

Synthetic Analogs of the Active Sites of Iron-Sulfur Proteins. II.¹ Synthesis and Structure of the Tetra[mercapto- μ_3 -sulfido-iron] Clusters, $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$

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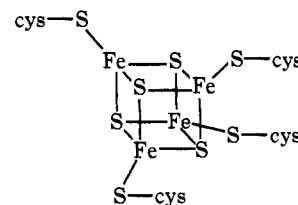
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Abstract: Reaction of ferric chloride in methanol with 3 equiv of sodium mercaptide followed by 1 equiv of a methanolic solution of sodium hydrosulfide and sodium methoxide affords the complexes $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ (R = alkyl, aryl), which may be precipitated and purified in the form of salts of quaternary cations. The crystal structure of a prototype member of the series, $[\text{Et}_4\text{N}]_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]$, has been determined from 4084 independent reflections collected by counter methods. The red-black crystals are monoclinic, space group $C_{2h}^5-P2_1/c$, with $a = 11.922(6)$, $b = 34.523(17)$, and $c = 12.762(5)$ Å and $\beta = 95.78(2)^\circ$. The measured density of 1.43(3) g cm⁻³ agrees with the density of 1.40 g cm⁻³, calculated for eight anions and four cations in the cell. The absorption corrected data gave a conventional R factor (on F) of 0.036 on least-squares refinement. The structure consists of discrete anions and cations; the geometry of the tetraethylammonium ion is unexceptional. The core (Fe_4S_4^*) of the anion exhibits distortions from cubic symmetry which are those of the point group $D_{2d}-4\bar{2}m$ such that each face of the polyhedron is a nonplanar rhomb. The bonded Fe-S* distances occur as sets of four (2.239(4) Å) and eight (2.310(3) Å), giving an average of 2.286 Å. The Fe-Fe distances occur as four short (2.732(3) Å) and two slightly longer (2.776 Å) separations and imply some direct metal-metal interactions. All four iron atoms are structurally indistinguishable. Comparisons of certain structural parameters of $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$ with those of the active sites of the reduced high-potential iron protein from *Chromatium* and the oxidized ferredoxin from *P. aerogenes* show that the three structures are unmistakably closely similar. This information together with comparative spectroscopic and magnetic evidence presented elsewhere demonstrates that the synthetic complexes $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ are true analogs of the active sites of bacterial iron-sulfur proteins.

Iron-sulfur proteins constitute one of the classes of metalloproteins and metalloenzymes which have been particularly extensively investigated in the last decade. Their biological, structural, and electronic properties have been reviewed in detail recently.⁵⁻⁸ The well characterized forms of these proteins contain one, two, four, and eight iron atoms; zero, two, four, and eight atoms of acid-labile or "inorganic" sulfur (S*); and a number of cysteinyl residues which equals or exceeds the number of iron atoms present. X-Ray structure determinations⁹⁻¹¹ and physicochemical studies^{7,8} have provided evidence for the minimal active site compositions as $\text{Fe}(\text{S-cys})_4$ (rubredoxins), $(\text{cys-S})_2\text{-FeS}^*_2\text{Fe}(\text{S-cys})_2$ (plant, mammalian, and certain bacterial proteins), and $(\text{cys-S})_4\text{Fe}_4\text{S}^*_4$ [4-Fe ("high-potential" iron proteins or HP) and 8-Fe bacterial pro-

teins]. Rubredoxin from *C. pasteurianum* contains a distorted Fe-S_4 tetrahedron.⁹ The active site of HP from *Chromatium* consists of an approximately cubic Fe_4S^*_4 cluster with Fe and S* at alternate vertices.¹⁰ The 8-Fe ferredoxin (Fd) from *P. aerogenes* contains two such clusters separated by 12 Å.¹¹ In these structures cysteinyl sulfurs act as terminal ligands to iron. No X-ray results are yet available for 2-Fe proteins, but the indicated active site formulation is considered fully consistent with a large body of magnetic and spectroscopic data.^{7,8,12}

As indicated by Tsibris and Woody,⁷ a detailed interpretation of the physical properties of the Fe-S proteins, many of which are unique, has been rendered difficult by the absence of well defined synthetic complexes whose structures and properties convincingly resemble those of the active sites of the proteins. We have initiated a research program directed toward preparation, isolation, and structural and electronic characterization of Fe-S complexes which may serve as meaningful analogs of active sites. Of particular relevance to the present work are the 4-Fe and 8-Fe proteins whose active site structures may be represented in an overall sense by 1. At the outset of this study



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(1) Part I: T. Herskovitz, B. A. Averill, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S. A.*, **69**, 2437 (1972).

(2) National Science Foundation Predoctoral Fellow, 1969-1972.

(3) Massachusetts Institute of Technology.

(4) Northwestern University.

(5) D. O. Hall and M. C. W. Evans, *Nature (London)*, **223**, 1342 (1969).

(6) B. B. Buchanan and D. I. Arnon, *Advan. Enzymol. Relat. Subj. Biochem.*, **33**, 119 (1970).

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

(8) G. Palmer and H. Brintzinger in "Electron and Coupled Energy Transfer in Biological Systems," T. E. King and M. Klingenberg, Ed., Vol. 1, Part B, Marcel Dekker, New York, N. Y., 1972, Chapter 9.

(9) (a) J. R. Herriott, L. C. Sieker, and L. H. Jensen, *J. Mol. Biol.*, **50**, 391 (1970); (b) K. D. Watenpaugh, L. C. Sieker, J. R. Herriott, and L. H. Jensen, *Cold Spring Harbor Symp. Quant. Biol.*, **36**, 359 (1971).

(10) C. W. Carter, Jr., S. T. Freer, Ng. H. Xuong, R. A. Alden, and J. Kraut, *ibid.*, **36**, 381 (1971).

(11) L. C. Sieker, E. Adman, and L. H. Jensen, *Nature (London)*, **235**, 40 (1972). The bacterial source of the ferredoxin whose structure is reported in this paper has been reclassified from *Micrococcus aerogenes* to *Peptococcus aerogenes* (L. H. Jensen, private communication).

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

Table I. Characterization Data for $(Q^+)_2[Fe_4S_4(SR)_4]^{2-}$

Q ⁺	R	Mp, ^a °C	Calcd, %					Found, %				
			C	H	N	S	Fe	C	H	N	S	Fe
<i>n</i> -Bu ₄ N	Me	238–239 ^b	42.19	8.26	2.73	25.03	21.80	42.31	8.24	2.75	24.85	21.72
Ph ₄ As ^c	Et	193–195 ^b	49.35	4.44		18.82	16.39	49.56	4.32		18.69	16.45
<i>n</i> -Bu ₄ N	<i>t</i> -Bu	240–243 ^b	48.31	9.12	2.35	21.50	18.72	48.10	9.09	2.46	21.32	18.47
Et ₄ N	CH ₂ Ph	123–124	47.83	6.20	2.54	23.21	20.22	47.72	6.35	2.59	23.14	20.25
Ph ₂ PCH ₂ Ph ^d	CH ₂ Ph	163–164 ^b	60.39	4.68		16.54	14.40	60.98	4.81		16.08	13.85
<i>n</i> -Pr ₄ N	CH ₂ C ₆ H ₁₁	248–249 ^b	50.31	8.77	2.26	20.66	18.00	50.54	8.58	2.48	20.78	17.82
<i>n</i> -Bu ₄ N	Ph	190–191	52.45	7.23	2.18	20.71	17.42	52.48	7.32	2.36	20.55	17.59
Me ₄ N	<i>p</i> -C ₆ H ₄ NO ₂	195–196 ^b	34.42	3.61	7.53	22.97	20.01	34.49	3.45	7.61	22.90	19.88
<i>n</i> -Bu ₄ N	C ₆ F ₅ ^e	154–157	41.19	4.44	1.72	15.71	13.68	40.92	4.54	1.85	16.04	13.77
Et ₄ N	C ₆ Cl ₅ ^f	192–193	27.65	2.32	1.61	14.76	12.86	27.68	2.33	1.76	14.72	12.80

^a Sealed tube, *in vacuo*. ^b Decomposes. ^c % As: calcd, 10.99; found, 11.10. ^d % P: calcd, 3.99; found, 3.81. ^e % F: calcd, 23.27; found, 23.38. ^f % Cl: calcd, 40.80; found, 40.42.

the only fully characterized synthetic species bearing any resemblance to **1** was $(h^5-C_5H_5)_4Fe_4S_4$, which has a similar cubane-type structure with cyclopentadienyl groups acting as terminal ligands.^{13,14} More recently, related structures have been established for $[(h^5-C_5H_5)_4Fe_4(CO)]^{0,+}$.¹⁵ Because of the non-physiological nature and specific electronic features of the cyclopentadienyl group, the utility of $(h^5-C_5H_5)_4Fe_4S_4$ as an active site analog is questionable. Consequently, synthetic routes to tetrameric complexes of the type $Fe_4S_4(SR)_4$, containing as terminal ligands simple organic mercaptides, were sought. This report describes the preparation and isolation of salts of the anion $[Fe_4S_4(SR)_4]^{2-}$ (R = alkyl, aryl) and a precise structural determination of a prototype member of the series, $[Et_4N]_2[Fe_4S_4(SCH_2Ph)_4]$. Elsewhere¹ we have described the essential structural features of the anion and certain magnetic and spectroscopic evidence which establish a relationship between it and the active sites of the reduced and oxidized forms of HP and 8-Fe clostridial proteins, respectively.

Experimental Section

Materials. Reagent grade methanol and acetonitrile were distilled from $Mg(OCH_3)_2$ and CaH_2 , respectively, and degassed by repeated evacuation and flushing with prepurified nitrogen gas (freed of oxygen by passage through a hot tower containing Badische Anilin und Soda Fabrik Catalyst R3-11) before use. The mercaptans employed were the best commercial grades available and, except for *p*-nitrothiophenol and pentachlorothiophenol, were not further purified. The former (technical grade, Eastern Chemical Co.) was treated with aqueous sodium hydroxide in boiling ethanol, the hot solution filtered, and the filtrate acidified with hydrochloric acid. The crude product was collected by filtration and recrystallized from 2-propanol to yield orange crystals, mp 75–77°. Technical grade pentachlorothiophenol (Chemicals Procurement Laboratory) was recrystallized twice from toluene-ethanol to afford off-white crystals, mp 238–241°. Sodium hydrosulfide was prepared by a published method.¹⁶

General Preparation of $[Fe_4S_4(SR)_4]^{2-}$ Salts. All operations were carried out in a pure nitrogen atmosphere. To a stirred solution of mercaptan (RSH, 90 mmol) and 4.86 g (90 mmol) of sodium methoxide in 200 ml of methanol, a filtered solution of 4.87 g (30 mmol) of anhydrous ferric chloride in 100 ml of methanol was added. The appearance of the reaction mixture at this point varied considerably depending on the nature of R (*vide infra*). A solution of 1.68 g (30 mmol) of sodium hydrosulfide and 1.62 g

(30 mmol) of sodium methoxide in 100 ml of methanol was immediately added; the mixture was stirred for 18 hr and filtered. The remaining solid was extracted with 50-ml portions of methanol until the extract was no longer intensely brown. The filtrate and extracts were combined and treated with 25 mmol of a salt of a quaternary cation (*cf.* Table I) in 100 ml of methanol. The resulting crystalline precipitate was collected by filtration, washed with 100-ml portions of methanol, water, and methanol, and dried *in vacuo* at room temperature. Purification was effected by twice dissolving the product in a minimum volume of warm (50°) acetonitrile, filtering the warm solution, adding methanol to incipient crystallization at 50°, and cooling slowly to –20°. The crystalline product was collected, washed with methanol, and dried *in vacuo* for 18 hr at room temperature. Yields of pure product, obtained as red-black crystals, varied from 30 to 77% depending on the nature of R. The benzyl mercaptan reaction was studied the most thoroughly and an average yield of 52% was obtained after one recrystallization. Notes on the preparation of individual compounds are given below. The salts isolated and their characterization data are summarized in Table I.

