

- (6) T. V. Long, T. M. Loehr, J. R. Allkins, and W. Lovenberg, *J. Amer. Chem. Soc.*, **93**, 1809 (1971).
 (7) S. W. Tang, T. G. Spiro, K. Mukai, and T. Kimura, *Biochem. Biophys. Res. Commun.*, **53**, 869 (1973).
 (8) S. Lindskog, *Struct. Bonding (Berlin)*, **8**, 153 (1970).
 (9) C. Lazdunski, C. Petitclerc, D. Chappellet, and M. Lazdunski, *Biochem. Biophys. Res. Commun.*, **35**, 744 (1969).
 (10) G. H. Tait and B. L. Vallee, *Proc. Nat. Acad. Sci. U. S.*, **56**, 1247 (1966).
 (11) W. N. Lipscomb, J. A. Hartsuck, F. A. Quijcho, and G. N. Reeke, Jr., *Proc. Nat. Acad. Sci. U. S.*, **64**, 28 (1969).
 (12) B. W. Matthews, J. N. Jansonius, P. M. Colman, B. P. Schoenborn, and D. Dupourque, *Nature (London), New Biol.*, **238**, 41 (1972).
 (13) A. Liljas, K. K. Kannan, P.-C. Bergstén, I. Waara, K. Fridborg, B. Strandberg, U. Carlborn, L. Järup, S. Lövgren, and M. Petet, *Nature (London), New Biol.*, **235**, 131 (1972).
 (14) W. J. Eibeck, F. Holmes, and A. E. Underhill, *J. Chem. Soc. A*, 757 (1967).
 (15) P. J. Morris and R. B. Martin, *J. Amer. Chem. Soc.*, **92**, 1543 (1970).
 (16) C. Perchard, A.-M. Bellocq, and A. Novak, *J. Chim. Phys.*, **62**, 1344 (1965).
 (17) A. G. Sykes and J. A. Weil, *Progr. Inorg. Chem.*, **13**, 1 (1970).
 (18) M. Cordes and J. L. Walter, *Spectrochim. Acta, Part A*, **24**, 237 (1968).
 (19) A. C. Albrecht and M. C. Hutley, *J. Chem. Phys.*, **55**, 4438 (1971).
 (20) E. D. Schmid and B. Brosa, *J. Chem. Phys.*, **58**, 637 (1973).
 (21) G. J. Kubas and T. G. Spiro, *Inorg. Chem.*, **12**, 1797 (1973).
 (22) W. Kiefer and H. J. Bernstein, *Appl. Spectrosc.*, **25**, 609 (1971).
 (23) B. M. Holcomb, M.S. Thesis, Pennsylvania State University, 1973.
 (24) L. Rimai, R. G. Kilponen, and D. Gill, *J. Amer. Chem. Soc.*, **92**, 3824 (1970).
 (25) J. S. Loehr, T. B. Freedman, and T. M. Loehr, *Biochem. Biophys. Res. Commun.*, **56**, 510 (1974).
 (26) R. E. Derry, M. S. Thesis, Portland State University, 1974.

Synthetic Analogs of the Active Sites of Iron-Sulfur Proteins. XI.¹ Synthesis and Properties of Complexes Containing the Fe₂S₂ Core and the Structures of Bis[*o*-xylyl- α,α' -dithiolato- μ -sulfido-ferrate(III)] and Bis[*p*-tolylthiolato- μ -sulfido-ferrate(III)] Dianions

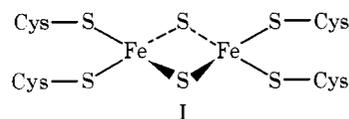
J. J. Mayerle,² S. E. Denmark,² B. V. DePamphilis,²
 James A. Ibers,^{*3} and R. H. Holm^{*2}

Contribution from the Departments of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Northwestern University, Evanston, Illinois 60201. Received August 13, 1974

Abstract: Although an extensive body of physicochemical data indicates that the active sites of plant ferredoxins (Fd) and similar 2-Fe proteins have the minimal formulation [Fe₂S₂(S-Cys)₄], the sites have not been defined by X-ray diffraction. Reaction of FeCl₃, *o*-C₆H₄(CH₂SH)₂, NaHS, and NaOMe in methanol affords the dimeric Fe(III) dianion [FeS(SCH₂)₂C₆H₄]₂²⁻ (**1**), isolated as its Et₄N⁺ and Ph₄As⁺ salts. The electronic spectra and other spectroscopic and magnetic properties of **1** indicate a clear electronic relationship to Fd_{ox} proteins. Ligand substitution reactions of **1** with arylthiols yield the dimers [Fe₂S₂(SAR)₄]₂²⁻ (Ar = Ph, *p*-tolyl (**4d**), *p*-C₆H₄Cl), isolated as Et₄N⁺ salts. The structures of **1** and **4d** (as their Et₄N⁺ salts) have been determined. Both salts crystallize with two formula units in space group C₂^{2h}-P2₁/n of the monoclinic system in unit cells of dimensions *a* = 9.549 (6) Å, *b* = 13.549 (6) Å, *c* = 14.748 (6) Å, and β = 95.42 (3)° (**1**) and *a* = 8.913 (3) Å, *b* = 16.132 (3) Å, *c* = 17.583 (3) Å, β = 97.14 (1)° (**4d**). The structures consist of well-separated cations and anions, the latter being sulfide-bridged dimers with crystallographically imposed centers of symmetry. Both anions contain planar and nearly isostructural Fe₂S₂* cores with Fe···Fe and mean Fe-S* distances of 2.698 (**1**) and 2.691 (**4d**) and 2.209 (**1**) and 2.201 Å (**4d**), respectively. The coordination units FeS₂*S₂ are distorted tetrahedra with bond angles of 104.7–112.3° (**1**) and 104.6–115.8° (**4d**). The structural and other properties of **1** indicate that it is a suitable minimal representation of the oxidized protein active sites and tend to confirm the previously proposed formulation of these sites. The reaction product of **1** with *p*-Me₃N⁺C₆H₄SH is identical with the previously reported complex prepared directly from FeCl₃, the thiol, and NaHS and is shown to be the cation dimer [Fe₂S₂(SC₆H₄NMe₃)₄]₂²⁺. Corresponding properties of [Fe₂S₂(SR)₄]₂²⁻ and [Fe₄S₄(SR)₄]₂²⁻ complexes at parity of R substituents are compared. Dimer Fe₂S₂* cores and tetramer Fe₂S₂* faces possess a high degree of dimensional similarity. Absorption spectra in the 400–600-nm region differ significantly. Dimeric complexes, as the tetramers, are reducible to 3– and 4– anions in steps which in most cases approach reversibility in DMF under dc and pulsed polarographic measurement conditions. Potentials for the [Fe₂S₂(SAR)₄]₂^{2-/3-} process show an approximate correlation with σ_p . Differences in potentials for 2–/3– and 3–/4– dimer reactions (*ca.* 300 mV) are much smaller than those for the corresponding tetramer reactions (*ca.* 700 mV). The comparative spectral and electrochemical properties should allow analysis of dimer–tetramer mixtures such as might result from the extrusion of active sites from complex Fe–S proteins with aryl thiols. The preparation of several arylthiolate tetramers from Fe₂S₂(CO)₆ is described.

Within the continually expanding group of purified iron-sulfur proteins,⁴ those containing two iron and two labile sulfur (S*) atoms and obtainable from plant, mammalian, and bacterial sources are at present the most numerous. Representative 2-Fe proteins have been subjected to extensive and elegant magnetic and spectroscopic characterization, and their physicochemical properties have been summarized in detail elsewhere.^{4–8} However, unlike the active centers of 1-Fe,⁹ 4-Fe,¹⁰ and 8-Fe^{10,11} proteins, the structure of the iron-sulfur unit apparently common to most, if not all, Fe₂S₂* proteins has not been conclusively estab-

lished by X-ray diffraction methods. Critical assessment of the physicochemical data has led to the generally accepted conclusion that the active site has the minimal composition [Fe₂S₂*(S-Cys)₄] and can be represented by the structure I.



In this formulation the Fe₂S₂* core of an oxidized protein

contains two Fe(III) ions which are high-spin, antiferromagnetically coupled, and tetrahedrally coordinated. This structure is consistent with the early considerations by Gibson, *et al.*,^{12a} and is the same as that explicitly set out for spinach ferredoxin and related proteins by Brintzinger, Palmer, and Sands^{12b} in 1966.

The lack of current structural definition of any 2-Fe protein has stimulated an investigation in these laboratories whose initial purpose has been to synthesize and to characterize structurally and electronically low molecular weight iron-sulfur complexes which might serve as reasonable representations of the active sites of these proteins. Prior to this study numerous discrete binuclear sulfur-bridged iron complexes had been prepared, the great majority of which contain metal centers bridged by SR fragments. As shown by structural studies, complexes of this type fall into two main classes: centrosymmetric Fe(II or III) dimers¹³ bridged by sulfur atoms included in chelate rings of the half-dimer (e.g., $[\text{Fe}(\text{mnt})_2]_2^{2-}$ ^{13a} and $[\text{Fe}(\text{SCH}_2\text{CH}_2\text{S})_2]_2^{2-}$ ^{13b}), and thiolate-bridged organometallic dimers^{13c,14} with varying degrees of direct metal-metal interactions (e.g., $[\text{Fe}(\text{S-Et})(\text{CO})_3]_2$,^{14a} $[\text{CpFe}(\text{CO})(\text{SR})]_2^{0,+}$ ^{14c,d} and $[\text{Fe}_2(\text{S-Me})_3(\text{CO})_6]^{+13e}$). The complexes $[\text{Fe}(\text{SR})(\text{S}_2\text{-CSR})_2]_2^{13d,15}$ are a unique class containing bridging thiolate and thioxanthate ligands. The only other structurally characterized binuclear complexes of possible interest are $\text{Fe}_2\text{S}_2(\text{CO})_6$ and $[\text{CpFeS}(\text{SEt})]_2$,¹⁷ both of which contain bridging S_2 units. Although the latter and the reaction product of $(\text{CF}_3)_2\text{C}_2\text{S}_2$, $\text{Fe}(\text{CO})_5$, and H_2S ¹⁸ have been considered as possible 2-Fe protein models, these and the other complexes referred to are not attractive in this respect because of one or more of the following features: presence of decidedly nonphysiological ligands, low formal metal oxidation states, room temperature diamagnetism, absence of terminal $-\text{CH}_2\text{S}$ ligands potentially similar to cysteinyl residues, and the absence of simple S bridging components. More promising as models are the complexes generated in aqueous solution by reaction of Fe(III) salts, sulfide, and thiols,^{19,20} some of which exhibit electronic spectral features similar to those of plant ferredoxins. However, certain of these complexes appear to be of limited stability and none has been isolated or otherwise characterized.

Recently we have reported the synthesis and essential structural and electronic features of the centrosymmetric dimer bis[*o*-xylyl- α,α' -dithiolato- μ -sulfido-ferrate(III)], $[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2^{2-}$ (**1**, Figure 1), whose properties reveal it to be the first well-characterized synthetic analog of the 2-Fe proteins.²¹ This article presents in more detail the synthesis and structural, spectral, and redox properties of this complex. In addition, it is shown that **1** undergoes thiolate ligand substitution reactions with aromatic thiols leading to the synthesis of a new class of dimers $[\text{Fe}_2\text{S}_2(\text{SAr})_4]^{2-}$ (**2d-4d**, Figure 1). The structure of a typical arylthiolate dimer, $[\text{Fe}_2\text{S}_2(\text{S-}i\text{-}p\text{-tol})_4]^{2-}$, as its tetraethylammonium salt, is described in full. Some properties of corresponding arylthiolate dimers and tetramers are compared, and it is shown that the previously reported²² reaction product from ferric chloride, sodium hydrosulfide, and *p*- $\text{Me}_3\text{N}^+\text{C}_6\text{H}_4\text{SH}$ is the cationic dimer $[\text{Fe}_2\text{S}_2(\text{SC}_6\text{H}_4\text{NMe}_3)_4]^{2+}$.

