC_2H_5)S]_2$ showing 33% probability ellipsoids.

Solution and Refinement of the Structure. The phases of the 272 largest ($E > 1.5$) normalized structure factors were determined by application of the tangent formula[8] using a CYBER 74 version of the MULTAN[8] direct-phasing program. The signs of three re-

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[8] G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27**, 368 (1971).

Table III. Distances and Angles of $[(C_5H_5)Fe(SC_2H_5)S]_2$ with Their Standard Deviations

Intramolecular Distances, Å

Fe1–Fe2	3.307 (1)	S3–S4	2.023 (3)
Fe1–S1	2.273 (2)	Fe2–S1	2.275 (2)
Fe1–S2	2.289 (2)	Fe2–S2	2.285 (2)
Fe1–S4	2.129 (2)	Fe2–S3	2.129 (2)
Fe1–C1	2.101 (7)	Fe2–C6	2.090 (8)
Fe1–C2	2.089 (8)	Fe2–C7	2.115 (8)
Fe1–C3	2.097 (8)	Fe2–C8	2.118 (8)
Fe1–C4	2.099 (7)	Fe2–C9	2.095 (7)
Fe1–C5	2.104 (8)	Fe2–C10	2.080 (7)
Av	2.098 (6)	Av	2.100 (6)
C1–C2	1.395 (13)	C6–C7	1.406 (14)
C2–C3	1.413 (14)	C7–C8	1.394 (12)
C3–C4	1.387 (12)	C8–C9	1.373 (14)
C4–C5	1.392 (12)	C9–C10	1.403 (13)
C5–C1	1.372 (13)	C10–C6	1.399 (11)
Av	1.392 (15)	Av	1.395 (13)
S1–C11	1.816 (5)	S2–C13	1.828 (6)
C11–C12	1.496 (8)	C13–C14	1.495 (10)
H1–C1	0.86 (7)	H6–C6	0.94 (6)
H2–C2	0.85 (7)	H7–C7	0.90 (7)
H3–C3	0.98 (8)	H8–C8	0.98 (7)
H4–C4	0.96 (7)	H9–C9	0.98 (7)
H5–C5	1.04 (8)	H10–C10	0.91 (6)
H1C11–C11	0.96 (5)	H1C13–C13	0.98 (8)
H2C11–C11	0.94 (6)	H2C13–C13	0.97 (8)
H1C12–C12	1.00 (8)	H1C14–C14	0.93 (8)
H2C12–C12	0.98 (8)	H2C14–C14	0.91 (9)
H3C12–C12	0.95 (7)	H3C14–C14	0.96 (9)

Closest Intermolecular Distances, Å

H6–H1C12[a]	2.43 (8)	H9–H2C11[c]	2.58 (7)
H6–H2C12[b]	2.61 (8)	H9–C2C13[d]	2.50 (8)