R = Me, Et, CH₂Ph, CH₂C₆H₁₁. In these cases addition of the ferric chloride solution to the mercaptide solution resulted in the immediate production of a bright green precipitate which formed a thick green slurry as all of the iron salt was added. Upon addition of the NaHS–NaOMe solution an immediate brown color appeared and increased in intensity during addition, upon completion of which most of the solid had dissolved. The insoluble green solid formed in the benzyl mercaptan reaction has been characterized by elemental analysis, which suggests the composition $[Fe(SCH_2Ph)_3]_n$. *Anal.* Calcd for $C_{21}H_{21}FeS_3$: C, 59.29; H, 4.97; Fe, 13.13; S, 22.61. Found: C, 57.40; H, 4.80; Fe, 12.73; S, 22.09; Cl, 2.36; Na, 0.70. This reaction was also run with anhydrous ferric bromide and no significant difference was observed.

R = *t*-Bu. Upon addition of a solution of ferric chloride to the mercaptide an immediate scarlet color was observed which increased in intensity as more iron salt was added. After addition was *ca.* two-thirds complete a rapid change to a pale khaki slurry occurred. Addition of the NaHS–NaOMe solution resulted in immediate dissolution of most of the solid to yield an orange-brown solution.

R = Ph. Addition of a solution of ferric chloride to the mercaptide resulted initially in the formation of a black precipitate. This material dissolved to give an intense green-brown solution as more ferric chloride was added and finally yielded a dark brown slurry when all of the iron salt had been added. The slurry reacted rapidly with NaHS–NaOMe to give an orange-brown solution. This reaction appears to be essentially quantitative inasmuch as there remained only 200–300 mg of black solid after methanol extraction. The crude product was isolated in 94% yield.

R = *p*-C₆H₄NO₂. Addition of the ferric chloride solution to the red mercaptide solution resulted in a marked increase in the intensity of the red color; a dark red solid precipitated after about one-half of the iron salt had been added. Most of the solid dissolved upon treatment with NaHS–NaOMe to give an intense red-orange solution.

R = C₆Cl₅. Upon addition of the ferric chloride solution to the lemon yellow mercaptide solution, a dark brown solid formed which gradually converted to a khaki-green slurry as all of the iron salt was added. Addition of NaHS–NaOMe resulted in the formation of a copious black precipitate and an intense brown solution.

(13) R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt, *Inorg. Chem.*, **5**, 892 (1966).

(14) C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *ibid.*, **5**, 900 (1966).

(15) (a) M. A. Neuman, Trinh-Toan, and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 3383 (1972); (b) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *ibid.*, **94**, 3389 (1972).

(16) R. E. Eibeck, *Inorg. Syn.*, **7**, 128 (1963).

$R = C_6F_5$. Addition of a solution of ferric chloride to the very pale yellow mercaptide solution gave a deep red solution and no solid. Upon addition of NaHS-NaOMe, a change in color to a brown-red solution and formation of a small amount of solid was observed. This compound is apparently less stable to heat than the others, as evidenced by partial decomposition of an acetonitrile solution at 50°; consequently, temperatures of solutions were not allowed to exceed 30° during the purification procedure.

Crystal Data for $[Et_4N]_2[Fe_4S_4(SCH_2Ph)_4]$. Because crystals of this compound are air sensitive, all transfers were done under pure nitrogen. Unit cell dimensions were obtained from a red-black crystal which had been sealed inside a glass capillary. On the basis of an extensive series of Weissenberg and precession photographs, it was found that the compound crystallizes in space group $C_{2h}^2-P2_1/c$ of the monoclinic system. Unit cell dimensions were obtained from the centering of 12 reflections on a FACS-1 automatic diffractometer using techniques previously described.¹⁷ Based on $\lambda(Mo K\alpha_1)$ of 0.70930 Å the dimensions are $a = 11.922$ (6), $b = 34.523$ (17), and $c = 12.762$ (5) Å and $\beta = 95.78$ (2)° at 23°. The density of 1.43 (3) g cm⁻³, observed by flotation of the crystals in aqueous ZnCl₂, is in good agreement with that of 1.40 g cm⁻³ calculated for 4 formula units in the cell. Thus no crystallographic symmetry need be imposed on the ions.

Data Collection and Reduction. The crystal selected for data collection was a plate of hexagonal cross section with plate faces {100} and the girdle faces {010} and {021}. The crystal had approximate dimensions 1.0 × 0.2 × 0.5 mm with a calculated volume of 0.0814 mm³.

Data were collected on a Picker FACS-1 diffractometer using Mo K α radiation that had been monochromatized from the (002) face of a highly mosaic graphite crystal. The takeoff angle used was 2.8°. The aperture was positioned 32 cm from the crystal and was set at 3 mm wide and 5 mm high to increase resolution, since a 35-Å cell dimension with Mo K α radiation could present overlap problems. There was no experimental evidence for overlapping reflections, as judged by the scan traces. Data were collected by the $\theta-2\theta$ scan method, using a scan from 0.8° 2θ below the K α_1 peak to 0.6° 2θ above the K α_2 peak. Backgrounds were counted at each end of the scan range. The scan rates (deg 2θ /min) and background counting times (sec) were as follows: $2\theta \leq 21^\circ$, 2.0, 4; $21^\circ < 2\theta \leq 28.5^\circ$, 2.0, 10; $28.5^\circ < 2\theta \leq 33^\circ$, 1.0, 10; $33^\circ < 2\theta \leq 40^\circ$, 1.0, 20. A total of 5047 independent reflections was collected. Of these 4084 obeyed the condition $I > 3\sigma(I)$, where $\sigma(I)$ is based on counting statistics and a p of 0.03. Six standards were monitored during the data collection. These showed a very slight, nearly uniform drop off with X-ray exposure, the average intensity being 97.5% of the initial at the termination of data collection. A linear correction was applied to the data for this presumed decomposition. Past 2θ of 40° the fraction of reflections of significant intensity was small and data collection was terminated. Data were processed in the usual way,^{17,18} and only the 4084 independent reflections above 3σ were carried in ensuing calculations.

Structure Solution and Refinement. The direct methods approach, based on 408 normalized structure factors, yielded the correct positions of the four Fe and eight S atoms of the anion.¹⁹ The other nonhydrogen atoms were found in a subsequent difference Fourier synthesis.

Refinement of the structure initially was by full-matrix least-squares methods. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and where the weights, w , were taken as $4F_o^2/\sigma^2(F_o^2)$. The agreement factors R and R_w are defined as $R = \sum ||F_o| - |F_c||/\sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. Atomic scattering factors were those of Cromer and Waber.²⁰ Anoma-

lous scattering factors for Fe and S were those calculated by Cromer and Liberman²¹ and were included in the calculated structure factors.²² Throughout the refinements the phenyl rings were constrained²³ to D_{6h} symmetry, with C-C taken as 1.392 Å. The data were corrected for absorption effects. Based on a linear absorption coefficient for Mo K α radiation of 13.6 cm⁻¹ the transmission factors were found to vary between 0.53 and 0.80. Refinement of a completely isotropic model for the two independent cations and the anion, with no contributions from H atoms, converged to an R factor of 0.11.

In a complete anisotropic refinement the number of variables exceeds that which may be handled on a computer with a memory of 64K words. Consequently, the anisotropic refinement was commenced using two blocks of the least-squares matrix. All nonhydrogen atoms were refined anisotropically, except for the C atoms in the rigid phenyl groups which were assigned variable, individual isotropic thermal parameters. Each of the matrix blocks included the scale factor and the parameters for the four Fe atoms. In addition block 1 contained the other atoms of the anion, while block 2 contained the atoms of the cations. A cycle of refinement of block 1 was followed by a cycle of refinement of block 2 and so forth until convergence was achieved. At this time the contributions of the H atoms were added. For the methylene H atoms the positions were calculated assuming C-H = 1.0 Å and a tetrahedral geometry and these atoms were assigned the equivalent isotropic thermal parameters of the C atoms to which they were attached. A difference Fourier synthesis revealed the positions of all of the methyl hydrogen atoms. These were idealized in a similar manner as were the phenyl hydrogens. After addition of the H atom contributions refinement was continued until convergence. At convergence R was 0.036, R_w was 0.047, and the error in an observation of unit weight was 2.19 e. A final difference Fourier synthesis showed a maximum density of 0.7 e/Å³, about 20% of that of a C atom in earlier syntheses. Analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of Miller indices, $|F_o|$, and scattering angle revealed no discernible trends. Calculation of $|F_c|$ for those reflections for which $I < 3\sigma(I)$ revealed none that was significantly above background. Thus these reflections are not included in the table²⁴ which gives the values of $10|F_o|$ and $10|F_c|$ (in electrons) for the 4084 reflections used in the refinement.

Table II lists the final parameters, together with the standard deviations of these parameters as estimated from the inverse matrices. Table III lists the positional parameters for the ring carbon atoms that may be derived from Table II. Table IV lists the calculated positions of the hydrogen atoms. Table V lists the root-mean-square amplitudes of vibration that may be derived from the data of Table II. The directions of the principal axes of vibration are discernible, at least approximately, from the figures.

Results and Discussion

Synthesis of $[Fe_4S_4(SR)_4]^{2-}$. The synthetic method affording these complexes was carried out in two stages. The initial reaction of ferric chloride with 3 equiv of sodium mercaptide (NaSR) in methanol resulted in the formation of a dark green solid when $R = Me, Et, CH_2Ph$, and $CH_2C_6H_{11}$. Analysis of the benzyl mercaptan reaction product suggests the composition $Fe(SCH_2Ph)_3$.²⁵ The highly insoluble nature of these

Crystallography," Vol. 4, Kynoch Press, Birmingham, England, in press, Table 2.2A.

(21) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(22) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, **17**, 781 (1964).

(23) See, for example, R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965).

(24) A tabular listing of structure amplitudes will appear immediately following this article 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 JACS-73-3523.

(25) Iron(III) mercaptides do not appear to have been reported previously. Reaction of iron(II) salts with excess ethanethiol in basic solution is claimed to yield $Fe(SET)_2$.²⁶ Ferric chloride is reduced to the ferrous state by pentafluorothiophenol but no mercaptide salt was isolated.²⁷

(26) W. Manchot and H. Gall, *Chem. Ber.*, **60**, 2318 (1927).