Experimental Section

Preparation of Compounds. All iron-sulfur complexes were prepared and purified under an atmosphere of pure dinitrogen gas. Melting points were determined in evacuated tubes and are uncorrected.

***o*-Xylene- α,α' -dithiol.** The following synthesis is more convenient than that described earlier.²³ α,α' -Dibromo-*o*-xylene (200 g, 0.76 mol) was combined with 115 g (1.52 mol) of thiourea in 600

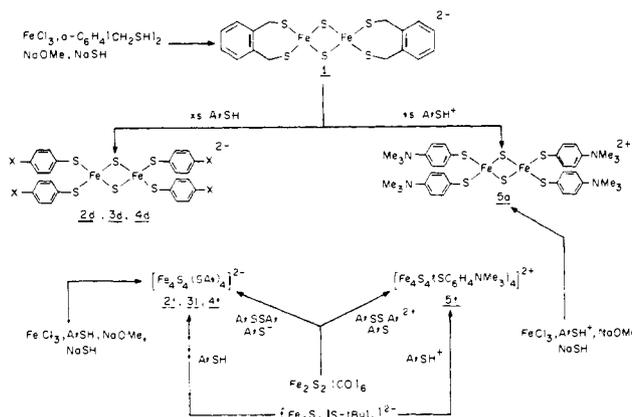


Figure 1. Scheme illustrating the preparation of $[\text{FeS}(\text{SC-H}_2)_2\text{C}_6\text{H}_4]_2^{2-}$ (**1**), arylthiolate dimers (**2d-5d**, X = H, CH_3 , Cl) from **1** by ligand substitution and arylthiolate tetramers (**2t-5t**, Ar = Ph, *p*-tolyl, *p*- $\text{C}_6\text{H}_4\text{Cl}$) by ligand substitution and direct synthesis. Dimer **5d** can also be prepared by direct synthesis.

ml of water and 100 ml of ethanol. The reaction mixture was refluxed for 3 hr. The system was purged of oxygen and the bis-(isothioronium) salt hydrolyzed by addition of a solution of 120 g (3.0 mol) of sodium hydroxide in 200 ml of water followed by refluxing for 90 min. The reaction mixture was cooled below 5° and acidified to pH 2 with 6 *N* sulfuric acid. The resultant white solid was collected by filtration, washed with 100 ml of 3 *N* sulfuric acid and repeatedly with water, and dried *in vacuo* to afford 125 g (97%) of the dithiol, mp $41-44^\circ$. This product can be employed in the following synthesis. Vacuum distillation of the product yielded a white solid: mp 44° (lit.²³ $44-46^\circ$); pmr (CDCl_3) δ 1.80 (t, 2, SH), 3.80 (d, 4, CH_2), 7.19 (s, 4, ring-H).

Bis[*o*-xylyl- α,α' -dithiolato- μ -sulfido-ferrate(III)], (a) Tetraphenylarsonium Salt. To a slurry of 1.7 g (10 mmol) of *o*-xylylene- α,α' -dithiol in 15 ml of methanol was added a solution of 1.1 g (20 mmol) of sodium methoxide in 20 ml of methanol. Anhydrous ferric chloride (0.81 g, 5.0 mmol) dissolved in 20 ml of methanol was added to the clear solution of sodium dithiolate, yielding a brown solution and some dark precipitate. The reaction mixture was stirred for 10 min and a freshly prepared solution of 0.27 g (5.0 mmol) of sodium methoxide and 0.28 g (5.0 mmol) of sodium hydrosulfide²⁴ in 20 ml of methanol was introduced. The solid dissolved immediately and a deep red-brown solution was obtained. After stirring for 2 hr, the solution was separated by filtration from a variable but usually slight quantity of black amorphous solid. Addition of the filtrate to a solution of 4.2 g (10 mmol) of tetraphenylarsonium chloride in 75 ml of DMF resulted in the precipitation of an amorphous brown material, which was collected by filtration and washed several times with small portions of methanol. The compound was obtained in analytically pure form by two recrystallizations from hot DMF-methanol, which afforded 0.80 g (25%) of a black microcrystalline solid. No definite melting point was found; some decomposition was evident at 73° and no further change was observed up to 360° . Analytical data are given elsewhere.²¹

(b) Tetraethylammonium Salt. The methanol filtrate containing $\text{Na}_2[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2$ was added to a stirred solution of 1.7 g (10 mmol) of tetraethylammonium chloride in 75 ml of DMF. Stirring during and after addition produced a microcrystalline red-brown solid in 35-50% yield which proved to be analytically pure, mp $\sim 190^\circ$ dec. Omission of stirring resulted in an amorphous brown solid which begins to crystallize only after prolonged contact with the parent solution. The compound can be recrystallized with difficulty from hot DMF-methanol or, more readily, from hot DMSO-ethanol yielding extremely fine dark red-brown crystals. Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{NS}_3\text{Fe}$: C, 49.73; H, 7.30; N, 3.62; S, 24.89; Fe, 14.45. Found: C, 49.42; H, 7.84; N, 3.72; S, 24.61; Fe, 14.32.

Tetraethylammonium Bis[bis(arylthiolato- μ -sulfido-ferrate(III)), (Et₄N)₂[Fe₂S₂(SAr)₄]. The following general ligand substitution reaction was used to prepare the benzenethiolate, *p*-tolylthiolate, and *p*-chlorobenzenethiolate complexes. To a stirred slurry of 0.77 g (1.0 mmol) of $(\text{Et}_4\text{N})_2[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2$ in 50 ml of acetoni-

trile was added a solution of *ca.* 20 mmol (five-fold excess) of the appropriate arylthiol in 50 ml of acetonitrile. The reaction solution immediately turned maroon and stirring was continued for several hours. The solution was warmed to 60°, diluted to three times its original volume with THF, and cooled to -20°. The resultant crystalline product was collected by filtration. (Spectral examination of the filtrate revealed the presence of some tetramer dianion $[\text{Fe}_4\text{S}_4(\text{SAR})_4]^{2-}$.) This product was twice recrystallized from acetonitrile-THF solutions (pronounced red-purple color) heated initially to *ca.* 60°. Red-black crystalline salts were obtained in 40–50% yields.

Ar = C₆H₅. *Anal.* Calcd for C₂₀H₃₀NS₃Fe: C, 55.03; H, 6.93; N, 3.21; S, 22.04; Fe, 12.79. Found: C, 55.04; H, 6.78; N, 3.23; S, 22.10; Fe, 12.74; mp 186–187° dec.

Ar = *p*-C₆H₄CH₃. *Anal.* Calcd for C₂₂H₃₄NS₃Fe: C, 56.88; H, 7.38; N, 3.02; S, 20.71; Fe, 12.02. Found: C, 56.94; H, 7.32; N, 3.07; S, 20.72; Fe, 12.09; mp 174–176°.

Ar = *p*-C₆H₄Cl. *Anal.* Calcd for C₂₀H₂₈Cl₂NS₃Fe: C, 47.53; H, 5.58; Cl, 14.03; N, 2.77; S, 19.03; Fe, 11.05. Found: C, 47.68; H, 5.50; Cl, 13.85; N, 2.84; S, 18.94; Fe, 11.12; mp 178–180°.

Bis[bis(*p*-trimethylammoniumbenzenethiolato)- μ -sulfido-ferrate-(III)] Hexafluorophosphate. This complex was prepared by the preceding method using (*p*-Me₃NC₆H₄SH)(PF₆)²² but with DMF as the reaction medium. Ethanol was used to precipitate the product, which was recrystallized from DMF-ethanol and obtained in 48% yield as small red-black crystals. A compound of the same stoichiometry had previously been obtained in low yield by direct synthesis²² and has been shown to be identical with the dimeric product from the ligand exchange reaction (see text).

(*n*-Bu₄N)₂[Fe₄S₄(SC₆H₄-*p*-Cl)₄]. This compound was prepared by the direct tetramer synthesis²⁵ and was purified by recrystallization from acetonitrile-methanol to afford the product in 67% yield as long black needles, mp 222–224°. *Anal.* Calcd for C₅₆H₈₈Cl₄N₂S₈Fe₄: C, 47.67; H, 6.29; N, 1.99; S, 18.18; Fe, 15.83. Found: C, 47.78; H, 6.12; N, 2.05; S, 18.08; Fe, 15.97.

Tetramer Dianions from Fe₂S₂(CO)₆. (a) **(Ph₄As)₂[Fe₄S₄(SPh)₄].** To a solution of 0.69 g (2.0 mmol) of Fe₂S₂(CO)₆²⁶ in 25 ml of methanol was added 0.44 g (2.0 mmol) of diphenyl disulfide in 25 ml of methanol followed by a solution of 0.41 ml (4 mmol) of benzenethiol and 0.21 g (4.0 mmol) of sodium methoxide in 10 ml of methanol. The red-brown reaction mixture was refluxed for 1 hr, and the progress of the reaction was monitored by loss of CO absorption at 1900–2100 cm⁻¹. Addition of 1.5 g (3.6 mmol) of tetraphenylarsonium chloride in 20 ml of ethanol gave a dark brown precipitate. This material was washed with methanol (two 20-ml portions), dried *in vacuo*, and recrystallized from hot acetonitrile to afford 1.44 g (65%) of pure product as black crystals, mp 192–194° (lit.²⁷ 191–193°). The electronic spectrum (Figure 2) is the same as that for an analyzed salt of this tetramer.²²

(b) **[Fe₄S₄(SC₆H₄-*p*-NMe₃)₄](PF₆)₂.** To a mixture of 0.688 g (2.00 mmol) of Fe₂S₂(CO)₆ and 1.25 g (2.00 mmol) of 4,4'-bis(trimethylammonium)diphenyl disulfide hexafluorophosphate, each in 25 ml of acetonitrile, was added a solution of 1.25 g (4.00 mmol)

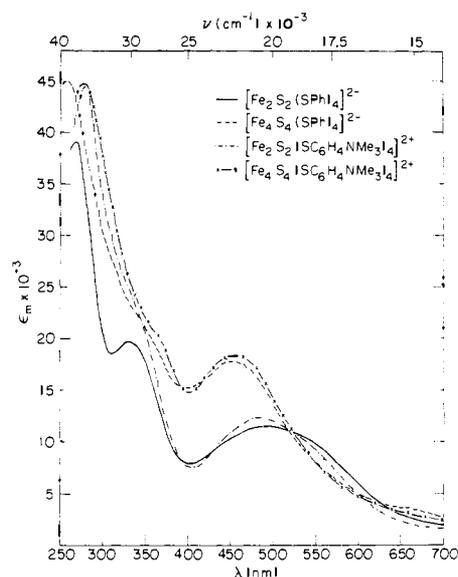


Figure 2. Electronic spectra of dimeric and tetrameric arylthiolate dianion and dication complexes in DMF solution.

of (*p*-Me₃NC₆H₄SH)(PF₆)²² and 0.216 g (4.00 mmol) of sodium methoxide in 25 ml of methanol. The reaction mixture was refluxed for 1 hr, during which time product precipitated from the red-brown solution. This material was isolated by addition of methanol and cooling of the reaction solution. After collection by filtration and drying, the solid was recrystallized from hot acetonitrile-ethanol to afford 0.59 g (45%) of black crystals, mp 160–161°. *Anal.* Calcd for C₃₆H₅₂F₁₂N₄P₂S₈Fe₄: C, 32.99; H, 4.00; N, 4.27; P, 4.73; S, 19.57; Fe, 17.04. Found: C, 32.81; H, 4.06; N, 4.30; P, 4.64; S, 19.43; Fe, 17.14.