Bond Angles, Deg

S1–Fe1–S2	76.44 (5)	S1–Fe2–S2	76.50 (5)
S1–Fe1–S4	94.31 (5)	S1–Fe2–S3	93.98 (5)
S2–Fe1–S4	93.43 (5)	S2–Fe2–S3	94.17 (5)
Fe1–S1–Fe2	93.28 (5)	Se1–S2–Fe2	92.62 (5)
Fe1–S1–C11	107.49 (15)	Fe1–S2–C13	111.28 (20)
Fe2–S1–C11	110.71 (15)	Fe2–S2–C13	106.41 (20)
Fe1–S4–S3	107.76 (7)	Fe2–S3–S4	107.33 (6)
S1–C11–C12	113.8 (5)	S2–C13–C14	114.0 (5)
C1–C2–C3	107.7 (6)	C6–C7–C8	107.3 (6)
C2–C3–C4	107.0 (6)	C7–C8–C9	109.2 (6)
C3–C4–C5	108.5 (6)	C8–C9–C10	108.0 (6)
C4–C5–C1	108.4 (6)	C9–C10–C6	107.8 (6)
C5–C1–C2	108.3 (6)	C10–C6–C7	107.7 (6)
Av	108.0 (6)	Av	108.0 (7)
H1–C1–C2	127 (5)	H6–C6–C7	125 (4)
H1–C1–C5	125 (5)	H6–C6–C10	128 (4)
H2–C2–C1	132 (5)	H7–C7–C6	125 (4)
H2–C2–C3	120 (s)	H7–C7–C8	127 (4)
H3–C3–C2	127 (5)	H8–C8–C7	126 (5)
H3–C3–C4	126 (s)	H8–C8–C9	125 (5)
H4–C4–C3	125 (4)	H9–C9–C8	123 (4)
H4–C4–C5	126 (4)	H9–C9–C10	128 (4)
H5–C5–C4	125 (4)	H10–C10–C9	126 (4)
H5–C5–C1	126 (4)	H10–C10–C6	127 (4)
H1C11–C11–H2C11	112 (4)	H1C13–C13–H2C13	114 (7)
H1C11–C11–S1	108 (3)	H1C13–C13–S2	107 (5)
H1C11–C11–C12	111 (3)	H1C13–C13–C14	105 (5)
H2C11–C11–S1	103 (3)	H2C13–C13–S2	107 (5)
H2C11–C11–C12	109 (3)	H2C13–C13–C14	111 (5)
H1C12–C12–C11	112 (4)	H1C14–C14–C13	111 (5)
H2C12–C12–C11	112 (5)	H2C14–C14–C13	111 (6)
H3C12–C12–C11	109 (4)	H3C14–C14–C13	102 (5)
H1C12–C12–H2C12	111 (7)	H1C14–C14–H2C14	111 (8)
H1C12–C12–H3C12	109 (6)	H1C14–C14–H3C14	108 (7)
H2C12–C12–H3C12	105 (6)	H2C14–C14–H3C14	113 (8)

[a] For position $-x + 2, -y + 1, -z + 1$. [b] For position $x, -y + {}^1/_2, z + {}^1/_2$. [c] For position $x, y - 1, z$. [d] For position $x, -y + {}^1/_2, z - {}^1/_2$.

flections, namely, $15,3,\overline{1}$, $87\overline{2}$, $2,3,\overline{11}$—their E's being 2.70, 2.72, and 2.34, respectively—were specified as positive for defining the origin. The signs of three more reflections were "known" from the application of the Σ_1 formula. Two were negative—$16,0,\overline{4}$, $E = 2.46$, and $20\overline{8}$, $E = 2.13$—and one was positive—060, $E = 1.71$. In addition, two further reflections—533, $E = 2.43$, and 666, $E = 3.55$—which occured frequently in the Σ_2 interactions were included in the starting set for the phase determination. The weighted tangent formula[8] was used then along with the Σ_2 relationships to determine additional signs. Four sets of signs were found and each set constitutes a possible solution. To find out which solution was the most probable one, three "figures of merit" were calculated for each solution—$\Sigma_h\alpha h$[8], M_{abs}[8] (absolute figure of merit), and R(KARLE).[9] All three "figures of merit" indicated strongly that solution 1 (in which the signs of both reflections, 666 and 533, were negative) was the most probable one. Using the signs of solution 1, an E map was calculated which clearly revealed the positions of all Fe and S atoms, as well as 10 carbon atoms. Only the positions of the Fe and S atoms were entered in the least-squares refinement and a Fourier map was calculated which revealed the positions of all C atoms. Refinement proceeded normally using the block-diagonal least-squares approximation, in blocks of 9 × 9, and converged initially to an R_1 ($=\Sigma||F_o| - |F_c||/\Sigma|F_o|$) of 0.097 varying positional and individual isotropic temperature factors for all nonhydrogen atoms and using unit weights. Inclusion of anisotropic temperature factors and a secondary extinction correction[10] reduced R_1 to 0.039. A difference map showed 20 peaks of 0.40–0.87 e/Å^3, which also appeared in a Fourier map, suggesting positions for all the hydrogens. Inclusion and refinement of these positions as well as the individual temperature factors for hydrogens reduced R_1 to 0.025. Letting the hydrogens as well to refine anisotropically gave an R_1 of 0.023. At this point a counting statistics weighting scheme was introduced giving $R_1 = 0.022$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2} = 0.026$ (observed data, 1781 reflections) and $R_2 = 0.029$ (including unobserved data, 1963 reflections). The function $\Sigma w(|F_o| - |F_c|)^2/N$, where N is the number of reflections in the particular range, showed no significant variation with $|F_o|$, h (the slowest varying index during data collection), or $(\sin\theta)/\lambda$. Average and maximum shifts in the final least-squares refinement were 0.2σ and 0.5σ, respectively. The scattering factors for all nonhydrogen atoms are from Cromer and Waber,[11] those for hydrogen are from Stewart, *et al.*,[12] and the anomalous dispersion components for Fe and S are from Cromer.[13]