(27) M. E. Peach, *Can. J. Chem.*, **46**, 2189 (1968).

(17) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).

(18) R. J. Doedens and J. A. Ibers, *ibid.*, **6**, 204 (1967).

(19) In addition to local programs for the CDC 6400 used in this work, local versions of the following programs were employed: MULTAN, direct methods program of Main, Germain, and Woolfson; FORDAP, Fourier program of Zalkin; AGNOST, absorption program of Cahen (employing the Gaussian integration logic of Coppens, Leiserowitz, and Rabinovich); ORFFE, function and error program of Busing and Levy; ORTEP, thermal ellipsoid plotting program of Johnson; TMA, thermal analysis program of Dunitz and White (employing the Schomaker-Trueblood algorithms). Our least-squares program, NUCLS, in its nongroup form, closely resembles the ORFLS program of Busing and Levy.

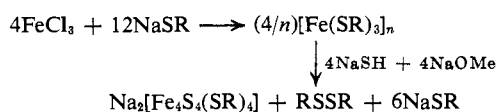
(20) D. T. Cromer and J. T. Waber, "International Tables for X-ray

Table II. Final Parameters for [Et₄N]₂[Fe₄S₄(SCH₂C₆H₅)₄]

Atom	x	y	z	10 ⁶ β ₁₁ ^a	10 ⁶ β ₂₂	10 ⁶ β ₃₃	10 ⁶ β ₁₂	10 ⁶ β ₁₃	10 ⁶ β ₂₃
Anion									
Fe(1)	0.18588 (6) ^b	0.10765 (2)	0.22477 (6)	599 (6)	87 (1)	628 (6)	-1 (2)	-25 (4)	42 (2)
Fe(2)	-0.00376 (6)	0.11121 (2)	0.07853 (5)	537 (6)	98 (1)	545 (5)	-26 (2)	25 (4)	9 (2)
Fe(3)	0.04297 (6)	0.16971 (2)	0.22079 (5)	539 (6)	94 (1)	527 (5)	-2 (2)	57 (4)	14 (2)
Fe(4)	0.17692 (6)	0.15797 (2)	0.05891 (5)	536 (6)	89 (1)	557 (5)	-5 (2)	97 (4)	23 (2)
S(1)	-0.01044 (11)	0.17450 (4)	0.04286 (10)	598 (11)	109 (2)	542 (9)	37 (3)	18 (8)	42 (3)
S(2)	0.23756 (10)	0.16992 (4)	0.23413 (10)	550 (10)	97 (2)	625 (10)	-34 (3)	19 (8)	8 (3)
S(3)	0.17654 (11)	0.09298 (4)	0.04729 (10)	668 (11)	96 (2)	703 (10)	24 (3)	93 (9)	-12 (3)
S(4)	-0.00072 (11)	0.10872 (4)	0.26021 (10)	659 (11)	111 (2)	552 (9)	-69 (3)	48 (8)	38 (3)
S(5)	0.29414 (13)	0.06688 (5)	0.32987 (13)	865 (14)	98 (2)	1078 (14)	3 (3)	-262 (11)	79 (4)
S(6)	-0.14829 (11)	0.07913 (4)	-0.00945 (10)	616 (11)	121 (2)	644 (10)	-48 (4)	5 (8)	-24 (3)
S(7)	-0.03766 (12)	0.21706 (5)	0.30763 (11)	805 (13)	116 (2)	728 (11)	45 (4)	179 (9)	4 (3)
S(8)	0.26820 (12)	0.19021 (4)	-0.06012 (11)	737 (12)	110 (2)	701 (10)	-17 (4)	223 (9)	43 (3)
C(1)	0.22253 (55)	0.02023 (20)	0.30503 (56)	975 (61)	117 (8)	1414 (66)	-37 (17)	-316 (50)	89 (18)
C(2)	-0.13879 (47)	0.02968 (18)	0.04208 (46)	763 (51)	117 (7)	1011 (50)	1 (16)	261 (41)	-39 (15)
C(3)	0.01575 (49)	0.26047 (18)	0.24720 (54)	779 (53)	105 (7)	1382 (63)	14 (16)	-10 (45)	65 (17)
C(4)	0.23350 (47)	0.24148 (18)	-0.04276 (49)	736 (50)	106 (7)	1125 (54)	-6 (15)	-34 (40)	93 (15)
Cation									
N(1)	-0.39489 (33)	0.16133 (14)	0.14377 (33)	501 (36)	112 (6)	807 (36)	77 (12)	54 (31)	6 (11)
C(5)	-0.49566 (48)	0.13793 (20)	0.09716 (50)	682 (52)	160 (9)	998 (53)	30 (18)	-61 (42)	-71 (18)
C(6)	-0.46775 (65)	0.10005 (26)	0.04646 (66)	1169 (74)	199 (12)	1557 (80)	78 (23)	-224 (59)	-225 (25)
C(7)	-0.44136 (49)	0.19772 (19)	0.18861 (48)	777 (53)	126 (8)	1043 (53)	100 (17)	103 (43)	-19 (16)
C(8)	-0.35626 (62)	0.22474 (22)	0.24538 (67)	1142 (71)	132 (9)	1825 (85)	76 (21)	-260 (62)	-132 (22)
C(9)	-0.32649 (58)	0.13802 (20)	0.22795 (58)	1085 (65)	126 (8)	1199 (65)	106 (19)	-388 (53)	-11 (18)
C(10)	-0.38907 (95)	0.12473 (25)	0.31827 (59)	3298 (157)	151 (10)	782 (59)	139 (33)	220 (77)	40 (20)
C(11)	-0.31404 (55)	0.17109 (24)	0.06350 (60)	885 (61)	185 (11)	1549 (74)	114 (21)	620 (57)	80 (23)
C(12)	-0.36478 (93)	0.19468 (31)	-0.02773 (72)	2777 (142)	275 (16)	1505 (86)	298 (39)	1189 (93)	299 (31)
N(2)	0.11162 (37)	0.40560 (13)	0.14557 (31)	864 (44)	92 (5)	647 (34)	-24 (12)	137 (31)	-16 (11)
C(13)	0.06468 (62)	0.43133 (20)	0.05549 (46)	1550 (82)	125 (8)	718 (48)	124 (21)	273 (49)	37 (16)
C(14)	-0.06089 (71)	0.42611 (28)	0.02154 (59)	1467 (89)	278 (15)	1008 (62)	237 (29)	-116 (58)	-54 (24)
C(15)	0.10193 (56)	0.36308 (18)	0.11521 (51)	1274 (69)	94 (7)	1019 (56)	-55 (17)	-29 (49)	-53 (16)
C(16)	0.16630 (72)	0.35192 (21)	0.02361 (53)	1998 (96)	136 (9)	864 (53)	202 (24)	-120 (57)	-82 (17)
C(17)	0.04445 (50)	0.41022 (20)	0.24073 (45)	919 (56)	136 (8)	824 (48)	-55 (17)	244 (41)	10 (16)
C(18)	0.03881 (58)	0.45075 (21)	0.28289 (50)	1279 (70)	152 (9)	980 (54)	-1 (20)	430 (49)	-105 (18)
C(19)	0.23388 (51)	0.41741 (18)	0.17227 (50)	902 (60)	106 (7)	1097 (56)	-48 (17)	302 (46)	-12 (16)
C(20)	0.29802 (57)	0.39550 (22)	0.26114 (54)	965 (61)	170 (10)	1100 (60)	23 (20)	4 (49)	47 (19)
Groups									
Ring ^c	x _c	y _c	z _c	δ	ε	η			
R(1)	0.37049 (21)	-0.04513 (8)	0.36935 (20)	2.625 (5)	2.007 (2)	2.709 (5)			
R(2)	-0.31816 (21)	0.01288 (8)	0.17293 (19)	-0.788 (4)	-2.355 (2)	1.963 (4)			
R(3)	-0.15265 (21)	0.31333 (8)	0.15307 (19)	-2.926 (6)	1.994 (2)	-1.042 (6)			
R(4)	0.40446 (21)	0.28506 (7)	0.08462 (19)	1.967 (5)	-2.084 (2)	1.338 (5)			

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b Here and in succeeding tables estimated standard deviations are parenthesized. ^c These group parameters have been defined previously. See, for example, S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).

green solids is similar to that of other metal (II, III) mercaptides for which polymeric structures have been proposed.²⁸ Reaction of the solids with NaHS-NaOMe in methanol produced a dark brown solution of the sodium salt of the tetranuclear anion and an amount of solid residue which, for a standard 18-hr reaction period, was variable with R. The following scheme appears to be a plausible representation of the overall reaction. In the cases of R = *t*-Bu, Ph, *p*-C₆H₄NO₂,



C₆Cl₅, and C₆F₅ addition of the ferric chloride to the mercaptide solution did not produce immediate precipitation of a green solid, and in several reaction mixtures color changes were observed during the course of

the addition. In these instances no attempts were made to determine the composition of the intermediate products. However, in all cases the products of the FeCl₃-NaSR reaction, when treated with NaHS-NaOMe solution, did afford intensely colored solutions from which crystalline salts of [Fe₄S₄(SR)₄]²⁻ could be precipitated by addition of an appropriate quaternary cation. These compounds were readily purified by recrystallization from acetonitrile-methanol, are soluble in polar organic solvents, and are stable in the solid and solution phases in the absence of oxygen.

The total oxidation level of [Fe₄S₄(SR)₄]²⁻, which implies the presence of two pairs of iron atoms in formal oxidation states (II) and (III) if bridging sulfur (*vide infra*) is considered as S²⁻, indicates that the overall preparative reaction involves oxidation-reduction. This process presumably occurs in the second stage, and in the benzyl mercaptan reaction dibenzyl disulfide was isolated from the reaction mixture. The amount of disulfide formed could not be directly related to the above reaction stoichiometry because the iron-mercap-

(28) G. Gorin and B. J. McCormick, *Inorg. Chem.*, **2**, 928 (1963); D. C. Bradley and C. H. Marsh, *Chem. Ind. (London)*, 361 (1967); C. J. Swann and D. L. Trimm, *ibid.*, 1363 (1967); D. A. Brown, W. K. Glass, and B. Kumar, *J. Chem. Soc. A*, 1510 (1969).