Reaction of *cis*-2-Butene-1,4-dithiol with Fe(III) and Sulfide. *cis*-2-Butene-1,4-dibromide, prepared²⁸ from *cis*-2-butene-1,4-diol (91% *cis*, Aldrich Chemical Co.) in 60% yield and fractionally recrystallized from hexane at -75° to remove any trans isomer, was converted to the dithiol by treatment with sodium trithiocarbonate²⁹ and unexceptional work-up. The dithiol was obtained in 41% yield after distillation: bp 39° (0.6 mm); bis(*p*-nitrobenzoate), mp 158–160° (lit.³⁰ 158–159°) (*cis* isomer). Ferric chloride (10 mmol) was treated with the dithiol (20 mmol) and sodium hydrosulfide (10 mmol) in a total reaction mixture volume of 90 ml of methanol using the procedure for the preparation of [FeS(SCH₂)₂C₆H₄]₂²⁻. The *n*-Bu₄N⁺ salt precipitated from the filtrate was isolated as a brown solid: λ_{max} (DMSO), 600 (sh, w), 400 nm (sh or maximum, s). This salt (*ca.* 250 mg) was treated with excess *p*-tolylthiol in acetonitrile, and the red-brown reaction mixture was stirred for 12 hr. The electronic spectrum of the filtrate was identical with that of [Fe₄S₄(*S-p*-tol)₄]²⁻ (Table I).

Table I. Electronic Spectra of Dimeric and Tetrameric Complexes

Complex	Solvent	λ_{max} , nm (ϵ_M^a)
Dimers		
[FeS(SCH ₂) ₂ C ₆ H ₄] ₂ ²⁻ <i>f</i>	DMF	294 (14,500), 338 (16,200), 414 (11,000), ~455 (sh, 9200), 590 (4800)
	DMSO	296 (15,300), 341 (16,600), 417 (11,200), ~450 (sh, 10,000), 593 (5200)
	Pyridine	g, 335 (16,600), 414 (8500), ~450 (sh, 7600), 585 (3400)
[Fe ₂ S ₂ (SPh) ₄] ²⁻ <i>b</i>	CH ₂ Cl ₂	~290 (sh, 14,500), 339 (13,700), 415 (9300), ~450 (sh, 8200), 590 (3600)
	DMF	270 (39,000), 333 (19,500), 490 (11,200)
	DMSO	270 (38,800), 334 (19,000), 493 (11,600)
[Fe ₂ S ₂ (<i>S-p</i> -tol) ₄] ²⁻ <i>b</i>	DMF	268 (42,400), 336 (18,600), 502 (11,200)
	DMSO	268 (42,200), 333 (19,500), 498 (11,200)
	DMF	277 (42,800), ~330 (sh, 22,100), 483 (12,800)
[Fe ₂ S ₂ (SC ₆ H ₄ - <i>p</i> -Cl) ₄] ²⁻ <i>b</i>	DMF	277 (42,800), ~330 (sh, 22,100), 483 (12,800)
	DMF	280 (44,500), ~350 (sh, 22,000), 486 (12,200)
[Fe ₂ S ₂ (SC ₆ H ₄ - <i>p</i> -NMe ₃) ₄] ²⁺ <i>c</i>	DMF	280 (44,500), ~350 (sh, 22,000), 486 (12,200)
	DMF	280 (44,500), ~350 (sh, 22,000), 486 (12,200)
Tetramers		
[Fe ₄ S ₄ (SPh) ₄] ²⁻	DMF ^b	260 (45,000), ~350 (sh, 22,000), 457 (17,700)
	DMSO ^d	259 (41,400), ~350 (sh, 21,000), 458 (17,600)
[Fe ₄ S ₄ (<i>S-p</i> -tol) ₄] ²⁻ <i>d</i>	DMF	262 (46,800), ~350 (sh, 22,000), 461 (18,600)
[Fe ₄ S ₄ (SC ₆ H ₄ - <i>p</i> -Cl) ₄] ²⁻ <i>e</i>	DMF	267 (44,800), ~360 (sh, 19,400), 449 (15,300)
[Fe ₄ S ₄ (SC ₆ H ₄ - <i>p</i> -NMe ₃) ₄] ²⁺ <i>c</i>	DMF	275 (44,700), ~350 (sh, 25,300), 454 (18,500)

^a Intensity data for bands with $\lambda_{\text{max}} \leq 270$ nm not as reliable for those at higher energy due to onset of solvent absorption. ^b Et₄N⁺ salt. ^c PF₆⁻ salt. ^d Me₄N⁺ salt. ^e *n*-Bu₄N⁺ salt. ^f Ph₄As⁺ salt. ^g Higher energy bands obscured by solvent.

Table II. Electrochemical Data for Dimeric and Tetrameric Complexes in DMF Solution

Complex	2-/3-			3-/4-		
	$E_{1/2}$ (V) ^a	i_d/C ($\mu\text{A}/\text{mM}$)	slope (mV) ^b	$E_{1/2}$ (V) ^a	i_d/C ($\mu\text{A}/\text{mM}$)	slope (mV) ^b
Dimers						
[FeS(SCH ₂) ₂ C ₆ H ₄] ₂ ²⁻ ^b	-1.49	1.66	-51 (95)	-1.73	1.48	-56 (96)
[Fe ₂ S ₂ (SPh) ₄] ²⁻ ^b	-1.09	1.86	-47 (88)	-1.37	1.39	-46 (90)
[Fe ₂ S ₂ (S- <i>p</i> -tol) ₄] ²⁻ ^b	-1.15	1.22	-52 (82)	-1.41	1.15	-51 (86)
[Fe ₂ S ₂ (SC ₆ H ₄ - <i>p</i> -Cl) ₄] ²⁻ ^b	-0.97	1.29	-50 (93)	-1.30	0.51	-55 (95)
[Fe ₂ S ₂ (SC ₆ H ₄ - <i>p</i> -NMe ₃) ₄] ²⁻ ^c	-0.83	1.36	-66	~ -1.25 ^g		
Tetramers						
[Fe ₄ S ₄ (SPh) ₄] ²⁻ ^{b,f}	-1.04	1.52	-56 (95)	-1.75	1.76	-48 (88)
[Fe ₄ S ₄ (S- <i>p</i> -tol) ₄] ²⁻ ^{d,f}	-1.09	1.49	-60	-1.76	1.46	-45
[Fe ₄ S ₄ (SC ₆ H ₄ - <i>p</i> -Cl) ₄] ²⁻ ^e	-0.95	1.40	-57	-1.63	1.39	-49
[Fe ₄ S ₄ (SC ₆ H ₄ - <i>p</i> -NMe ₃) ₄] ²⁻ ^c	-0.80	1.16	-59	-1.36	1.19	-114

^a vs. sce at 25°. ^b Et₄N⁺ salt. ^c PF₆⁻ salt. ^d Me₄N⁺ salt. ^e *n*-Bu₄N⁺ salt. ^f Data from ref 22. ^g Poorly developed irreversible wave. ^h Half-widths of peaks (mV) in differential pulse polarograms measured with 25-mV pulse amplitude are given in parentheses.

2,2'-Bis(benzo[*d*]thiazoline)-4,4'-dinitrodiphenyl Disulfide, H₂(bnps)₂. 2,2'-Diformyl-4,4'-dinitrodiphenyl disulfide³¹ (3.6 g, 10 mmol) was combined with 2.6 g (21 mmol) of *o*-aminobenzenethiol in 150 ml of ethanol and refluxed for 18 hr. The resulting precipitate was collected and washed with ethanol and ether to afford after drying 5.4 g (92%) of product as an orange powder, mp 178–179°. *Anal.* Calcd for C₂₆H₁₈N₄O₄S₄: C, 53.96; H, 3.14; N, 9.68; S, 22.16. Found: C, 53.81; H, 3.27; N, 9.50; S, 21.95.

Reactions of H₂(bnps)₂. (a) With Fe(III) and Sulfide. To a slurry of 0.58 g (1.0 mmol) of H₂(bnps)₂ in 20 ml of ethanol was added a solution of 0.16 g (3.0 mmol) of sodium methoxide in 20 ml of ethanol. The mixture was warmed until all the solid dissolved. Anhydrous ferric chloride (0.16 g, 1.0 mmol) in 20 ml of ethanol was added followed by a solution of 0.056 g (1.0 mmol) of sodium hydrosulfide and 0.054 g (1.0 mmol) of sodium methoxide in 20 ml of ethanol. The intense red-brown solution was stirred for 18 hr and filtered. Addition of a solution of 0.84 g (2.0 mmol) of tetraphenylarsonium chloride in 50 ml of ethanol to the filtrate resulted in the separation of a red-brown solid. This material was washed with ethanol, dried *in vacuo*, and recrystallized from acetonitrile-methanol: mp 160–161°; ir (mull): 1316 (s), 1241 (m), 1070 (s), 945 (w), 811 (w), 734 (s), 681 (m), 655 (w) cm⁻¹. The analysis is consistent with a 1:1 salt (see text). *Anal.* Calcd for C₃₇H₂₈AsN₂O₂S₃Fe: C, 58.51; H, 3.72; As, 9.86; S, 12.66; Fe, 7.35. Found: C, 58.38; H, 3.79; As, 9.98; S, 12.76; Fe, 7.20.

(b) With Fe₂S₂(CO)₆. To a slurry of 5.8 g (1.0 mmol) of H₂(bnps)₂ in 30 ml of ethanol was added 0.11 g (2.0 mmol) of sodium methoxide in 25 ml of ethanol, and the mixture warmed until solution resulted. Fe₂S₂(CO)₆ (0.34 g, 1.0 mmol) in 15 ml of methanol was added, producing a brown solution which was refluxed for 1 hr. After filtration the filtrate was treated with 0.84 g (2.0 mmol) of tetraphenylarsonium chloride in 25 ml of water. The resulting solid was shown by its infrared spectrum to be the same as that obtained in the preceding preparation.

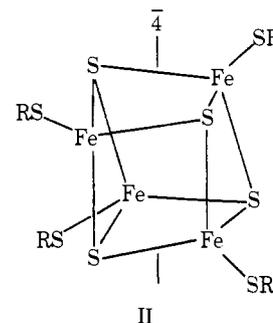
Physical Measurements. Owing to the sensitivity of the Fe-S complexes to dioxygen, all manipulations and measurements were performed under a pure dinitrogen atmosphere. Electronic spectra were recorded on a Cary Model 14 spectrophotometer. Dc and differential pulse polarographic and cyclic voltammetric measurements were carried out at 25 ± 0.1° with a Princeton Applied Research Model 170 electrochemistry system. The data collected in Table II were obtained by dc polarography using a dropping mercury working electrode; slopes were evaluated from plots of log [$i/(i_d - i)$] vs. E . A hanging mercury drop or stationary Pt electrode was used in cyclic voltammetry. Current-voltage curves corresponding to scan rates faster than 500 mV/sec were recorded oscillographically. Differential pulse polarograms were obtained with a dropping mercury electrode. Solvents were purified as previously²² and solutions contained 0.05 *M* (*n*-Pr₄N)(ClO₄) supporting electrolyte. All potentials were measured vs. a saturated calomel electrode.