The observed and calculated structure factor amplitudes are available.[14] The final positional and thermal parameters for the nonhydrogen atoms are presented in Table I, and those for the hydrogen atoms, in Table II.

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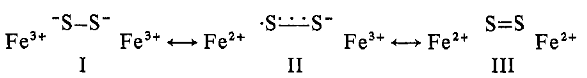
Results and Discussion

A discussion of the possible electronic structure of the Fe-S core and the relevance of this model to the chemistry and structure of the 2Fe-2S proteins has appeared in a preliminary report.[15] The crystal structure consists of dimeric $[(C_5H_5)Fe(SC_2H_5)S]_2$ units, one of which is shown in Figure 1.

There is a planar Fe-S-S-Fe bridge and the ethyl sulfide ligands also bridge the two irons while each is bonded to a π-cyclopentadienyl group. The coordination polyhedron about each iron can be viewed as a distorted octahedron, the S-Fe-S angles varying between 76 and 94° (Table III).

The iron-iron separation, 3.307 Å, is nonbonding. In the analogous monocharged $[(C_5H_5)Fe(SCH_3)CO]_2^+$ cation the Fe-Fe distance is 2.925 Å and a bond order of 0.5 (a one-electron metal-metal bond) has been assigned to the Fe-Fe bond.[16] In the neutral $[(C_5H_5)Fe(SC_6H_5)(CO)]_2$,[17] which has a structure very similar to the present one, the Fe-Fe distance is 3.39 Å and no metal-metal bond has been invoked.

The planar Fe-S-S-Fe bridge (Table V) is unprecedented while there are several analogous peroxide and superoxide bridges in binuclear cobalt(III) complexes.[18] Recently, the structures of nickel(II) and zinc(II) perthioarylates have been reported[19,20] and they contain an essentially planar M-S-S-C (M = Ni, Zn) structure. One could write three resonance forms for the Fe_2S_2 system and we believe that



$$\underset{\text{I}}{Fe^{3+}\ \overset{^-S-S^-}{}\ Fe^{3+}} \longleftrightarrow \underset{\text{II}}{Fe^{2+}\ \overset{\cdot S\text{:-:}S^-}{}\ Fe^{3+}} \longleftrightarrow \underset{\text{III}}{Fe^{2+}\ \overset{S=S}{}\ Fe^{2+}}$$

form II predominates. The dihedral angle about the S-S bond is 0°, as one finds in the superoxide bridge in the binuclear cobalt(III) complexes,[18] while a dihedral angle of close to 90° is normal for the disulfides.[21,22] From extensive structural studies of a series of compounds containing unsaturated five-member disulfide rings Hordvik[21,23] has found a (bond length)-(dihedral angle) relationship as well as suggested a linear (bond length)-(bond order) graph for S-S bonds in cis planar disulfide groups. According to this a S-S bond of 2.023 Å has a π-bond order of about $^1/_3$. The S-S-Fe angles are not greatly strained, having a mean value of 107.55°.

The cyclopentadienyl rings are planar within experimental error (Table IV). The ring C-C distances range from 1.372 (10) to 1.413 (10) Å, with an average of 1.393 Å. On the basis of a χ^2 test the deviations of the individual values from the mean are not significant at 1% probability level.