Table III. Derived Parameters for the Ring Carbon Atoms

Atom	x	y	z	B, Å ²
R(1)C(1)	0.30002 (30)	-0.01375 (10)	0.33341 (28)	4.8 (1)
R(1)C(2)	0.35646 (33)	-0.01663 (10)	0.43388 (25)	5.2 (1)
R(1)C(3)	0.42692 (32)	-0.04800 (12)	0.45982 (23)	5.8 (1)
R(1)C(4)	0.44095 (33)	-0.07650 (10)	0.38529 (31)	6.6 (2)
R(1)C(5)	0.38452 (36)	-0.07363 (10)	0.28482 (27)	6.3 (1)
R(1)C(6)	0.31405 (32)	-0.04226 (12)	0.25888 (22)	5.7 (1)
R(2)C(1)	-0.23220 (27)	0.02054 (11)	0.10996 (25)	4.4 (1)
R(2)C(2)	-0.32599 (32)	-0.00066 (12)	0.06986 (22)	5.5 (1)
R(2)C(3)	-0.41196 (27)	-0.00832 (13)	0.13283 (30)	6.4 (2)
R(2)C(4)	-0.40413 (28)	0.00521 (13)	0.23591 (28)	6.5 (2)
R(2)C(5)	-0.31033 (33)	0.02641 (12)	0.27601 (21)	5.9 (1)
R(2)C(6)	-0.22436 (27)	0.03408 (11)	0.21304 (26)	5.1 (1)
R(3)C(1)	-0.07516 (28)	0.28671 (10)	0.19899 (25)	4.1 (1)
R(3)C(2)	-0.12282 (31)	0.31401 (11)	0.26121 (20)	4.9 (1)
R(3)C(3)	-0.20031 (33)	0.34063 (10)	0.21530 (28)	5.9 (1)
R(3)C(4)	-0.23014 (32)	0.33995 (11)	0.10716 (29)	6.4 (1)
R(3)C(5)	-0.18248 (34)	0.31265 (12)	0.04493 (20)	6.2 (1)
R(3)C(6)	-0.10499 (32)	0.28602 (11)	0.09085 (24)	5.5 (1)
R(4)C(1)	0.32325 (27)	0.26333 (11)	0.02489 (24)	4.1 (1)
R(4)C(2)	0.40987 (31)	0.28080 (12)	-0.02309 (20)	5.3 (1)
R(4)C(3)	0.49108 (29)	0.30253 (12)	0.03663 (29)	6.5 (2)
R(4)C(4)	0.48567 (30)	0.30678 (12)	0.14433 (28)	6.3 (1)
R(4)C(5)	0.39904 (33)	0.28931 (12)	0.19231 (20)	5.6 (1)
R(4)C(6)	0.31784 (27)	0.26758 (11)	0.13259 (25)	5.1 (1)

Table IV. Calculated Coordinates of Hydrogen Atoms

Atom	x	y	z	Atom	x	y	z
C(5)H(1)	-0.5423	0.1541	0.0430	C(18)H(3)	0.0077	0.4694	0.2264
C(5)H(2)	-0.5453	0.1315	0.1551	C(19)H(1)	0.2366	0.4457	0.1885
C(6)H(1)	-0.4267	0.0824	0.0986	C(19)H(2)	0.2738	0.4133	0.1055
C(6)H(2)	-0.5376	0.0867	0.0133	C(20)H(1)	0.2863	0.3665	0.2511
C(6)H(3)	-0.4175	0.1054	-0.0120	C(20)H(2)	0.3810	0.4008	0.2650
C(7)H(1)	-0.4989	0.1907	0.2381	C(20)H(3)	0.2701	0.4028	0.3301
C(7)H(2)	-0.4826	0.2133	0.1284	C(1)H(1)	0.1940	0.0186	0.2289
C(8)H(1)	-0.2891	0.2275	0.2055	C(1)H(2)	0.1569	0.0189	0.3487
C(8)H(2)	-0.3892	0.2509	0.2570	C(2)H(1)	-0.0645	0.0265	0.0858
C(8)H(3)	-0.3301	0.2133	0.3175	C(2)H(2)	-0.1432	0.0111	-0.0181
C(9)H(1)	-0.2612	0.1541	0.2592	C(3)H(1)	0.0640	0.2524	0.1915
C(9)H(2)	-0.2960	0.1142	0.1952	C(3)H(2)	0.0629	0.2754	0.3032
C(10)H(1)	-0.3346	0.1080	0.3717	C(4)H(1)	0.1615	0.2432	-0.0091
C(10)H(2)	-0.4153	0.1463	0.3605	C(4)H(2)	0.2233	0.2542	-0.1138
C(10)H(3)	-0.4529	0.1069	0.2953	R(1)H(2)	0.3462	0.0040	0.4879
C(11)H(1)	-0.2826	0.1459	0.0368	R(1)H(3)	0.4680	-0.0500	0.5325
C(11)H(2)	-0.2480	0.1860	0.1000	R(1)H(4)	0.4924	-0.0991	0.4038
C(12)H(1)	-0.4184	0.1779	-0.0776	R(1)H(5)	0.3948	-0.0942	0.2307
C(12)H(2)	-0.4081	0.2171	-0.0058	R(1)H(6)	0.2730	-0.0402	0.1862
C(12)H(3)	-0.3048	0.2045	-0.0735	R(2)H(2)	-0.3318	-0.0106	-0.0044
C(13)H(1)	0.1093	0.4269	-0.0072	R(2)H(3)	-0.4798	-0.0238	0.1044
C(13)H(2)	0.0792	0.4598	0.0776	R(2)H(4)	-0.4661	-0.0003	0.2821
C(14)H(1)	-0.0805	0.3981	0.0243	R(2)H(5)	-0.3044	0.0364	0.3508
C(14)H(2)	-0.1068	0.4410	0.0699	R(2)H(6)	-0.1564	0.0496	0.2420
C(14)H(3)	-0.0804	0.4360	-0.0524	R(3)H(2)	-0.1009	0.3145	0.3393
C(15)H(1)	0.0186	0.3564	0.0989	R(3)H(3)	-0.2346	0.3604	0.2604
C(15)H(2)	0.1304	0.3469	0.1796	R(3)H(4)	-0.2864	0.3592	0.0740
C(16)H(1)	0.1595	0.3225	0.0104	R(3)H(5)	-0.2044	0.3121	-0.0335
C(16)H(2)	0.1323	0.3650	-0.0424	R(3)H(6)	-0.0706	0.2663	0.0454
C(16)H(3)	0.2466	0.3585	0.0375	R(4)H(2)	0.4138	0.2777	-0.1013
C(17)H(1)	0.0777	0.3929	0.2994	R(4)H(3)	0.5538	0.3152	0.0016
C(17)H(2)	-0.0361	0.4012	0.2202	R(4)H(4)	0.5446	0.3226	0.1873
C(18)H(1)	-0.0112	0.4525	0.3428	R(4)H(5)	0.3952	0.2925	0.2701
C(18)H(2)	0.1163	0.4602	0.3113	R(4)H(6)	0.2552	0.2550	0.1672

tide polymer did not react completely with the NaHS-NaOMe solution. The formation of a partially reduced tetramer as opposed to, *e.g.*, Fe₄S₄(SR)₄ (which might be a transient intermediate), is not unexpected in view of the inherent instability of a number of Fe(III)-mercaptide complexes. For example, in systems containing Fe(III) and cysteine²⁹ or thioglycollate,³⁰

(29) J. E. Taylor, J. F. Yen, and J. Wang, *J. Amer. Chem. Soc.*, **88**,

the initially formed Fe(III) complexes are unstable to intramolecular electron transfer under ambient conditions, affording RSSR and Fe(II) species which may be reoxidized by molecular oxygen in the presence of excess thiol to give the original complex. This reaction

1663 (1966); A. Tomita, H. Hirai, and S. Makishima, *Inorg. Chem.*, **7**, 760 (1968).

(30) D. L. Leussing and L. Newman, *J. Amer. Chem. Soc.*, **78**, 552 (1956).

Table V. Root-Mean-Square Amplitudes of Vibration (Å)

Atom	Cations			Atom	Anion		
	Min	Int	Max		Min	Int	Max
N(1)	0.171 (7)	0.257 (6)	0.273 (6)	Fe(1)	0.195 (1)	0.216 (1)	0.251 (1)
C(5)	0.215 (9)	0.271 (8)	0.331 (8)	Fe(2)	0.192 (1)	0.211 (1)	0.247 (1)
C(6)	0.264 (9)	0.282 (10)	0.433 (10)	Fe(3)	0.196 (1)	0.206 (1)	0.240 (1)
C(7)	0.204 (9)	0.288 (8)	0.303 (8)	Fe(4)	0.190 (1)	0.211 (1)	0.237 (1)
C(8)	0.254 (10)	0.273 (10)	0.421 (10)	S(1)	0.190 (2)	0.216 (2)	0.265 (2)
C(9)	0.208 (10)	0.282 (9)	0.369 (9)	S(2)	0.192 (2)	0.226 (2)	0.248 (2)
C(10)	0.247 (10)	0.297 (10)	0.491 (12)	S(3)	0.212 (2)	0.238 (2)	0.247 (2)
C(11)	0.196 (9)	0.316 (9)	0.394 (9)	S(4)	0.194 (2)	0.212 (2)	0.278 (2)
C(12)	0.246 (10)	0.344 (11)	0.541 (13)	S(5)	0.203 (2)	0.246 (2)	0.336 (2)
N(2)	0.223 (6)	0.230 (7)	0.258 (6)	S(6)	0.198 (2)	0.235 (2)	0.277 (2)
C(13)	0.233 (8)	0.249 (9)	0.355 (9)	S(7)	0.218 (2)	0.249 (2)	0.275 (2)
C(14)	0.265 (9)	0.297 (9)	0.447 (11)	S(8)	0.197 (2)	0.250 (2)	0.270 (2)
C(15)	0.219 (9)	0.291 (8)	0.316 (8)	C(1)	0.234 (8)	0.254 (9)	0.379 (8)
C(16)	0.232 (9)	0.268 (8)	0.417 (10)	C(2)	0.217 (8)	0.261 (8)	0.300 (7)
C(17)	0.223 (8)	0.273 (8)	0.297 (8)	C(3)	0.229 (8)	0.249 (9)	0.345 (8)
C(18)	0.221 (9)	0.302 (9)	0.343 (8)	C(4)	0.223 (8)	0.234 (8)	0.325 (7)
C(19)	0.224 (9)	0.260 (8)	0.311 (8)				
C(20)	0.256 (9)	0.298 (8)	0.330 (9)				

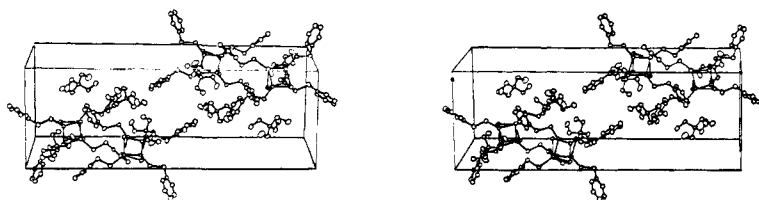


Figure 1. A stereoscopic view of the unit cell of $(\text{Et}_4\text{N})_2[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]$. Hydrogen atoms have been omitted for the sake of clarity. The atoms depicted are drawn with vibrational ellipsoids at the 20% probability level. In the drawing the origin is at the upper right, with the y axis running from right to left, the x axis from top to bottom, and the z axis into the paper.

sequence is the basis of the well known Fe(III)-catalyzed oxidation of thiols to disulfides and has been observed in the system Fe(III)-HS⁻-HOCH₂CH₂SH where the Fe(III) complex has been proposed as a model for Fe₂S₂ proteins.³¹ However, it has been possible in a number of cases to produce stable Fe(III)-mercaptide complexes³²⁻³⁴ and several of these, *viz.*, $[\text{Fe}(\text{S}_2\text{-CSR})_2(\text{SR})_2]^{3-}$ and $[\text{Fe}(\text{SCH}_2\text{CH}_2\text{S})_2]^{2-}$,³⁴ are referred to below.