Crystal Structure Determinations. Pertinent details regarding the crystal parameters and the collection of intensity data are given in Table III. Both structures were solved by direct methods. Details of the course of the refinement are summarized in Table IV. Particulars on methods of data collection, computer programs

employed, sources of atomic scattering factors, and related matters have been given previously for related structures^{25,27} and are not repeated here. The final coordinates for (Et₄N)₂[FeS(SCH₂)₂C₆H₄]₂ and (Et₄N)₂[Fe₂S₂(S-*p*-tol)₄] are presented in Tables V and VI, respectively. The calculated positions for the hydrogen atoms are given in Tables VII and VIII for the xylyl- and tolylthiolate complexes, respectively.³² The root-mean-square amplitudes of vibration for the nonhydrogen atoms of the two structures are listed in Tables IX and X.³² In Tables XI and XII values of $10|F_d|$ and $10|F_c|$ (in electrons) are presented for those reflections used in the refinements of the structures of the xylyl- and tolylthiolate complexes, respectively.³²

Results and Discussion

Previous investigations in this series have dealt primarily with the synthesis and structural and electronic characterization of the tetrameric³³ dianions [Fe₄S₄(SR)₄]²⁻ (II),^{22,25,27,34,35} whose properties reveal them to be close



representations of the active centers of 4-Fe and 8-Fe ferredoxin (Fd_{ox}) and reduced "high-potential" proteins.⁴ Both alkyl- and arylthiolate tetramers were initially synthesized from FeCl₃, an appropriate thiol, NaHS, and NaOMe as indicated for [Fe₄S₄(SAr)₄]²⁻ in Figure 1. Variations in the Fe(III)/thiol mole ratio from that of the proposed reaction stoichiometry²⁵ afforded the dianions II as the only isolable product. Although such experiments were not extensively pursued, the results were suggestive of a considerable stability of the D_{2d} cubane-type structure II relative to other possible Fe-S reaction products. Consequently, routes to binuclear and other complexes were investigated employing potentially chelating dithiols whose "bite" distances render them incapable of spanning the ca. 7 Å distance between thiolate coordination positions within a tetramer. The first reaction of this sort attempted utilized 1,2-ethanedithiol in place of a monofunctional thiol and yielded a highly crystalline salt containing no sulfide despite the presence of NaHS in the reaction mixture. The anion of this salt has been identified as the Fe(III) dimer [Fe₂(SCH₂CH₂S)₄]²⁻.^{13b,36}

Table III. Summary of Crystal Data and Intensity Collection

	(Et ₄ N) ₂ (Fe ₂ S ₂ (C ₆ H ₄ (CH ₂ S) ₂) ₂)	(Et ₄ N) ₂ (Fe ₂ S ₂ (SC ₆ H ₄ CH ₃) ₂)
Formula	Fe ₂ S ₆ N ₂ C ₃₂ H ₅₆	Fe ₂ S ₆ N ₂ C ₄₄ H ₆₈
a, Å	9.549 (6)	8.913 (3)
b, Å	13.549 (6)	16.132 (3)
c, Å	14.748 (6)	17.583 (3)
β, deg	95.42 (3)	97.14 (1)
V, Å ³	1899	2508
Z	2	2
d _{calc'd} , g/cm ³	1.353	1.230
Space group	C _{2h} ⁵ -P2 ₁ /n	C _{2h} ⁵ -P2 ₁ /n
Crystal dimensions, mm	0.64 × 0.23 × 0.15	0.40 × 0.23 × 0.21
Crystal volume, mm ³	0.0187	0.0219
Crystal shape	Needle in [100] direction pentagonal cross section with faces (001), (012̄), (012̄), {010}	Parallelepiped along [100] tetragonal cross section with faces {011}
Radiation	Mo (λKα ₁ 0.70930 Å) monochromatized from (002) face of mosaic graphite	Cu (λKα ₁ 1.540562 Å) pre- filtered with 1 mil of Ni foil
Transmission factors	0.78 to 0.87	0.20 to 0.33
μ, cm ⁻¹	11.05	71.81
Receiving aperture	4 mm wide by 6.5 mm high 32 cm from crystal	3 mm wide by 5 mm high 32 cm from crystal
Takeoff angle, deg	2.3	2.6
Scan speed	2 deg in 2θ/min	2 deg in 2θ/min
Scan range	0.75 below Kα ₁ to 0.70 above Kα ₂	0.75 below Kα ₁ to 0.75 above Kα ₂
Background counts	10 sec 2θ ≤ 35°; 20 sec thereafter	10 sec 2θ ≤ 104°; 20 sec thereafter
2θ limit (deg)	47.5	120
Unique data (F _o ² > 3σ(F _o ²))	2087	2576

belonging to the structural class described above. Although this complex is antiferromagnetic, as are 2-Fe Fd_{ox} proteins, the details of this and other physical properties together with the presence of only thiolate sulfur show that it is not an acceptable model of the protein active sites.⁴⁻⁸

Following characterization of [Fe₂(SCH₂CH₂S)₄]²⁻, a similar reaction system containing *o*-xylyl- α,α' -dithiol (Figure 1) was investigated. As reported recently,²¹ this system affords the binuclear dianion [FeS(SCH₂)₂C₆H₄]₂²⁻ (**1**), whose tetraphenylarsonium and tetraethylammonium salts have been isolated as air-sensitive red-brown crystalline solids. Both are insoluble in water but moderately soluble in polar organic solvents where they undergo oxidative decomposition; the tetraphen-

ylarsonium salt is the more soluble.

Description of the Structure of (Et₄N)₂[FeS(SCH₂)₂-C₆H₄]₂. This compound crystallizes in space group C_{2h}⁵-P2₁/n of the monoclinic system with two formula units per unit cell. Crystal data are collected in Table III. The crystal structure consists of the packing of well-separated cations and anions. The closest calculated interionic contacts are cation-anion H \cdots H interactions of 2.38 Å. Stereoviews of the unit cell and the anion **1** are shown in Figures 3 and 4, respectively. The stereochemistry of the nonhydrogen atoms of **1** together with the labeling scheme and selected bond distances and angles is depicted in Figure 5. Structural parameters for the anion are collected in Tables XIII and XIV. The tetraethylammonium ions have their expected tetrahedral geometry with a mean C-N-C angle of 109.5°. Bond distances are foreshortened somewhat as a result of thermal motion. Cation distances and angles are summarized in Table XV.

The anion is a centrosymmetric dimer of C_i symmetry which, however, can be regarded as effectively C_{2h} because of the marginal difference between Fe-S(2) and Fe-S(3) bond lengths. Its structure is entirely consistent with the proposed active site formulation I, the cysteinyl residues being replaced with -CH₂S groups of chelating *o*-xylyldithiolate ligands. Two Fe(III) centers with somewhat distorted tetrahedral coordination are bridged by two sulfide ions and terminally coordinated by two thiolate sulfurs. The Fe₂S₂* core (S* = S(1), S(1')) is planar with an Fe \cdots Fe distance of 2.698 Å, indicative of a stabilizing metal-metal interaction, and an S* \cdots S* distance of 3.498 Å, far too long for any significant bonding between the two atoms (*vide infra*). The core structure possesses the unexpected feature of two pairs of unequal Fe-S* distances, differing by 0.047 (2) Å, for which there is no clear rationalization at present. Inasmuch as the dihedral angle between the S*-Fe-S* and S(2)-Fe-S(3) coordination planes is 89.95 (5)°, the reduction of Fe(III) site symmetry below tetrahedral

Table IV. Structure Refinement

Model	[FeS(SCH ₂) ₂ -C ₆ H ₄] ₂ ²⁻ ^a		[Fe ₂ S ₂ (S- <i>p</i> -tol) ₄] ₂ ²⁻ ^a	
	R	R _w	R	R _w
Anion (isotropic)	0.237	0.307		
Anion and cation isotropic, no H atoms	0.079	0.100	0.081	0.105
Anisotropic, no H atoms	0.057	0.072	0.061	0.086
Anisotropic, with idealized H positions	0.033	0.037	0.034	0.039
Error in observation of unit weight (e ⁻)	1.38		1.44	
No. of variables	190		244	
Maximum electron density on final difference Fourier map (e ⁻ /Å ³)	0.23 (5)		0.19 (3)	
No. of unobserved reflections	1029		1360	
No. of unobserved reflections having F _o ² - F _c ² > 3σ(F _o ²)	0		3	
Trends of Σw(F _o - F _c) ² with F _o , setting angles, Miller indices	None		None	

^a Et₄N⁺ salt.

Table V. Final Parameters for $(Et_4N)_2[FeS(SCH_2)_2C_6H_4]_2$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.04707 (5) ^b	0.03543 (4)	0.58278 (3)	0.00903 (7)	0.00501 (3)	0.00439 (3)	0.00024 (4)	0.00084 (3)	-0.00056 (3)
S(1)	-0.16298 (10)	0.05478 (7)	0.51238 (7)	0.00892 (12)	0.00623 (7)	0.00543 (6)	0.00114 (7)	0.00103 (6)	-0.00093 (5)
S(2)	0.15954 (10)	0.18387 (7)	0.61424 (6)	0.01034 (12)	0.00482 (6)	0.00438 (5)	0.00005 (7)	0.00080 (6)	0.00022 (5)
S(3)	0.04080 (10)	-0.04421 (7)	0.72025 (7)	0.01068 (13)	0.00496 (6)	0.00525 (6)	-0.00075 (7)	0.00163 (6)	-0.00007 (5)
C(1)	0.32538 (39)	0.13904 (29)	0.67296 (26)	0.00949 (50)	0.00668 (27)	0.00573 (23)	0.00011 (29)	0.00116 (27)	0.00116 (29)
C(2)	0.23240 (41)	-0.05658 (26)	0.74958 (27)	0.01060 (51)	0.00484 (25)	0.00598 (23)	0.00040 (28)	-0.00012 (27)	-0.00011 (19)
C(3)	0.29044 (36)	0.02678 (26)	0.80821 (23)	0.00903 (45)	0.00454 (23)	0.00447 (20)	0.00008 (26)	0.00069 (24)	0.00019 (18)
C(4)	0.30919 (44)	0.01345 (30)	0.90186 (27)	0.01388 (60)	0.00629 (29)	0.00526 (24)	-0.00133 (32)	0.00045 (30)	0.00120 (21)
C(5)	0.35446 (46)	0.08774 (36)	0.96035 (28)	0.01489 (65)	0.00859 (35)	0.00490 (24)	-0.00029 (39)	-0.00018 (31)	-0.00004 (25)
C(6)	0.38152 (42)	0.17895 (32)	0.92705 (29)	0.01133 (56)	0.00680 (31)	0.00646 (27)	-0.00021 (33)	0.00000 (30)	-0.00181 (23)
C(7)	0.36812 (38)	0.19462 (27)	0.83467 (28)	0.00921 (49)	0.00454 (25)	0.00681 (26)	-0.00009 (27)	-0.00036 (28)	0.00043 (21)
C(8)	0.32500 (35)	0.11926 (27)	0.77327 (24)	0.00732 (43)	0.00507 (24)	0.00496 (21)	0.00036 (26)	0.00054 (24)	0.00037 (19)
N	0.35878 (30)	0.26648 (23)	0.35183 (20)	0.00844 (38)	0.00651 (23)	0.00506 (18)	-0.00074 (23)	0.00221 (20)	0.00056 (16)
C(9)	0.38590 (49)	0.26378 (35)	0.25260 (29)	0.01891 (76)	0.00889 (35)	0.00538 (25)	-0.00126 (42)	0.00560 (36)	0.00041 (25)
C(10)	0.26566 (65)	0.22541 (42)	0.18894 (31)	0.0304 (11)	0.01224 (48)	0.00544 (29)	-0.00465 (61)	0.00306 (45)	-0.00149 (31)
C(11)	0.22691 (41)	0.32423 (31)	0.36474 (28)	0.01047 (54)	0.00722 (31)	0.00683 (26)	0.00051 (33)	0.00253 (30)	0.00012 (23)
C(12)	0.22473 (55)	0.42842 (37)	0.33049 (38)	0.01854 (84)	0.00784 (37)	0.01224 (44)	0.00271 (43)	0.00220 (48)	-0.00021 (32)
C(13)	0.48809 (44)	0.31540 (39)	0.40073 (32)	0.00988 (57)	0.01193 (44)	0.00804 (32)	-0.00294 (39)	0.00161 (34)	0.00156 (30)
C(14)	0.48384 (63)	0.32659 (54)	0.50119 (41)	0.01984 (92)	0.02487 (84)	0.00765 (34)	-0.01000 (73)	-0.00230 (45)	-0.00054 (45)
C(15)	0.33182 (43)	0.16391 (31)	0.38811 (29)	0.01146 (54)	0.00747 (30)	0.00705 (27)	0.00000 (33)	0.00348 (31)	0.00187 (24)
C(16)	0.45084 (55)	0.09119 (39)	0.38355 (40)	0.01794 (82)	0.00925 (40)	0.01360 (46)	0.00367 (48)	0.00553 (50)	0.00409 (36)

^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.