Table IV. Least-Squares Planes[a-c]

Plane 1		Plane 2		Plane 3	
Atom	Dist, Å	Atom	Dist, Å	Atom	Dist, Å
C1	0.002 (7)	C6	0.001 (6)	Fe1	0.003 (1)
C2	−0.002 (7)	C7	−0.003 (6)	Fe2	−0.003 (1)
C3	0.001 (7)	C8	0.005 (6)	S3	0.012 (2)
C4	0.000 (7)	C9	−0.004 (6)	S4	−0.014 (3)
C5	−0.001 (7)	C10	0.002 (5)		
H1	−0.03 (7)	H6	−0.05 (5)		
H2	−0.04 (7)	H7	0.00 (5)		
H3	0.03 (7)	H8	−0.07 (7)		
H4	0.02 (6)	H9	−0.06 (6)		
H5	−0.05 (6)	H10	−0.00 (5)		
Fe1	−1.732 (1)	Fe2	−1.732 (1)		

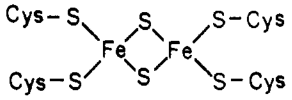
	Values		
Parameters	Plane 1	Plane 2	Plane 3
l	−0.6926	0.5787	0.6876
m	0.5007	−0.8146	0.5451
n	−0.5193	−0.0377	−0.4793
d	−5.2466	6.7773	7.7909
w[d]	142.1°	91.6°	

[a] The equations of the planes have the form $lx + my + nz = d$. [b] Distances in braces indicate atoms included in the calculation of the planes. [c] Standard deviations in parentheses. [d] Angle between normals to the planes.

These results, therefore, do not suggest any localization of ring electron density, although such localization has been suggested in π-cyclopentadienyl-metal complexes to explain differences in C-C bond lengths.[24-26] The ring carbon-Fe distances for ring 1 (C1-C5) range from 2.089 (7) to 2.104 (7) Å and are therefore equal within experimental errors, while for ring 2 (C6-C10) they range between 2.080 (5) and 2.118 (6) Å and on the basis of a χ^2 test the deviations of the individual values are significant. This is probably a reflection of the close intermolecular distances that exist for ring 2 and not for ring 1 (Table III). The metal-cyclopentadienyl bonding is therefore somewhat weaker than in ferrocene, where a value of 2.058 Å[27] was obtained for the Fe-C distance in an electron diffraction analysis.

Some close contacts of interest involve the disulfide bridge. The distance of H1C11 to both S3 and S4 (Figure 1) is 2.89 (4) Å, and on the other side of the S-S bridge, the distance of H2C13 from both S3 and S4 is 2.86 (7) Å.

Several models[5,28-30] have been proposed for the active site of plant ferredoxins and the most widely accepted one[5,30] contains two sulfide ions bridging two iron atoms as in structure A (Cys = cysteine).



A

The present work suggests new models containing a Fe-S-S-Fe bridge

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(14) A listing of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2132.

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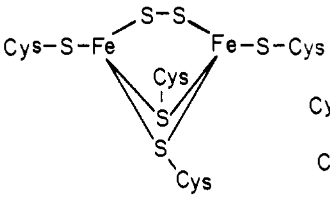
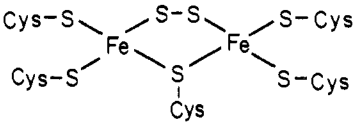


B



C

Structure C requires a fifth cysteine which is in fact present in all plant ferredoxins except in *Equisetum* ferredoxin.[31]

Registry No. $[(C_5H_5)Fe(SC_2H_5)S]_2$, 39796-99-1.

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Crystal Structure of Manganese Pyrophosphate Dihydrate, $Mn_2P_2O_7 \cdot 2H_2O$

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Manganese pyrophosphate dihydrate, $Mn_2P_2O_7 \cdot 2H_2O$, crystallizes in the monoclinic space group $P2_1/n$. A unit cell with dimensions $a = 6.461$ (2), $b = 14.325$ (4), and $c = 7.570$ (4) Å, and $\beta = 95.20$ (4)° contains four formula units. The manganese ions are each coordinated to five oxygen atoms and a water molecule in a distorted octahedral arrangement with a mean manganese–oxygen distance of 2.192 (1) Å. Chains of octahedra with shared edges run through the structure. The two ends of the pyrophosphate anion are 20° from the completely eclipsed conformation and the P–O–P bridge angle is 127.5 (2)°. The mean P–O distance for the terminal P–O bonds is 1.520 (2) Å while for the bridge oxygen the mean P–O bond distance is 1.613 (3) Å. The structure was solved by the symbolic addition method, based on diffractometer data collected with Mo Kα radiation, and it was refined by block-diagonal least squares to a conventional R value of 0.038 for 1506 reflections.