As the preceding results demonstrate, variation of the mercaptan used in the synthetic method over a wide range of R groups results in the formation of complex anions with the same stoichiometry (Table I). Examination of the electronic and redox properties, some of which have been reported earlier,¹ for this series of complexes reveals that certain of these properties are influenced by the nature of R. Conspicuous among the properties influenced by substituent changes are the polarographic half-wave potentials for the process $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{3-} \rightleftharpoons [\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-} + e^-$ which span the extremes of -1.38 (R = *t*-Bu) to -0.73 V (R = *p*-C₆H₄NO₂) *vs.* sce in acetonitrile solution.³⁵ However, there is no indication from the spectroscopic, magnetic susceptibility, Mössbauer, and nmr results currently at

hand that substituent variation results in any significant structural change in the $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ series. Consequently, the structure of any one complex should be representative of all members of the series. The structure of $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$ as its tetraethylammonium salt has been determined. A brief description of the essential structural features of the anion has been given elsewhere.¹

Description of the Structure. 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 cations and anions. Figure 1 is a stereoscopic view of the contents of the unit cell. As may be seen, the anions occur in layers which are separated by layers of cations. Selected distances and angles for the ions are presented in Table VI. The cations have their expected geometry, with no evidence of disorder, and their structure is evident in Figure 1. The Fe₄S₄ core of the anion is a distorted cube with Fe and S* atoms at alternate vertices. The principal dimensions of the core together with the atom labeling scheme are given in Figure 2. Figure 3 is a stereoview of the complete anion.

As is seen in the figures and from the data of Table VI, the Fe₄S₄ core exhibits perceptible distortions from cubic (T_d) symmetry. Moreover, these distortions are not the result of the effects of thermal motion on the derived bond distances. Corrections for librational motion of the Fe₄S₄ portion of the anion result in bond distances which are uniformly 0.006-0.008 Å longer than those given in Table VI. As discussed below and in the Appendix the distortions from cubic symmetry of the Fe₄S₄ portion of the anion are those of the point group $D_{2d}\bar{4}2m$, where the $\bar{4}$ axis passes through the top and bottom faces of the polyhedron in Figure 2.

(31) C. S. Yang and F. M. Huennekens, *Biochemistry*, **9**, 2127 (1970).

(32) D. L. Leussing and J. P. Mislán, *J. Phys. Chem.*, **64**, 1908 (1960).

(33) (a) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, **92**, 3342 (1970); (b) D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2773 (1970).

(34) (a) T. Herskovitz and R. H. Holm, results to be submitted for publication; (b) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 249 (1973).

(35) B. A. Averill, T. Herskovitz, and R. H. Holm, results to be submitted for publication.

Table VI. Selected Distances (Å) and Angles (deg)

Cations		Anion	
N-C		C-N-C	
N(1)-C(5)	1.519 (7)	C(5)-N(1)-C(7)	106.6 (4)
N(1)-C(7)	1.509 (7)	C(5)-N(1)-C(9)	110.1 (5)
N(1)-C(9)	1.513 (8)	C(5)-N(1)-C(11)	112.7 (5)
N(1)-C(11)	1.514 (8)	C(7)-N(1)-C(9)	111.4 (4)
N(2)-C(13)	1.515 (8)	C(7)-N(1)-C(11)	110.8 (5)
N(2)-C(15)	1.520 (8)	C(9)-N(1)-C(11)	105.3 (5)
N(2)-C(17)	1.529 (7)	C(13)-N(2)-C(15)	111.1 (4)
N(2)-C(19)	1.519 (7)	C(13)-N(2)-C(17)	111.0 (5)
Mean	1.517 (3) ^a	C(13)-N(2)-C(19)	106.6 (5)
C-C		N-C-C'	
C(5)-C(6)	1.511 (10)	C(6)-C(5)-N(1)	115.4 (5)
C(7)-C(8)	1.509 (9)	C(8)-C(7)-N(1)	116.2 (5)
C(9)-C(10)	1.506 (11)	C(10)-C(9)-N(1)	115.6 (6)
C(11)-C(12)	1.498 (11)	C(12)-C(11)-N(1)	114.3 (6)
C(13)-C(14)	1.527 (10)	C(14)-C(13)-N(2)	115.0 (6)
C(15)-C(16)	1.512 (10)	C(16)-C(15)-N(2)	114.3 (6)
C(17)-C(18)	1.503 (9)	C(18)-C(17)-N(2)	115.3 (5)
C(19)-C(20)	1.506 (9)	C(20)-C(19)-N(2)	115.9 (5)
Mean	1.509 (3)	Mean	115.3
Anion		Anion	
Fe-S		S-C	
Fe(1)-S(5)	2.258 (2)	S(5)-C(1)	1.835 (7)
Fe(2)-S(6)	2.251 (2)	S(6)-C(2)	1.829 (6)
Fe(3)-S(7)	2.245 (2)	S(7)-C(3)	1.829 (6)
Fe(4)-S(8)	2.250 (2)	S(8)-C(4)	1.836 (6)
Mean	2.251 (3)	Mean	1.832 (3)
Fe...S*		C-ring	
Fe(1)-S(1)	3.886 (2)	C(1)-R(1)C(1)	1.515 (8)
Fe(2)-S(2)	3.896 (2)	C(2)-R(2)C(1)	1.511 (8)
Fe(3)-S(3)	3.894 (2)	C(3)-R(3)C(1)	1.497 (8)
Fe(4)-S(4)	3.882 (2)	C(4)-R(4)C(1)	1.508 (8)
Mean	3.890 (3)	Mean	1.507 (4)
S*...S*		Fe-Fe-Fe	
S(1)-S(2)	3.643 (3)	Fe(4)-Fe(1)-Fe(3)	60.78 (4)
S(3)-S(4)	3.647 (2)	Fe(4)-Fe(2)-Fe(3)	60.87 (4)
Mean	3.645	Fe(1)-Fe(3)-Fe(2)	61.23 (4)
S(1)-S(3)	3.587 (2)	Fe(1)-Fe(4)-Fe(2)	61.41 (4)
S(1)-S(4)	3.578 (2)	Mean	61.11
S(2)-S(3)	3.595 (2)	Fe(4)-Fe(1)-Fe(2)	59.15 (3)
S(2)-S(4)	3.583 (2)	Fe(3)-Fe(1)-Fe(2)	59.40 (3)
Mean	3.586 (4)	Fe(4)-Fe(2)-Fe(1)	59.45 (4)
Fe-S*-Fe		S-Fe-S*	
Fe(2)-S(1)-Fe(4)	73.97 (5)	S(5)-Fe(1)-S(2)	115.4 (1)
Fe(2)-S(1)-Fe(3)	74.20 (5)	S(5)-Fe(1)-S(3)	114.4 (1)
Fe(4)-S(1)-Fe(3)	73.98 (5)	S(5)-Fe(1)-S(4)	113.4 (1)
Fe(1)-S(2)-Fe(3)	73.96 (5)	S(6)-Fe(2)-S(1)	111.7 (1)
Fe(1)-S(2)-Fe(4)	73.72 (5)	S(6)-Fe(2)-S(3)	117.3 (1)
Fe(3)-S(2)-Fe(4)	73.43 (5)	S(6)-Fe(2)-S(4)	114.5 (1)
Fe(4)-S(3)-Fe(2)	73.31 (5)	S(7)-Fe(3)-S(1)	110.2 (1)
Fe(4)-S(3)-Fe(1)	73.58 (5)	S(7)-Fe(3)-S(2)	116.0 (1)
Fe(2)-S(3)-Fe(1)	74.06 (6)	S(7)-Fe(3)-S(4)	116.9 (1)
Fe(3)-S(4)-Fe(1)	73.80 (5)	S(8)-Fe(4)-S(1)	110.4 (1)
Fe(3)-S(4)-Fe(2)	73.79 (5)	S(8)-Fe(4)-S(2)	116.0 (1)
Fe(1)-S(4)-Fe(2)	73.95 (6)	S(8)-Fe(4)-S(3)	116.5 (1)
Mean	73.81	Mean	114.4
S*-S*-S*		S-C-ring	
S(4)-S(1)-S(3)	61.20 (5)	S(5)-C(1)-R(1)C(1)	112.1
S(4)-S(2)-S(3)	61.08 (5)	S(6)-C(2)-R(2)C(1)	112.2
S(1)-S(3)-S(2)	60.97 (5)	S(7)-C(3)-R(3)C(1)	113.6
S(1)-S(4)-S(2)	61.17 (5)	S(8)-C(4)-R(4)C(1)	113.3
Mean	61.11	Mean	112.8
S(4)-S(1)-S(2)	59.48 (4)		
S(3)-S(1)-S(2)	59.62 (4)		
S(4)-S(2)-S(1)	59.35 (4)		
S(3)-S(2)-S(1)	59.42 (4)		
S(1)-S(3)-S(4)	59.27 (4)		
S(2)-S(3)-S(4)	59.30 (4)		
S(1)-S(4)-S(3)	59.53 (4)		
S(2)-S(4)-S(3)	59.62 (5)		
Mean	59.45		

^a If given, the value in parentheses is the standard deviation of the mean, based on the larger of that estimated from the agreement among the *n* averaged values or that estimated from the average standard deviation of a single observation divided by \sqrt{n} . The estimated standard deviation of the mean is not given for any angular quantity, as the variations exceed those expected from a sample taken from the same population.

Table VII. Best Weighted Least-Squares Planes for the Anion

Plane no.	$Ax + By + Cz = D$ (monoclinic coordinates)			
	A	B	C	D
1	7.817	-4.951	-10.255	-1.385
2	8.894	-1.461	7.480	19.069
3	9.315	21.286	-2.236	3.520
4	7.100	-27.726	-0.534	-3.154
5	-0.637	-22.785	9.584	-1.779
6	1.645	26.261	7.876	4.903
7	1.569	34.115	-1.166	3.634
8	11.797	-4.504	-2.057	-0.776
9	0.682	2.609	12.566	1.207
10	11.790	-4.599	-2.108	1.297
11	0.687	2.513	12.568	3.301
12	1.499	34.127	-1.226	5.649

Atom	Deviations (\AA) from plane no.					
	1	2	3	4	5	6
Fe(1)	0.0001 (7)		0.0007 (7)			-0.0001 (8)
Fe(2)	-0.0001 (7)			0.0016 (8)	-0.0003 (7)	
Fe(3)		0.0012 (7)	-0.0006 (7)		0.0003 (7)	
Fe(4)		-0.0012 (7)		-0.0015 (7)		0.0001 (8)
S(1)	0.000 (1)		0.002 (1)			0.000 (1)
S(2)	0.000 (1)			0.004 (1)	-0.001 (1)	
S(3)		0.004 (1)	-0.002 (1)		0.001 (1)	
S(4)		-0.003 (1)		-0.005 (2)		0.000 (1)

Atom	Deviations (\AA) from plane no.					
	7	8	9	10	11	12
Fe(1)	0.0681 (8)		0.0680 (7)	-0.0745 (7)	-0.0779 (7)	
Fe(2)	0.0623 (8)	0.0689 (7)				
Fe(3)		0.0641 (7)			-0.0702 (7)	-0.0632 (8)
Fe(4)			0.0666 (7)	-0.0619 (7)		-0.0647 (8)
S(1)		-0.222 (1)	-0.220 (1)			0.238 (2)
S(2)				0.229 (1)	0.232 (1)	0.219 (1)
S(3)	-0.240 (2)		-0.249 (1)	0.257 (1)		
S(4)	-0.230 (2)	-0.258 (1)			0.242 (1)	

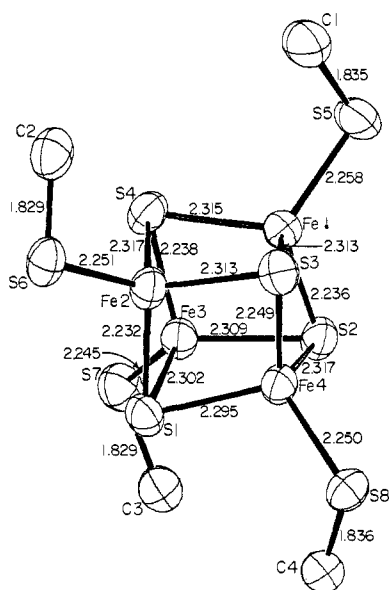


Figure 2. A portion of the $\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4$ core, showing 50% probability ellipsoids, principal interatomic distances, and the atom labeling scheme.