Table VI. Final Parameters for $(Et_4N)_2[Fe_2S_2(SC_6H_4CH_3)_4]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.47373 (6)	0.06532 (3)	-0.45593 (3)	0.01450 (9)	0.00379 (2)	0.00374 (2)	-0.00038 (4)	0.00126 (3)	-0.00025 (2)
S(1)	0.30615 (10)	-0.01729 (6)	-0.51942 (5)	0.01391 (14)	0.00451 (4)	0.00433 (4)	-0.00075 (6)	0.00118 (6)	-0.00025 (3)
S(2)	0.48156 (11)	0.05864 (6)	-0.32417 (5)	0.01575 (15)	0.00584 (5)	0.00386 (4)	0.00146 (7)	0.00065 (6)	0.00002 (4)
S(3)	0.41229 (11)	0.19720 (6)	-0.50092 (6)	0.01659 (16)	0.00430 (4)	0.00473 (4)	-0.00053 (7)	-0.00005 (6)	0.00017 (3)
C(1)	0.30270 (38)	0.08091 (19)	-0.29697 (19)	0.01521 (58)	0.00326 (15)	0.00353 (14)	0.00043 (23)	0.00059 (22)	-0.00005 (11)
C(2)	0.17732 (42)	0.10484 (22)	-0.34771 (20)	0.01600 (62)	0.00432 (16)	0.00388 (15)	0.00062 (26)	0.00103 (25)	-0.00010 (13)
C(3)	0.03931 (43)	0.12027 (23)	-0.32175 (22)	0.01686 (67)	0.00494 (19)	0.00423 (17)	0.00058 (28)	0.00012 (26)	-0.00018 (14)
C(4)	0.01966 (44)	0.11270 (24)	-0.24562 (23)	0.01609 (67)	0.00523 (20)	0.00494 (19)	0.00038 (29)	0.00168 (28)	-0.00068 (16)
C(5)	0.14363 (48)	0.08897 (25)	-0.19512 (21)	0.01992 (75)	0.00583 (22)	0.00377 (16)	0.00105 (30)	0.00217 (28)	0.00017 (14)
C(6)	0.28150 (44)	0.07319 (21)	-0.21985 (20)	0.01916 (68)	0.00441 (17)	0.00361 (15)	0.00080 (28)	0.00066 (24)	0.00008 (13)
C(7)	-0.13147 (50)	0.13015 (32)	-0.21727 (27)	0.01892 (80)	0.01055 (35)	0.00694 (24)	0.00101 (42)	0.00345 (34)	-0.00079 (23)
C(8)	0.55633 (41)	0.26813 (22)	-0.46863 (19)	0.01727 (64)	0.00402 (17)	0.00356 (15)	-0.00039 (26)	0.00189 (24)	-0.00036 (12)
C(9)	0.68200 (43)	0.24833 (23)	-0.41773 (23)	0.01667 (68)	0.00472 (19)	0.00594 (20)	0.00032 (29)	-0.00010 (29)	-0.00058 (15)
C(10)	0.79140 (47)	0.30786 (28)	-0.39511 (26)	0.01919 (77)	0.00571 (23)	0.00669 (22)	-0.00051 (35)	-0.00012 (31)	-0.00135 (18)
C(11)	0.77799 (51)	0.38834 (27)	-0.42074 (24)	0.02132 (80)	0.00561 (22)	0.00535 (20)	-0.00310 (35)	0.00167 (32)	-0.00116 (17)
C(12)	0.65096 (62)	0.40791 (26)	-0.46985 (27)	0.0335 (11)	0.00495 (21)	0.00585 (22)	-0.00350 (39)	0.00129 (39)	0.00072 (17)
C(13)	0.54206 (49)	0.34949 (26)	-0.49392 (24)	0.02653 (92)	0.00502 (21)	0.00499 (18)	-0.00216 (35)	-0.00089 (32)	0.00085 (16)
C(14)	0.89708 (62)	0.45288 (31)	-0.39514 (31)	0.0318 (11)	0.00784 (31)	0.00938 (32)	-0.00730 (46)	0.00152 (44)	-0.00199 (24)
N	0.42434 (33)	0.33346 (17)	-0.18076 (16)	0.01816 (54)	0.00368 (13)	0.00444 (13)	0.00013 (21)	0.00226 (21)	-0.00089 (10)
C(15)	0.40126 (49)	0.28900 (25)	-0.25688 (25)	0.02424 (85)	0.00567 (22)	0.00545 (20)	-0.00008 (34)	0.00367 (33)	-0.00252 (17)
C(16)	0.34429 (60)	0.34128 (36)	-0.32488 (26)	0.0368 (12)	0.01071 (37)	0.00418 (20)	-0.00088 (53)	0.00249 (39)	-0.00149 (22)
C(17)	0.27770 (47)	0.37415 (25)	-0.16442 (23)	0.02043 (78)	0.00563 (22)	0.00546 (20)	0.00122 (33)	0.00296 (31)	-0.00138 (16)
C(18)	0.14468 (50)	0.31650 (32)	-0.16354 (28)	0.02000 (84)	0.00950 (32)	0.00820 (27)	-0.00163 (43)	0.00486 (37)	-0.00111 (24)
C(19)	0.47708 (51)	0.26958 (29)	-0.12094 (28)	0.02508 (93)	0.00670 (25)	0.00668 (25)	0.00139 (38)	0.00206 (38)	0.00210 (21)
C(20)	0.49560 (56)	0.30297 (43)	-0.03938 (29)	0.0250 (10)	0.01760 (53)	0.00571 (23)	0.00017 (60)	0.00056 (40)	0.00250 (29)
C(21)	0.53854 (51)	0.40275 (25)	-0.18173 (25)	0.02305 (83)	0.00535 (20)	0.00583 (20)	-0.00243 (34)	0.00262 (33)	-0.00078 (16)
C(22)	0.69378 (52)	0.37707 (32)	-0.19863 (26)	0.02037 (85)	0.00990 (34)	0.00629 (22)	-0.00200 (42)	0.00303 (35)	-0.00045 (22)

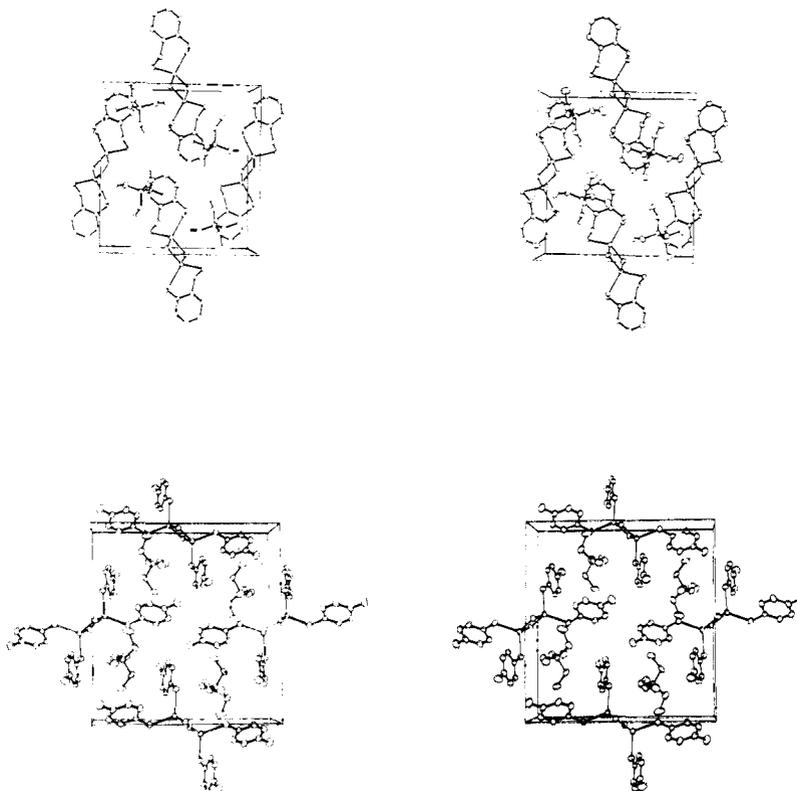


Figure 3. Stereoviews of the contents of the unit cells of $(\text{Et}_4\text{N})_2[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2$ (top) and $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{S-}i>p\text{-tol})_4]$ (bottom). Hydrogen atoms have been omitted for the sake of clarity. The thermal ellipsoids are drawn at their 20% probability levels. In the drawings the y axis is horizontal from left to right, the z axis is vertical from top to bottom, and the x axis is normal to the page with positive direction toward the viewer.