Introduction

In the solid state, the pyrophosphate ion is found to assume a rather wide range of conformations. The anhydrous pyrophosphate salts of the divalent metal ions, magnesium, zinc, and copper, exist in two phases. In the high-temperature (β) phase and in $Mn_2P_2O_7$, the pyrophosphate ion has a linear P–O–P bridge with considerable disorder in the bridge oxygen atoms.[1-4] The terminal PO_3 groups are oriented so as to present a staggered conformation when the ion is viewed along the P–P direction. In the low-temperature (α) phases of magnesium[5] and copper[6] pyrophosphate, the pyrophosphate ion is in a staggered conformation but with a bent P–O–P bridge. The high-temperature (α) phases of $Ca_2P_2O_7$[7] and $Sr_2P_2O_7$[8] contain pyrophosphate ions with bent bridge bonds but with an exactly eclipsed conformation in $Sr_2P_2O_7$ and an almost eclipsed conformation in $Ca_2P_2O_7$. The low-temperature form (β) of $Ca_2P_2O_7$ (and presumably the isostructural β-$Sr_2P_2O_7$) has bent P–O–P bonds and is almost eclipsed.[9] The crystal structure of only one hydrated pyrophosphate has been determined, $Na_4P_2O_7 \cdot 10H_2O$.[10,11] In that structure the bridge bonds are bent and the conformation is staggered. The crystal structure determination of $Mn_2P_2O_7 \cdot 2H_2O$ was undertaken to study the conformation of the $P_2O_7^{4-}$ ion in another type of crystal environment and to assess more fully the conformational range available to the pyrophosphate anion.

Experimental Section

Amorphous manganese pyrophosphate was prepared by mixing together solutions of manganese chloride and sodium pyrophosphate.[12] The precipitate was dissolved with sulfur dioxide and the sulfur dioxide was then removed slowly by bubbling carbon dioxide through the solution. A pink precipitate formed that was a mixture of microcrystals under 2 μ and larger prismatic crystals measuring up to 0.1 mm in length.

One of the larger crystals with dimensions 0.09 × 0.07 × 0.03 mm was chosen for X-ray analysis and mounted on a goniometer head. Preliminary examination of the reciprocal lattice and a determination of approximate lattice constants were made with a Buerger precession camera and Mo K radiation. The reciprocal lattice symmetry indicated that the crystal was monoclinic and the systematic extinction of $h0l$ reflections for $h + l$ odd and $0k0$ reflections for k odd established the space group uniquely as $P2_1/n$. This space group has the equivalent positions x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $\bar{x} + {}^1/_2, y + {}^1/_2, \bar{z} + {}^1/_2$; $x + {}^1/_2, \bar{y} + {}^1/_2, z + {}^1/_2$ and is merely a nonstandard orientation of $P2_1/c$. The lattice constants were refined by centering 12 high-angle reflections on the detector of an automated Picker four-circle diffractometer and using the 2θ angles measured with Mo Kα_1 radiation ($\lambda = 0.70926$ Å) as input to a least-squares adjustment. The final lattice constants obtained in this way were $a = 6.461$ (2), $b = 14.325$ (4), and $c = 7.570$ (4) Å and $\beta = 95.20$ (4)° at 25.5°. The density measured by flotation in a mixture of benzene and *s*-tetrabromoethane was 2.95 g/cm³. The density calculated for four molecules of $Mn_2P_2O_7 \cdot 2H_2O$ per unit cell is 3.06 g/cm³.

The intensity data were collected by the 2θ scan method with Zr-filtered Mo Kα radiation on an automated Picker four-circle diffractometer. A 3° target take-off angle was used and the scan range was increased from a minimum value of 1.0° to allow for dispersion as 2θ increased. The scans were made at 1°/min and the total number of counts recorded. Net intensities were calculated by sub-

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