The angles $\text{S}^*-\text{Fe}-\text{S}^*$ average 104.09° while the angles $\text{Fe}-\text{S}^*-\text{Fe}$ average 73.81° , so that each face of the polyhedron is a rhomb. These rhombs are distinctly non-planar as the weighted least-squares planes in Table VII illustrate. There are six planes through the Fe_4S_4^*

core which are perfect within experimental error. These are the diagonal planes defined by the $\text{Fe}(n)$, $\text{Fe}(m)$, $\text{S}(n)$, and $\text{S}(m)$ where $1 \leq n \leq 3$ and $n < m \leq 4$.

Under D_{2d} symmetry the angles and distances of the Fe_4S_4^* core divide into the following sets: $\text{Fe}-\text{Fe}$ (2 + 4), $\text{Fe}-\text{S}^*$ (4 + 8), and $\text{Fe}-\text{Fe}-\text{Fe}$, $\text{S}^*-\text{Fe}-\text{S}^*$, $\text{Fe}-\text{S}^*-\text{Fe}$ (all 4 + 8). Except for the last two types of angles, the intrinsic differences in structural parameters for this symmetry were resolvable. The $\text{Fe}-\text{Fe}$ distances occur as *four* short (mean 2.732 \AA) and *two* slightly longer (mean 2.776 \AA) distances. With reference to the orientation of the core in Figure 2, the latter distances are found in the horizontal faces (perpendicular to the $\bar{4}$ axis) and the four short distances lie in the vertical faces. The average of all metal-metal distances is 2.746 \AA . The mean of the four $\text{Fe}-\text{Fe}-\text{Fe}$ angles whose legs lie in the vertical faces is 61.11° while that of the remaining eight angles is 59.46° . The two sets of bonded $\text{Fe}-\text{S}^*$ distances are four in the vertical faces (mean 2.239 \AA) and eight in the horizontal faces (mean 2.310 \AA) giving an average $\text{Fe}-\text{S}^*$ distance of 2.286 \AA . From these and other data in Tables VI and VII and inspection of the stereoview in Figure 3, the following structural features are evident: (i) the D_{2d} core polyhedron is slightly compressed along the $\bar{4}$ axis; (ii) in a qualitative sense the sulfur atoms are toward the outside of the polyhedron; (iii) the structural parameters of each iron site are insignificantly different. While static disorder of the anion cannot be rigorously ruled out, the apparent equivalence of all four iron atoms is consistent with a

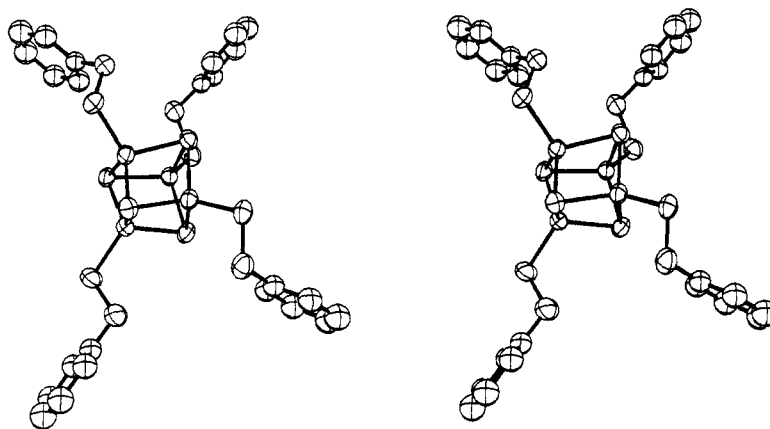


Figure 3. A stereoscopic view of the $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$ ion, complete except for hydrogen atoms. The 50% probability ellipsoids are shown.

Table VIII. Comparison of Mean Values for Selected Angles and Distances in Fe_4S_4 Cores

Dist, Å, or angle, ^a deg	$[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$ ^b	HP_{red}^c	Fd_{ox}^c	$[(\text{C}_5\text{H}_5)\text{FeS}]_4^d$	$[(\text{tfd})\text{FeS}]_4^{2-}$ ^e
Fe-Fe	2.776 (2), ^f 2.732 (4) ^g	2.81	2.85	2.650 (2), ^f 3.365 (4) ^g	3.23 (2), ^f 2.73 (4) ^g
Fe-S*	2.310 (8), ^h 2.239 (4) ⁱ	2.32	2.30	2.204 (8), ^h 2.250 (4) ⁱ	2.26 (8), ^h 2.16 (4) ⁱ
Fe-S	2.251	2.22	2.19		2.21
S*...S*	3.645 (2), ^j 3.586 (4) ^k	l	l	3.334 (2), ^j 2.880 (4) ^k	l
Fe-Fe-Fe	59.46 (8), ^m 61.11 (4) ⁿ	l	l	l	54 (8), ^m 73 (4) ⁿ
Fe-S*-Fe	73.81	76	78	73.9 (4), ^o 98.0 (8) ^p	l
S*-Fe-S*	104.1	104	101	98.2 (4), ^q 80.6 (8) ^r	79 (4), ^q 103 (8) ^r
S*-Fe-S	114.4	116	116		
S*-S*-S*	59.45 (8), ^s 61.11 (4) ^t	l	l	70.8 ^t	l

^a Type of distance or angle identified where necessary by reference to Figure 2; number of values averaged indicated in parentheses where two distances or angles are given. ^b This work. ^c Reference 40. ^d Monoclinic form, ref 14. ^e Reference 45. ^f Fe(1)-Fe(2). ^g Fe(1)-Fe(3). ^h Fe(1)-S(3). ⁱ Fe(1)-S(2). ^j S(3)-S(4). ^k S(3)-S(2). ^l Not reported. ^m Fe(4)-Fe(1)-Fe(2). ⁿ Fe(4)-Fe(1)-Fe(3). ^o Fe(1)-S(3)-Fe(2). ^p Fe(1)-S(3)-Fe(4). ^q S(3)-Fe(1)-S(4). ^r S(3)-Fe(1)-S(2). ^s S(4)-S(1)-S(2). ^t S(4)-S(1)-S(3).

variety of spectroscopic measurements on $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ in crystalline and solution phases which thus far have detected only one type of iron.^{1,35}

The terminal Fe-S bond lengths (mean 2.251 Å) are comparable to other iron-mercaptide sulfur distances in, e.g., $[\text{EtSFe}(\text{CO})_3]_2^{36}$ (2.26 Å), $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{SPh})]_2^{37}$ (2.26 Å), $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{SMe})]_2^{38}$ (2.23 Å), $[\text{Fe}(\text{S}_2\text{-CSEt})_2(\text{SEt})]_2^{33b}$ (2.22 Å), and $[\text{Fe}(\text{SCH}_2\text{CH}_2\text{S})_2]_2^{2-}$ ^{34b} (2.24 Å). Other than noting that the terminal distances are substantially shorter than the mean Fe(II)-S bond length of 2.36 Å in high-spin $\text{Fe}[\text{SPMe}_2\text{NPM}_2\text{S}]_2$,³⁹ no inferences concerning the effective oxidation state of iron in $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ can be drawn from comparison of bond lengths.

Comparison with Protein Active Site Structures. In part I¹ we have reported electronic spectral, Mössbauer, magnetic susceptibility, and pmr results which serve to demonstrate that the total oxidation levels of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$, the active site of the reduced form of HP (HP_{red}), and the active sites of the 8-Fe ferredoxins (Fd_{ox}) are the same. At that time information reported from ongoing X-ray investigations defined the overall active site structure of $\text{HP}_{\text{red,ox}}$ at 2.25 Å resolution¹⁰ as **1** and showed that *P. aerogenes* Fd_{ox} contained two

apparently similar clusters.¹¹ Very recently, the refined structures of HP_{red} and Fd_{ox} at 2.0 Å resolution have been described.⁴⁰ Comparison of selected angles and distances for these structures with those of the synthetic analog $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$ is presented in Table VIII. Despite the relatively large range of values for the protein structures at the reported stage of resolution,⁴¹ the similarity of all three structures is unmistakable. Indeed, comparison of the present data for the high-potential protein with those reported earlier¹⁰ indicates that upon further refinement the structural parameters of the active site are converging to those of the analog. No precise symmetry can as yet be assigned to the active site structure of either protein. Carter, *et al.*,⁴⁰ have argued that the protein Fe_4S_4^* geometry (and, by inference, that of the analog) is intermediate between limiting cubic and stellated tetrahedral structures, both of which have T_d symmetry. Clearly, a D_{2d} arrangement represents one compromise between these structural extremes and, in addition to $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$, has also been found in $(\text{C}_5\text{H}_5)_4\text{-Fe}_4\text{S}_4$.^{13,14} The results in Table VIII demonstrate that an $\text{S}_4\text{Fe}_4\text{S}_4^*$ unit structurally closely related to active site geometries can be stabilized in other than a

(40) C. W. Carter, Jr., J. Kraut, S. T. Freer, R. A. Alden, L. C. Sieker, E. Adman, and L. H. Jensen, *Proc. Nat. Acad. Sci. U. S.*, **69**, 3526 (1972).

(41) The following ranges have been reported:⁴⁰ Fe-Fe, 2.74-2.87 Å (HP_{red}), 2.65-3.04 Å (Fd_{ox}); Fe-S*, 2.18-2.45 Å (HP_{red}), 1.93-2.67 Å (Fd_{ox}); Fe-S*-Fe, 72-80° (HP_{red}), 66-91° (Fd_{ox}); S*-Fe-S*, 99-107° (HP_{red}), 88-116° (Fd_{ox}).

(36) L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, **2**, 328 (1963).

(37) G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Commun.*, 1165 (1968).

(38) N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7472 (1970).

(39) M. R. Churchill and J. Wormald, *Inorg. Chem.*, **10**, 1778 (1971).