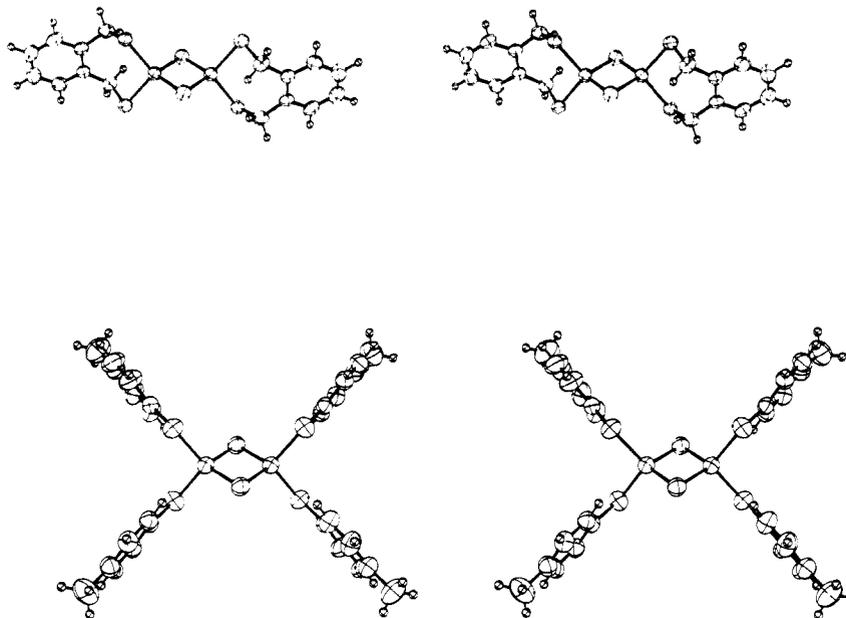


Figure 4. Stereoviews of $[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2^{2-}$ (top) and $[\text{Fe}_2\text{S}_2(\text{S-}i>p\text{-tol})_4]^{2-}$ (bottom). The 50% probability ellipsoids are shown except for the hydrogen atoms, which have been drawn artificially small.

occurs as a consequence of the *ca.* 0.1 Å difference between Fe-S* and Fe-S bond lengths and the angular variations evident in Figure 5. The smallest of the angles around the metal is S*-Fe-S*, internal to the core. The core dimensions of **1** are strikingly similar to other compounds containing planar or nearly planar Fe_2S_2 or $\text{Fe}_2(\text{SR})_2$ units and variant metal stereochemistry and oxidation state. Examples are $[\text{Fe}(\text{SEt})(\text{S}_2\text{CSEt})_2]_2$,^{13d,15} $\text{Fe}_2(\text{SEt})_2(\text{NO})_4$,^{14c} KFeS_2 ,³⁷ $\text{Cs}[\text{Fe}_4\text{S}_3(\text{NO})_7] \cdot \text{H}_2\text{O}$,³⁸ cubanite³⁹ (CuFe_2S_3), and the Fe_3S_7 units in $\text{Ba}_7\text{Fe}_6\text{S}_{14}$.⁴⁰ Other considerations of the core structure are deferred to a later section.

The chelate rings in **1** adopt a chair conformation. The phenyl rings are approximately planar, the best weighted least-squares plane through atoms C(3) to C(8) having the equation

$$9.148x - 3.820y - 2.087z = 0.887$$

Atoms C(1) and C(2) are significantly out of this plane by about 0.1 Å. The observed variations in ring C-C distances (Table XIV) are expected as a consequence of thermal motion, with the shortest distance being furthest away from the presumed center of libration.⁴¹ The chelate portion of

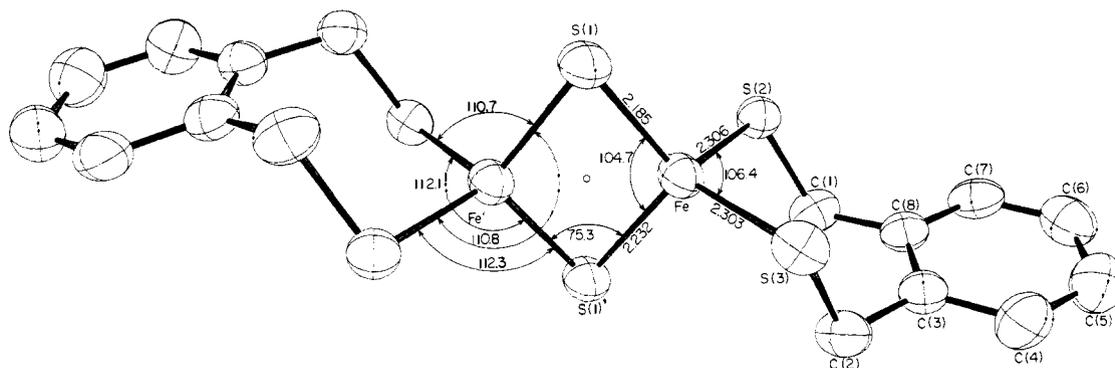


Figure 5. A drawing of the nonhydrogen atoms of the centrosymmetric $[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2^{2-}$ anion, showing the labeling scheme and selected bond distances and angles. Labeling errors on the drawing presented earlier²¹ have been corrected.

Table XIII. Comparison of the $\text{Fe}_2\text{S}_2^*\text{S}_4$ Geometries in the $[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2^{2-}$ (Xylyl) and $[\text{Fe}_2\text{S}_2(\text{SC}_6\text{H}_4\text{CH}_3)_4]^{2-}$ (Toly) Complexes (Distances in Å, Angles in deg)

Distance	Xylyl	Toly	Angle	Xylyl	Toly
Fe...Fe' ^a	2.698 (1)	2.691 (1)	S(1)-Fe-S(1)'	104.73 (5)	104.61 (4)
Fe-S(1)	2.185 (2)	2.200 (1)	S(1)-Fe-S(2)	112.33 (5)	114.48 (4)
Fe-S(1)'	2.232 (1)	2.202 (1)	S(1)-Fe'-S(2)'	110.78 (5)	105.32 (4)
Fe-S(2)	2.306 (1)	2.312 (1)	S(1)-Fe-S(3)	112.05 (5)	105.48 (4)
Fe-S(3)	2.303 (1)	2.312 (1)	S(1)-Fe'-S(3)'	110.66 (5)	115.81 (4)
S(1)...S(1)'	3.498 (3)	3.483 (3)	Fe-S(1)-Fe'	75.27 (5)	75.39 (4)
S(1)...S(2)	3.732 (2)	3.794 (1)			
S(1)...S(2)'	3.736 (2)	3.589 (1)	Dihedral angle ^b		
S(1)...S(3)	3.722 (2)	3.591 (1)	S(1)-Fe-S(1)'		
S(1)...S(3)'	3.730 (2)	3.824 (2)	S(2)-Fe-S(3)	-89.95 (5)	-97.00 (4)
S(2)...S(3)	3.690 (2)	3.816 (1)			

^a Primed atoms are related to the corresponding unprimed atoms by the center of symmetry within the anion. ^b This is the angle between the normals to the planes formed by the two groups of atoms.

the anion is characterized by an average Fe-S distance of 2.305 Å, an S...S bite distance of 3.690 Å, and a bite angle of 106.4°. In contrast the mean bite distance and angle in $[\text{Fe}_2(\text{SCH}_2\text{CH}_2\text{S})_4]^{2-}$ ^{13b} are 3.16 Å and 89.6°, with the mean Fe-S distance in the half-dimer being 2.24 Å. On this basis it appears that one necessary criterion for the formation of binuclear structures such as **1** from dithiols is structural flexibility of the latter sufficient to accommodate near-tetrahedral angles around the metal in a relatively strain-free fashion with retention of normal (*ca.* 2.3 Å) Fe-S distances. Consistent with this observation are the solution studies by Sugiura, *et al.*,²⁰ who found that Fe(III) complexes of 1,2-ethanedithiol and 1,3-propanedithiol did not react with sulfide whereas complexes of higher homologs ($\text{HS}(\text{CH}_2)_{4-6}\text{SH}$) did undergo reaction. The electronic spectra of the species so formed were described as resembling those of oxidized plant ferredoxins. The affinity of the dithiol complexes for sulfide was reported to be largest in the 1,4-butanedithiol case where, interestingly, a seven-membered chelate ring roughly similar to that in **1** presumably was formed. With the precise structure of **1** in hand, past²¹ and continuing efforts are being directed toward an elucidation of its electronic and reactivity properties.

[FeS(SCH₂)₂C₆H₄]₂²⁻ as an Active Site Analog. Characteristic electronic features of plant, mammalian, and bacterial 2-Fe proteins in their oxidized and reduced forms are summarized elsewhere.⁴⁻⁸ Absorption spectra of both redox forms in the 250-650-nm region are sufficiently similar to suggest a common chromophore for all proteins. Spectra of the oxidized forms of spinach^{42,43} and parsley⁴⁴ Fd, adrenodoxin,^{8,42,45} and putidaredoxin⁴⁶ are representative of proteins from diverse sources and in this region consist of three prominent bands superimposed on rising absorbance into the ultraviolet. The absorption spectra of oxidized proteins are adequately summarized by the following λ_{max} (nm) and

ϵ_{m} data: 325-333, 12,000-15,000; 410-425, 9000-10,000; 455-470, 8500-9500. The spectra of **1** in several nonhydroxylic polar solvents are given in Figure 6 and spectral data in these and other solvents are summarized in Table I. The spectral features are not too solvent dependent, and a rather close similarity to the aqueous protein spectra is evident. In DMF solution, for example, the features at 338, 414, and 455 nm correlate well with the three protein bands. The latter absorptions, somewhat increased in intensity and red-shifted, are retained in the spectra of adrenodoxin in 98% DMF and DMSO solutions.⁴⁷ In addition, the spectra of **1** contain a maximum at 585-593 nm and a very weak shoulder near 520 nm. One or more features in the 500-600-nm interval are found in the solution spectra of certain bacterial proteins⁴⁸ and adrenodoxin^{45,47} and are more clearly developed in the low-temperature spectra of the latter^{42,45,49} and spinach Fd.^{42,49} The peak at 290-296 nm in the spectra of **1** may correspond to the shoulder near about 285 nm discernible in the published spectra of many proteins, but nearly obscured by a strong band at *ca.* 276 nm, which derives considerable intensity from the aromatic residues of the polypeptide chain. We conclude that the spectral similarities between **1** and the oxidized proteins are sufficient to demonstrate that both contain essentially the same iron-sulfur chromophore.

Results from investigations of Mössbauer and pmr spectra and magnetic susceptibility properties, some of which have been briefly described earlier,²¹ further support a definite electronic relationship between $[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2^{2-}$ and the active centers of the oxidized 2-Fe proteins. Magnetic and Mössbauer properties have been more thoroughly examined and will be reported separately.⁵⁰ The collective electronic features of **1** are taken to confirm the proposed formulation I for the oxidized protein active sites, the detailed structure of which we conclude to be closely related