Table IX. Comparison of Core Structures of $X_nM_4Y_4$ Complexes

Complex	M_4Y_4 core	Space group	Z^a	Imposed symmetry ^b	$Q, ^\circ \text{\AA}$	$\sigma^2 ^c$	Probable symmetry
$\text{Ph}_4\text{Al}(\text{NPh})_4^d$	Al_4N_4	$I4_1/a$	4	$\bar{4}$	0.0006	0.006, 0.76, 0.82	T_d
$(\text{C}_5\text{H}_5)_4\text{Fe}_4\text{S}_4^e$	Fe_4S_4	$C2/c$	4	2	0.0055	1.8, 1900, 2250	D_{2d}
$(\text{C}_5\text{H}_5)_4\text{Fe}_4\text{S}_4^f$	Fe_4S_4	$Pnam$	4	m	0.0036	14.2, 3350, 3350	D_{2d}
$[(\text{PhCH}_2\text{S})_4\text{Fe}_4\text{S}_4]^{2- \circ}$	Fe_4S_4	$P2_1/c$	4	None	0.0042	25.4, 289, 350	D_{2d}
$(\text{C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_4^h$	Fe_4C_4	$Pbca$	8	None	0.0069	16.0, 20.0, 21.0	T_d
$[(\text{C}_5\text{H}_5)_4\text{Fe}_4(\text{CO})_4]^{+ i}$	Fe_4C_4	$Pnma$	4	m	0.0133	26.8, 40.0, 40.0	D_{2d}
$(\text{C}_5\text{H}_5)_4\text{Co}_4\text{P}_4^j$	Co_4P_4	$Pmnb$	4	m	0.0033	11.1, 910, 910	D_{2d}
$(\text{C}_5\text{H}_5)_4\text{Co}_4\text{S}_4^k$	Co_4S_4	$C2/c$	4	2	0.0111	112, 530, 1100	$<D_{2d}$
$[(\text{C}_5\text{H}_5)_4\text{Co}_4\text{S}_4]^{+ k}$	Co_4S_4	$I\bar{4}$	2	$\bar{4}$	0.0034	0.55, 212, 212	D_{2d}
$(\text{OC})_{12}\text{Co}_4\text{Sb}_4^l$	Co_4Sb_4	$I4_1/amd$	4	$\bar{4}2m$	0	0, 6.8, 6.8	T_d
$(\text{OC})_{12}\text{Re}_4(\text{SMe})_4^m$	Re_4S_4	$P3_121$	3	2	0.0247	79, 108, 210	$<D_{2d}$
$(\text{EtOH})_4(\text{sal})_4\text{Ni}_4(\text{OMe})_4^n$	Ni_4O_4	$I4_1/a$	4	$\bar{4}$	0.0095	1.19, 13.1, 13.1	T_d
$(\text{MeOH})_4(\text{acac})_4\text{Co}_4(\text{OMe})_4^o$	Co_4O_4	$C2/c$	4	2	0.0238	8.4, 14.9, 23.5	T_d
$\text{Cu}_4(\text{EIA})_4^p$	Cu_4O_4	$P4_2/c$	2	2	0.0062	0.1, 280, 280	D_{2d}
$\text{Me}_{12}\text{Pt}_4(\text{OH})_4^q$	Pt_4O_4	$I\bar{4}3m$	2	$\bar{4}3m$	0	0, 0, 0	T_d (required)
$\text{Et}_{12}\text{Pt}_4\text{Cl}_4^r$	Pt_4Cl_4	$P2_1/n$	4	None	0.0311	15.9, 16.0, 19.1	T_d

^a Number of formula units in the cell. ^b Symmetry imposed by crystallographic symmetry elements. ^c See Appendix for definition. The value of Q given is for the orientation with the smallest σ^2 . ^d T. R. R. McDonald and W. S. McDonald, *Acta Crystallogr., Sect. B*, **28**, 1619 (1972). ^e Reference 14. ^f Reference 13. ^g This work. ^h Reference 15a. ⁱ Reference 15b. ^j Reference 52. ^k Reference 53. ^l Reference 51. ^m W. Harrison, W. C. Marsh, and J. Trotter, *J. Chem. Soc., Dalton Trans.*, 1009 (1972). ⁿ sal = salicylaldehyde anion: J. E. Andrew and A. B. Blake, *J. Chem. Soc. A*, 1456 (1969). ^o Ni(II) complex isomorphous: J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **10**, 240 (1971). ^p EIA = MeC(O)CHC(Me)NCH₂CH₂O: J. A. Bertrand and J. A. Kelley, *Inorg. Chim. Acta*, **4**, 203 (1970). ^q Reference 44. ^r R. N. Hargreaves and M. R. Truter, *J. Chem. Soc. A*, 90 (1970).

protein environment, and, together with the spectroscopic and magnetic evidence presented earlier,¹ constitute sufficient proof that the complexes $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ are true analogs of the active sites of clostridial Fe-S proteins.

Other Tetranuclear Cluster Systems. The active sites of 4-Fe and 8-Fe proteins and their synthetic analogs may now be recognized as members of a series of tetranuclear cluster systems of general formulation $[\text{X}_n\text{M}_4\text{Y}_4]$ ($n \geq 4$) which have the cubane-type structure containing bridging atoms Y and terminal ligands X. A number of structurally characterized complexes of this type are listed in Table IX. Other members of the series whose structures have been determined include $[\text{Me}_3\text{PtX}]_4$ ($X = \text{Cl},^{42} \text{I},^{43} \text{OH}^{44}$), $[(\text{tfd})\text{FeS}]_4^{2-}$ ⁴⁵ ($\text{tfd} = (\text{CF}_3)_2\text{C}_2\text{S}_2$), $[(\text{CO})_2(\text{NO})\text{Mo}(\text{OH})]_4$,⁴⁶ $[(\text{CO})_3\text{OsO}]_4$,⁴⁷ $[(\text{Et}_3\text{As})\text{Cu}]_4$,⁴⁸ $[\text{MeZn}(\text{OMe})]_4$,⁴⁹ and the linked double cluster $[\text{Me}_6\text{Zn}_7(\text{OMe})_8]$.⁵⁰ The diversity of M, X, and Y components which stabilize the cubane-type structure is impressive, as are the occurrences of cases in which direct metal-metal bonding may be considered to make a significant contribution (e.g., $[(\text{C}_5\text{H}_5)\text{FeS}]_4$,^{14,51} $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$,¹⁵ $[(\text{C}_5\text{H}_5)\text{CoP}]_4$ ⁵²) or little if any contribution (e.g., $[(\text{C}_5\text{H}_5)\text{CoS}]_4$,⁵³ $[(\text{CO})_3\text{CoSb}]_4$ ⁵¹) to

(42) R. E. Rundle and J. H. Sturdivant, *J. Amer. Chem. Soc.*, **69**, 1561 (1947).

(43) G. Donnay, L. B. Coleman, N. G. Krieghoff, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **24**, 157 (1968).

(44) H. S. Preston, J. C. Mills, and C. H. L. Kennard, *J. Organometal. Chem.*, **14**, 447 (1968); see also T. G. Spiro, D. H. Templeton, and A. Zalkin, *Inorg. Chem.*, **7**, 2165 (1968).

(45) I. Bernal, B. R. Davis, M. L. Good, and S. Chandra, *J. Coord. Chem.*, **2**, 61 (1972).

(46) V. Albano, P. Bellon, G. Ciani, and M. Manaserro, *Chem. Commun.*, 1242 (1969).

(47) D. Bright, *ibid.*, 1169 (1970).

(48) A. F. Wells, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **94**, 447 (1936).

(49) H. M. M. Shearer and C. B. Spencer, *Chem. Commun.*, 194 (1966).

(50) M. L. Ziegler and J. Weiss, *Angew. Chem., Int. Ed. Engl.*, **9**, 905 (1970).

(51) A. S. Foust and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7337 (1970).

(52) G. L. Simon and L. F. Dahl, *ibid.*, **95**, 2175 (1973).

(53) G. L. Simon and L. F. Dahl, *ibid.*, **95**, 2164 (1973).

the stability of the cluster. Inasmuch as explicit criteria for assignment of M_4Y_4 core symmetries have not been presented in all previous structural investigations, a procedure has been developed for assessing probable symmetries and is described in the Appendix. The results of this analysis for those structures for which the necessary data are in the literature are presented in Table IX. As may be seen, the probable core symmetries vary from T_d to $<D_{2d}$.

The only synthetic species other than $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ which have been shown by X-ray methods to possess the cubane-type Fe_4S_4^* core are $[(\text{C}_5\text{H}_5)\text{FeS}]_4^{2-}$ ($z = 0,^{13,14} 2+^{54}$) and $[(\text{tfd})\text{FeS}]_4^{2-}$.⁴⁵ It is pertinent to inquire whether these complexes, which are of considerable interest in their own right, serve as meaningful active site models. Like the proteins^{5-8,40} and their $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ analogs,^{1,35} they maintain the Fe_4S_4^* core in multiple oxidation levels.^{55,56} However, certain differences are evident. A structural comparison with the protein active sites is presented in Table VIII. The probable core symmetry of $[(\text{C}_5\text{H}_5)\text{FeS}]_4$ is D_{2d} (Table IX) whereas that of $[(\text{tfd})\text{FeS}]_4^{2-}$ appears to be lower on the basis of the preliminary report.⁴⁵ The average structural parameters for the latter have been calculated for idealized D_{2d} stereochemistry. It is apparent that the structures of the indicated oxidation levels are not congruent with those of $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$, HP_{red} , or Fd_{ox} . In addition, Mössbauer data^{45,56} for the series $[(\text{tfd})\text{FeS}]_4^{0,-,2-}$ show only slight changes with oxidation level and reveal substantially smaller ⁵⁷Fe isomer shifts and larger quadrupole coupling constants than found for $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$,^{1,35} $\text{HP}_{\text{red,ox}}$,⁵⁷ and Fd_{ox} .⁵⁸

(54) L. F. Dahl, private communication.

(55) J. A. Ferguson and T. J. Meyer, *Chem. Commun.*, 623 (1971).

(56) A. L. Balch, *J. Amer. Chem. Soc.*, **91**, 6962 (1969).

(57) M. C. W. Evans, D. O. Hall, and C. E. Johnson, *Biochem. J.*, **119**, 289 (1970).

(58) D. C. Blomstrom, E. Knight, Jr., W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U. S. A.*, **51**, 1085 (1964); T. H. Moss, A. J. Bearden, R. G. Bartsch, M. A. Cusanovich, and A. San Pietro, *Biochemistry*, **7**, 1591 (1968).