Table XIV. Other Distances (Å) and Angles (deg) within the Anions

Xylyl			
S(2)-C(1)	1.835 (4)	C(1)-C(8)-C(3)	122.8 (3)
S(3)-C(2)	1.847 (4)	C(2)-C(3)-C(8)	123.2 (3)
C(1)-C(8)	1.504 (5)		
C(2)-C(3)	1.497 (5)	C(3)-C(4)-C(5)	122.3 (4)
		C(4)-C(5)-C(6)	119.9 (4)
C(3)-C(4)	1.388 (5)	C(5)-C(6)-C(7)	119.6 (4)
C(4)-C(5)	1.369 (6)	C(6)-C(7)-C(8)	121.5 (4)
C(5)-C(6)	1.364 (6)	C(7)-C(8)-C(3)	118.5 (3)
C(6)-C(7)	1.373 (6)	C(8)-C(3)-C(4)	117.9 (3)
C(7)-C(8)	1.401 (5)	Mean	120.0
C(3)-C(8)	1.406 (5)		
Mean	1.384 (17) ^a	Fe-S(2)-C(1)-C(8)	-85.0 (3) ^b
		S(2)-C(1)-C(8)-C(3)	90.5 (4)
Fe-S(2)-C(1)	99.8 (1)	C(1)-C(8)-C(3)-C(2)	-8.5 (5)
Fe-S(3)-C(2)	98.1 (1)	C(8)-C(3)-C(2)-S(3)	-82.0 (4)
S(2)-C(1)-C(8)	116.2 (3)	C(3)-C(2)-S(3)-Fe	94.0 (3)
S(3)-C(2)-C(3)	111.8 (3)	C(2)-S(3)-Fe-S(2)	-62.4 (1)
		S(3)-Fe-S(2)-C(1)	56.2 (1)
C(14)H(3)···C(4)H 2.38 ^c			
Tolyl			
S(2)-C(1)	1.758 (4)	Fe-S(2)-C(1)	110.4 (1)
S(3)-C(8)	1.760 (4)	Fe-S(3)-C(8)	110.8 (1)
C(4)-C(7)	1.520 (5)		
C(11)-C(14)	1.515 (5)	C(3)-C(4)-C(7)	121.8 (4)
		C(5)-C(4)-C(7)	120.7 (4)
C(1)-C(2)	1.395 (4)	C(10)-C(11)-C(14)	121.5 (4)
C(2)-C(3)	1.387 (5)	C(12)-C(11)-C(14)	121.4 (4)
C(3)-C(4)	1.377 (5)	Mean	121.4 (5)
C(4)-C(5)	1.383 (5)		
C(5)-C(6)	1.377 (5)	S(2)-C(1)-C(2)	124.3 (3)
C(6)-C(1)	1.398 (4)	S(2)-C(1)-C(6)	118.8 (3)
Mean	1.386 (9)	S(3)-C(8)-C(9)	124.0 (3)
		S(3)-C(8)-C(13)	118.5 (3)
C(8)-C(9)	1.381 (5)	Mean	121.4
C(9)-C(10)	1.391 (5)		
C(10)-C(11)	1.375 (6)	C(1)-C(2)-C(3)	120.8 (3)
C(11)-C(12)	1.373 (6)	C(2)-C(3)-C(4)	122.0 (3)
C(12)-C(13)	1.381 (5)	C(3)-C(4)-C(5)	117.4 (4)
C(13)-C(8)	1.387 (5)	C(4)-C(5)-C(6)	121.4 (4)
Mean	1.381 (7)	C(5)-C(6)-C(1)	121.6 (3)
		C(6)-C(1)-C(2)	116.8 (3)
Fe-S(1)-Fe'		Mean	120.0
C(1)-C(2)-C(6)	118.1 (1)		
		C(8)-C(9)-C(10)	120.6 (4)
Fe-S(1)-Fe'		C(9)-C(10)-C(11)	121.9 (4)
C(8)-C(9)-C(13)	-59.2 (2)	C(10)-C(11)-C(12)	117.0 (4)
		C(11)-C(12)-C(13)	121.9 (4)
Fe-S(2)-S(3)		C(12)-C(13)-C(8)	121.0 (4)
C(1)-C(2)-C(6)	118.3 (3)	C(13)-C(8)-C(9)	117.5 (4)
		Mean	120.0
Fe-S(2)-S(3)			
C(8)-C(9)-C(13)	-63.3 (3)		
C(3)H···C(9)H	2.49 ^c		

^a If given, the value in parentheses is the standard deviation of a single observation as estimated from the agreement among the averaged values. ^b The torsion angles are given for the seven-membered Fe-S(2)-C(1)-C(8)-C(3)-C(2)-S(3) ring. The sign of the torsion angle of the atoms I-J-K-L is positive if when looking from J to K a clockwise motion of atom I would superimpose it on atom L. ^c This is the closest calculated H···H intermolecular interaction.

to that shown in Figure 5. In particular, the S*···S* distance (3.498 Å) is much longer than those found in Fe₂S₂(CO)₆¹⁶ (2.01 Å), [CpFeS(SEt)]₂¹⁷ (2.02 Å), FeS₂⁵¹ (2.18, 2.22 Å), and Na₂S₂ and K₂S₂⁵² (av 2.13 Å), which contain bridging or discrete S₂ units. The S···S* separations in the FeS₂*S₂ tetrahedra average to 3.730 Å, also a nonbonding distance, and are to be contrasted with, e.g., the S-S bond lengths of 2.03–2.05 Å in L-cystine and its derivatives.⁵³ Consequently, active site structures considered as alternatives^{17,54} to I and involving bridging S₂ fragments,

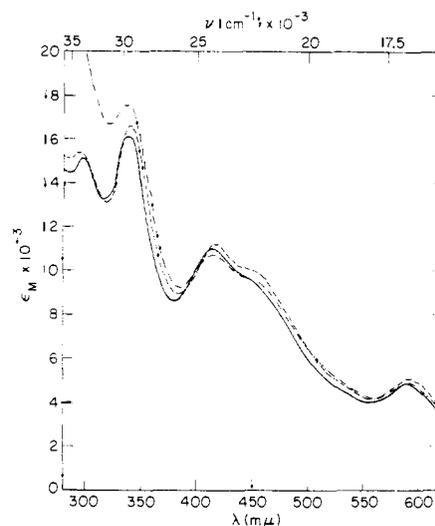


Figure 6. Absorption spectra of (Ph₄As)₂[FeS(SCH₂)₂C₆H₄]₂ in several different solvents: —, DMF; ---, DMSO; - · -, benzonitrile.

perthiocysteinyl linkages (Cys-S-S-Fe), and bridging Cys-S groups may now be safely discounted. As previously,²¹ we stress that **1** is regarded as a *minimal* representation, inasmuch as it does not incorporate any minor metal site inequivalencies, additional coordination interactions, and hydrogen-bonding, charge distribution, and other environmental effects such as may be present in the oxidized proteins. The lack of large perturbations in the spectra of **1** when the solvent is varied from essentially noncoordinating (dichloromethane) to potentially strongly coordinating (pyridine) is suggestive of little tendency of Fe(III) to bind additional ligands.

Thiolate Ligand Substitution Reactions of [FeS(SCH₂)₂C₆H₄]₂²⁻. The tetranuclear complexes [Fe₄S₄(SR)₄]²⁻ exhibit two types of reactivity, oxidation-reduction²² and thiolate ligand substitution.^{22,27} Substitution reactions are effected by addition of free thiol to a solution of the tetramer, and the extent²⁷ as well as the rate¹ of substitution is dominated by the acid-base properties of coordinated thiolate and added thiol. Addition of ca. 4.5–6 equiv of arylthiol to a solution of an alkylthiolate tetramer such as [Fe₄S₄(S-*t*-Bu)₄]²⁻ results in complete formation of [Fe₄S₄(SAr)₄]²⁻. This reaction, illustrated in Figure 1, offers a second synthetic route to anionic tetramers²⁵ (**2t**–**4t**) and allows generation of the cationic tetramer **5t** in solution.²² Both types of reactivity extend to the alkylthiolate dimer **1**; redox properties are described in a later section.

Treatment of a slurry of (Et₄N)₂[FeS(SCH₂)₂C₆H₄]₂ in acetonitrile with a fivefold mole excess of benzenethiol, *p*-tolylthiol, or *p*-chlorobenzenethiol afforded maroon solutions from which crystalline salts were isolated in 40–50% yield after purification. These compounds are air-sensitive and rather soluble in polar organic solvents. In DMF solutions the spectra of the Fe-S anions are characterized by an asymmetric band at 483–502 nm, a shoulder or maximum at ca. 330–336 nm, and a stronger absorption near 270 nm. These results together with Mössbauer and magnetic properties, currently under study, serve to show that these complexes (**2d**–**4d**) are electronically very similar and to differentiate them from the corresponding arylthiolate tetramer dianions (**2t**–**4t**). However, they are insufficient to establish conclusively the dimeric structure (Figure 1) anticipated from the method of synthesis. Consequently, the structure of the *p*-tolylthiol reaction product was determined by X-ray diffraction.

Table XV. Distances (Å) and Angles (deg) in the NEt_4 Cations

	Xylyl	Tolyl		Xylyl	Tolyl
N–C(a) ^a	1.511 (5)	1.510 (4)	N–C(a)–C(b)	115.0 (4)	115.6 (4)
N–C(c)	1.510 (5)	1.522 (5)	N–C(c)–C(d)	115.5 (3)	115.5 (3)
N–C(e)	1.522 (5)	1.505 (5)	N–C(e)–C(f)	114.7 (4)	113.8 (4)
N–C(g)	1.520 (5)	1.513 (3)	N–C(g)–C(h)	115.3 (3)	115.7 (4)
Mean	1.516 (6)	1.513 (7)	Mean	115.1	115.2
C(a)–C(b)	1.505 (7)	1.499 (6)	C(a)–N–C(c)	110.9 (3)	110.3 (3)
C(c)–C(d)	1.499 (6)	1.508 (6)	C(a)–N–C(e)	105.3 (3)	106.9 (3)
C(e)–C(f)	1.494 (7)	1.522 (6)	C(a)–N–C(g)	111.7 (3)	111.0 (3)
C(g)–C(h)	1.510 (6)	1.509 (6)	C(c)–N–C(e)	111.3 (3)	111.3 (3)
Mean	1.502 (7)	1.510 (10)	C(c)–N–C(g)	105.0 (3)	106.2 (3)
			C(e)–N–C(g)	112.8 (3)	111.2 (3)
			Mean	109.5	109.5

^a In the xylyl structure C(a) through C(h) correspond to C(9) through C(16), respectively. In the tolyl structure C(a) through C(h) correspond to C(15) through C(22), respectively.

Description of the Structure of $(\text{Et}_4\text{N})_2[\text{Fe}_2\text{S}_2(\text{S}-p\text{-tol})_4]$. This compound also crystallizes in space group $C^5_{2h}-P2_1/n$ with two formula units per unit cell. Crystal data, structural parameters, and stereoviews of the unit cell and anion are presented in the same tables and figures as for $(\text{Et}_4\text{N})_2[\text{FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2$. The closest calculated interionic contacts are cation–anion $\text{H}\cdots\text{H}$ interactions of 2.49 Å. The same comments apply to the tetraethylammonium ions as in the previous structure.

The stereochemistry of the nonhydrogen atoms of the anion **4d** with its labeling scheme and selected bond angles and distances is shown in Figure 7. It, as **1**, is a dimer with a crystallographically imposed center of symmetry. The point group symmetry of the $\text{Fe}_2\text{S}_2^*\text{S}_4$ portion of $[\text{Fe}_2\text{S}_2(\text{S}-p\text{-tol})_4]^{2-}$ is essentially perfect C_{2h} . It is degraded from D_{2h} by the dihedral angle of 97° between $\text{S}^*-\text{Fe}-\text{S}^*$ and $\text{S}(2)-\text{Fe}-\text{S}(3)$ planes, in contrast to **1** where markedly unequal $\text{Fe}-\text{S}^*$ distances are responsible. These distances in **4d** are within experimental uncertainty of each other. The coordination around iron involves a larger variation in bond angles than is found for **1**. Further comparisons of the structures of the two dimers are available in Table XIII and Figure 8. The most important conclusion to be drawn from the structural results is that the Fe_2S_2^* core in **1** is retained upon thiolate ligand substitution with no significant changes in dimensions.

The tolyl rings in the structure of **4d** are planar, their best weighted least-squares planes being

$$2.131x + 15.478y + 2.083z = 1.277$$

for C(1)–C(7) and

$$5.239x - 3.806y - 14.786z = 8.815$$

for C(8)–(14). The two planes make an angle of 101.6° with each other. S(2) lies -0.018 Å out of the first plane while S(3) is in the second plane. Small but consistent distance and angular variations, presumably arising from some combination of motional and electronic effects, are evident in the structures of the two tolyl rings (Table XIV).