The structural and spectral differences noted above for the various even-electron species must ultimately be accountable in terms of different core electronic structures, which are influenced by the nature of the terminal ligands. While no detailed electronic structural descriptions can be offered at present, several comments are in order. The similarity between mercaptide ligands in $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ and cysteinyl residues in the proteins is apparent. Mercaptides are innocent ligands and in 1-Fe and 2-Fe proteins exert ligand fields of moderate strength.⁵² Cyclopentadienyl and dithiolene ligands are noninnocent and of the strong field, relatively covalent type leading to low-spin behavior and frequently indistinct metal and ligand formal oxidation levels. For $[\text{X}_n\text{M}_4\text{Y}_4]^z$ systems of the latter type Dahl and coworkers^{15b,51-53,60} have proposed a qualitative MO description of bonding, whose basic assumption is the (approximate) factorization of M-X and M-Y bonding from M-M interactions, thereby generating sets of symmetry orbitals assumed to be principally tetrametal in character. When the 76 valence electrons of $[(\text{C}_5\text{H}_5)\text{FeS}]_4$ are apportioned to terminal and bridge bonding and S^* lone pairs, the remaining 20 electrons are assigned to bonding ($a_1 + e + t_2$) and antibonding ($t_1 + t_2$) Fe_4 orbitals such that the D_{2d} core symmetry and the existence of two short and four long Fe-Fe interactions have been rationalized.⁵¹⁻⁵³ Previous work¹ has shown that $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$, HP_{red} , and Fd_{ox} possess equivalent levels of oxidation. These species contain 62 valence electrons and a similar treatment leaves 22 core electrons which, according to this description,^{15b,52,53} could be assigned the configuration $(a_1 + e + t_2)^{12} (e + t_1 + t_2)^{10} (t_1 + t_2)^0$ with the second set of orbitals neither strongly bonding nor antibonding. By these or equivalent considerations the cores of $[(\text{C}_5\text{H}_5)\text{FeS}]_4^{0,2+}$ and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ are not electronically analogous. The cases of $[(\text{tfd})\text{FeS}]_4^z$ ($z = 0, 1-, 2-$) are ambiguous with respect to the total number of valence and core electrons. If the dithiolene ligand is treated as a neutral two- or three-electron donor (equivalently, di- or monoanionic four-electron donors), there are 66 valence and 18 core or 70 valence and 22 core electrons in $[(\text{tfd})\text{FeS}]_4^{2-}$. A structural comparison of this complex with $[(\text{C}_5\text{H}_5)\text{FeS}]_4^{2+}$ suggests that the 18 electron formulation may be more appropriate.⁵⁴ However, if the 22 electron case is assumed,⁴⁵ thereby implying a similarity with $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ and the proteins, the slight sensitivity of Mössbauer parameters to total oxidation level in the $[(\text{tfd})\text{FeS}]_4^z$ series^{45,56} may be interpreted in terms of redox processes affecting principally the dithiolene ligands rather than the metal centers. Analogous behavior cannot obtain in clusters containing simple mercaptide terminal ligands.

The applicability of the delocalized MO bonding model to $[\text{Fe}_4\text{S}_4(\text{SR})_4]^z$ and the protein active sites must await further experimentation. The average Fe-Fe distance of 2.746 Å in $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$ is substantially longer than the values in $[(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_4]$ (2.520 Å) and its monocation (2.484 Å), which are considered to contain completely bonding Fe_4 units,¹⁵ but are comparable with the sets of short distances in $[(\text{C}_5\text{H}_5)\text{FeS}]_4$ and $[(\text{tfd})\text{FeS}]_4^{2-}$ (Table VII). The above electronic

configuration for $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ is consistent with a degree of net Fe-Fe bonding. However, the most sensitive test of a delocalized description *vs.* one in terms of localized or "trapped" mixed valence Fe(II, III) oxidation states⁶¹ must derive from measurements with a shorter *effective* molecular time scale than the spectroscopic techniques applied heretofore.¹ Toward this end low-temperature optical spectra of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ are being investigated. The results of this study and investigations of the structural and electronic relationship of the $z = 1-, 3-$ forms of the synthetic analogs to oxidation levels of HP and Fd proteins will be the subjects of future reports.

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Appendix

Symmetry of the M_4Y_4 Core. It is difficult to assess the true symmetry of a generalized M_4Y_4 core in a crystal structure where the positions of M and Y atoms are expressed in fractional coordinates along the crystallographic axes. For this reason the following procedure was adopted and, for the sake of simplicity, is illustrated only with the fractional coordinates x .

Given are the x_i for the eight atoms, together with the corresponding values of the standard deviations $\sigma(x_i)$. By standard matrix methods an approximate orientation of the M_4Y_4 core in an orthonormal coordinate system is first found, where the principal ($\bar{4}$) axis is taken perpendicular to particular $\text{M}_i\text{-M}_j$ vectors. In this coordinate system the transformed coordinates are now X_i with standard deviations $\sigma(X_i)$. A least-squares analysis is next performed in order to adjust rotations about the orthonormal axes to obtain the best fit to D_{2d} symmetry. In this symmetry, if a given M atom is at X, X, Z , then the other three M atoms are at \bar{X}, \bar{X}, Z ; \bar{X}, X, \bar{Z} ; and X, \bar{X}, \bar{Z} . A similar relationship holds (with different X and Z) for the Y atoms. The coordinate of the center of the axis system is defined as

$$X_c = 1/8 \sum_{i=1}^8 X_i$$

and new atomic coordinates are defined as

$$X_i' = X_i - X_c$$

Then for the M and Y atoms the

$$\bar{X}_i' = 1/3 \sum |X_i'|$$

are separately determined and we let $D_i = \bar{X}_i' \text{sign}(X_i') - X_i'$. The quantity $\sum D_i^2 / \sigma^2(X_i)$ is minimized over all 24 coordinates of the eight atoms. The process is cycled until convergence is reached. The final agreement factors are defined as the mean square deviation

(59) W. A. Eaton and W. Lovenberg, *J. Amer. Chem. Soc.*, **92**, 7195 (1970); W. A. Eaton, G. Palmer, J. A. Fee, T. Kimura, and W. Lovenberg, *Proc. Nat. Acad. Sci. U. S. A.*, **68**, 3015 (1971).

(60) B. K. Teo and L. F. Dahl, to be submitted for publication.

(61) Localized Co(II, III) valence states in the cubane-type complex $[\text{Co}_4(\text{acac})_4(\text{MeO})(\text{OAc})_2]$ have recently been established by X-ray diffraction: J. A. Bertrand and T. C. Hightower, *Inorg. Chem.*, **12**, 206 (1973).

$Q = (\sum D_i^2/21)^{1/2}$ and the variance in an observation of unit weight as

$$\sigma^2 = 1/21 \sum D_i^2 / \sigma^2(X_i)$$

The quantity σ^2 may be tested as $(\chi^2/21)$ with 21 degrees of freedom (24 observations, three variables—the rotation angles). The values of $(\chi^2/21)$ with probability P of being exceeded in a random sampling for 21 degrees of freedom are 10%, 1.41; 5%, 1.56; and 1%, 1.84. On this basis we may assess whether D_{2d} symmetry holds for this orientation of the M_4Y_4 core. The process is repeated for the other two possible orientations of the principal axis with respect to the M–M vectors. If D_{2d} symmetry holds for all three orientations, then the molecular symmetry is T_d .

Inspection of Table IX leads to the conclusion that for the majority of the entries the values of σ^2 are too large to enable one to assign symmetry by the above criterion. Thus either the hypothesis of D_{2d} or T_d symmetry is not true, or the standard deviations associated with the atomic parameters are too small. (Because

the information is lost in publication, the effects of correlation between atomic parameters were not included in this analysis, and only a diagonal weight matrix was employed. This could have some effect on the values of σ^2 .) On the basis of evidence accumulated over the years⁶² on careful X-ray structure determinations, in particular from comparative studies of the same structure carried out in different laboratories, it is reasonable to assume that the σ 's reported in crystal structure investigations should be increased by a factor of 3 or 4 before chemical information is derived from the structure. It is on this basis that the probable symmetry assignments are made in Table IX. It is clear that the definite assignment of symmetry to molecules in a crystal structure is very difficult, unless such symmetry is required by crystallographic constraints. Thus the assessment of minor apparent variations in symmetry between related molecules in different crystal structures is risky at best and cannot be used objectively to support theoretical calculations.

(62) See, for example, S. C. Abrahams, *Acta Crystallogr., Sect. B*, **28**, 2886 (1972).

Complex Formation between $\text{Eu}(\text{fod})_3$, a Lanthanide Shift Reagent, and Organic Molecules

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Abstract: The complex formation between $\text{Eu}(\text{fod})_3$, a lanthanide shift reagent, and acetone, dimethyl sulfoxide (DMSO), 2-propanol, and β -picoline dissolved in carbon tetrachloride was studied as a function of the reagent-to-substrate ratio, ρ , using the chemical shifts induced in the methyl proton resonances as an indicator. Detailed data analysis shows that the total stoichiometry of the reagent–substrate adduct is 1:2, with complexes of the type RS and RS_2 present in equilibrium. The dissociation constants of the two complexes differ greatly in magnitude: $K_2 > 4K_1$ for acetone and DMSO; $K_2 < 4K_1$ for 2-propanol and β -picoline. A substrate-induced ligand rearrangement around the central lanthanide ion is suggested to account for these observations. The calculated relative contributions of the two complexes to the observed shifts vary with ρ and with the substrate. The approach to the data analysis is presented in detail.

Following the original communication of Hinckley¹ in 1969 and as a result of the methodological investigations subsequently conducted by him and his coworkers, by Williams and coworkers,² as well as by others,³ some paramagnetic lanthanide β -diketonates that are soluble in organic solvents and are able to expand their coordination sphere and form adducts with organic molecules are now routinely used as chemical shift inducing agents in organic nmr spectroscopy. The proper interpretation of chemical shifts induced by lanthanide shift reagents in the spectra of substrate molecules requires some knowledge regarding the nature of the complex species present in solution, *viz.*, their stoichiometry, structure, and dissociation constants. In most of the published work

1:1 stoichiometry is implied. However, the existence in the solid state of reagent–substrate adducts of 1:2 stoichiometry has been demonstrated with $\text{Eu}(\text{dpm})_3$ both chemically¹ and crystallographically.^{4–6} Recently Evans and Wyatt showed that a 1:2 adduct is formed at low temperatures (-80°) between the deuterated analog of $\text{Eu}(\text{fod})_3$ and DMSO in CD_2Cl_2 solution.⁷ It is possible that an equilibrium between 1:1 and 1:2 adduct is present in solution at room temperature. Such an equilibrium may have unexpected effects on the chemical shifts induced on nuclei at different parts of the organic molecule thereby com-

(4) W. D. Horrocks, Jr., J. P. Sipe, III, and J. R. Luber, *J. Amer. Chem. Soc.*, **93**, 5258 (1971).

(5) R. E. Cramer and K. Seff, *J. Chem. Soc., Chem. Commun.*, 400 (1972).

(6) Abbreviations used: dpm, dipivaloylmethanate; fod, 1,1,1-, 2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate; pta, pivaloyltrifluoroacetate; DMSO, dimethyl sulfoxide; TMS, tetramethylsilane.

(7) D. F. Evans and M. Wyatt, *J. Chem. Soc., Chem. Commun.*, 312 (1972).

(1) C. C. Hinckley, *J. Amer. Chem. Soc.*, **91**, 5160 (1969).

(2) J. K. M. Sanders, S. W. Hanson, and D. H. Williams, *ibid.*, **94**, 5325 (1972), and references cited therein.

(3) For a recent review, see J. Reuben, *Progr. Nucl. Magn. Resonance Spectrosc.*, **9**, Part 1 (1973).