Other Synthetic Results. The direct synthesis of **1** and the preparation of **2d–4d** ($X = \text{H}, \text{Cl}, \text{CH}_3$) (Figure 1) by thiolate substitution reactions have prompted a search for new alkylthiolate dimers and alternate and possibly more convenient routes to arylthiolate dimers. Tetramer dianions of both types are accessible by direct synthesis²⁵ (Figure 1). No such general synthesis has yet been found for dimer dianions. In an attempt to secure a second alkylthiolate dimer, isomerically pure *cis*-2-butene-1,4-dithiol was used in place of *o*-xylyldithiol in the reaction system yielding **1**. Based on the following observations the product, isolated as

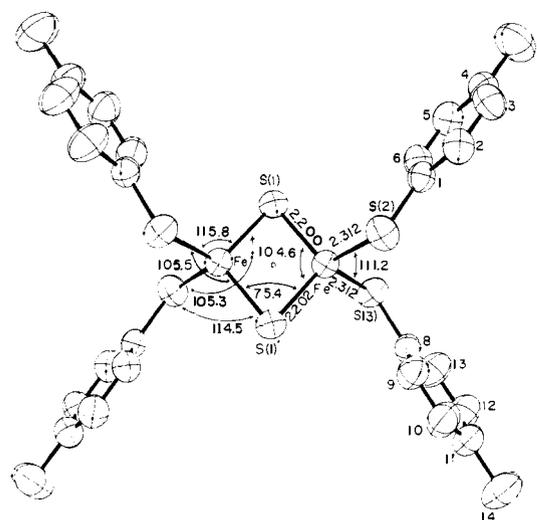


Figure 7. A drawing of the nonhydrogen atoms of the centrosymmetric $[\text{Fe}_2\text{S}_2(\text{S}-p\text{-tol})_4]^{2-}$ anion, showing the labeling scheme and selected bond distance and angles.

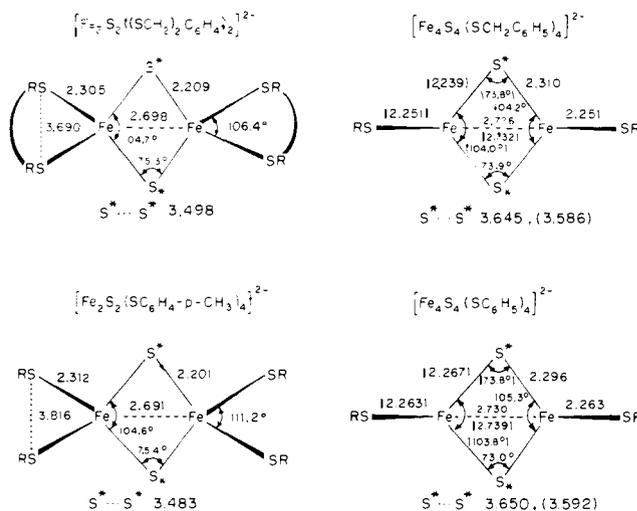
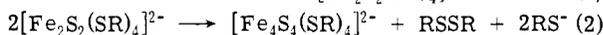
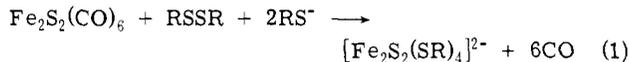


Figure 8. Structural comparison of alkylthiolate and arylthiolate dimers and tetramers.^{25,27} In the tetramer structures one face of the Fe_4S_4^* core is shown; the numbers with and without parentheses refer to faces approximately parallel and perpendicular, respectively, to the $\bar{4}$ axis of $I\bar{4}$.

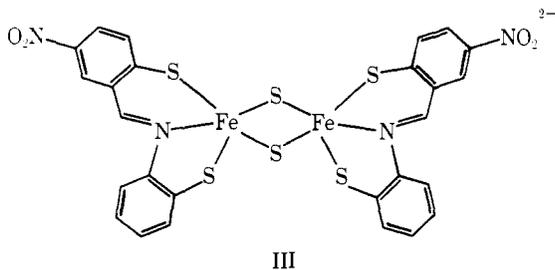
a tetra-*n*-butylammonium salt, is presumably an oligomer of tetranuclear clusters: its spectrum is consistent with those of alkylthiolate tetramer dianions,²² and its reaction with

p-tolylthiol in acetonitrile afforded $[\text{Fe}_4\text{S}_4(\text{S-}i\text{p-tol})_4]^{2-}$, identified spectrally (Table I). Inasmuch as the two dithiols should form chelate rings of quite similar dimensions, it is apparent that other factors, as yet unclear, are required for the formation of discrete dimeric species. The oligomeric reaction product is under further investigation.

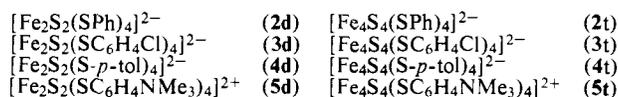
The reaction of FeCl_3 , NaHS , and *p*- $\text{Me}_3\text{N}^+\text{C}_6\text{H}_4\text{SH}$ in methanol was recently reported to produce an Fe-S complex cation in low yield whose properties are not consistent with those of an arylthiolate tetramer of structure II.²² In this work an identical complex was isolated from the reaction of **1** and excess thiol in DMF solution. On the basis of spectral comparison (Figure 2) this complex is now identified as the cation dimer $[\text{Fe}_2\text{S}_2(\text{SC}_6\text{H}_4\text{NMe}_3)_4]^{2+}$ (**5d**, Figure 1). To date this is the only arylthiolate dimer prepared directly from a simple iron salt. Another potential route to dimers was explored using $\text{Fe}_2\text{S}_2(\text{CO})_6$,^{16,26} whose Fe_2S_2 portion requires oxidation by two electrons to achieve the core oxidation level of the dimer dianions. Reaction mixtures containing the appropriate $\text{Fe}_2\text{S}_2(\text{CO})_6$:PhSSPh:PhS⁻ mole ratio of 1:1:2 in methanol gave $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ as the only isolable product. The cation tetramer $[\text{Fe}_4\text{S}_4(\text{SC}_6\text{H}_4\text{NMe}_3)_4]^{2+}$ (**5t**, Figure 1) was prepared by an analogous reaction. It seems plausible that dimers may have been formed initially by reaction 1 and then thermally or catalytically transformed to tetramers by reaction 2 (*vide*



infra). The oxidation of $\text{Fe}_2\text{S}_2(\text{CO})_6$ with disulfides was further investigated in its reaction with 2,2'-bis(benzothiazoline)-4,4'-dinitrodiphenyl disulfide and sodium methoxide. An anionic complex containing no carbon monoxide was isolated as its tetraphenylarsonium salt. Analytical and other data suggest the formulation III containing five-coordinate Fe(III). The same complex can be obtained from the reaction of FeCl_3 , NaHS , base, and the thiazoline disulfide. The postulated rearrangement of the thiazoline to a Schiff base ligand in the presence of a metal ion has a number of well-established precedents.⁵⁵

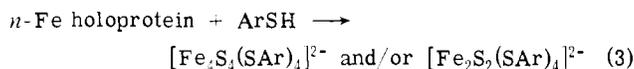


Comparative Properties of Dimers and Tetramers. By the methods outlined in Figure 1 the following pairs of dimers and tetramers^{25,56} containing the same arylthiolate ligands have been synthesized. The thiolate substitution reactions **1** → **2d-5d** and $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ ($\text{R} = t\text{-Bu, Et}$) → $[\text{Fe}_4\text{S}_4$



$(\text{SAr})_4]^{2-}$,^{22,27} effected with arylthiols, reveal that dimer and tetramer cores can be transformed from one ligand environment to another with retention of structure.²⁷ Further, glycyl-L-cysteinylglycyl oligopeptide complexes have recently been prepared by substitution reactions and readily form **2t** upon treatment with a small excess of benzene-thiol.⁵⁷ The latter process may be considered an extrusion reaction in which the Fe_4S_4 core is removed from a polypep-

ptide ligand environment of moderate complexity. These reactions are clear precedents for extrusion of intact clusters from proteins, reaction 3. Very recently such reactions have been accomplished



with several 2-Fe and 4-Fe proteins by Bale and Orme-Johnson⁵⁸ and in these laboratories, where it has been found that the Fe_2S_2^* core of the algal protein *Spirulina maxima* Fd_{ox} may be removed and identified in the form of **2d**.⁵⁹ Under appropriate conditions extrusion reactions may be applicable to complex Fe-S proteins and enzymes in which the organization of active sites into 2-Fe and 4-Fe types cannot be adequately established by spectroscopic methods. Because arylthiols at present appear to be the most promising extrusion reagents for both types of sites, some comparative properties of arylthiolate dimers and tetramers are briefly examined. Structural features are considered first followed by spectral and electrochemical properties which, under appropriate conditions, might be adopted to an assay of dimer-tetramer mixtures in solutions resulting from protein extrusion reactions.

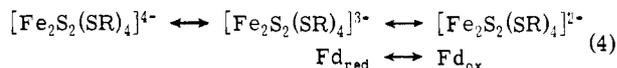
(a) Core Structures. The structures of $[\text{Fe}_4\text{S}_4(\text{SCH}_2\text{Ph})_4]^{2-}$ ²⁵ and $[\text{Fe}_4\text{S}_4(\text{SPh})_4]^{2-}$ ²⁷ have been reported earlier. Average values of distances and angles in dimeric and tetrameric cores are summarized in Figure 8. In dimer-dimer and tetramer-tetramer comparisons it is seen that core structures are essentially independent of the nature of the thiolate ligands. In dimer-tetramer comparisons several points should be noted. Formal metal oxidation states are different, being 3+ in the dimers and apparently 2.5+ in the electronically delocalized tetramers.³⁵ Owing to the D_{2d} tetramer symmetry Fe_2S_2^* faces approximately perpendicular and parallel to the 4 axis of II are not quite equidimensional, as indicated in the figure. The dimer cores are planar whereas all tetramer faces are nonplanar rhombs with average displacements from best weighted least-squares planes being *ca.* +0.07 and -0.24 Å for Fe and S*, respectively, in the two structures. These differences notwithstanding, it is evident that the Fe_2S_2^* dimer core and the Fe_4S_4^* tetramer faces possess a high degree of dimensional similarity. Corresponding bonded distances and angles do not differ by more than 0.11 Å⁶⁰ and 2.4°, respectively. In view of this structural relationship the dimer core may be considered a fragment or building block of the tetramer, leading to the possibility that the two might be interconvertible by a redox process such as reaction 2. Indeed, the slow conversion **2d** → **2t** has been observed in 80% DMSO-H₂O over an *ca.* 10-hr period and is under further study.⁵⁹

(b) Electronic Spectra. Spectral data for the four dimer-tetramer pairs given in Table I reveal that in DMF solution the principal dimer band at 483–502 nm is red-shifted compared to the main tetramer absorption at 449–461 nm. Extinction coefficients per iron are also appreciably different, being 5600–6100 for dimers and 3800–4600 for tetramers in DMF. The spectra of the pairs **2d-2t** and **5d-5t** shown in Figure 2 serve to illustrate the differences between dimers and tetramers with the same arylthiolate ligands. Spectra of dimer-tetramer mixtures have been examined and found to be additive with respect to those of the components measured separately. For example, the spectrum of a mixture of **2d** ($1.95 \times 10^{-4} M$) and **2t** ($3.27 \times 10^{-4} M$) at 400–600 nm in DMF agreed to within 4% of that calculated from extinction coefficient data of the components and remained unchanged for at least 5.5 hr.

The dimer bands in the 483–502-nm range, each of

which contains an additional unresolved feature at lower energy, appear to correspond to the absorptions of **1** near 415 and 450 nm. A low energy shift of about 30 nm or more between alkyl- and arylthiolate tetramers has been observed.²² All dimers except **5d** show a maximum or pronounced shoulder near 335 nm, which is thought to be related to the 338-nm absorption of **1**. Bands in the 300–700-nm interval of both dimer and tetramer spectra are believed to arise, in simple terms, from S → Fe charge transfer excitations. In the dimer series the near constancy of the feature at 335–340 nm and the energy variation of the lower energy absorptions with changes from alkyl- to arylthiolate suggest the assignments S* → Fe and RS → Fe, respectively.

Redox Properties. The electrochemical behavior of the dimer dianions **1** and **2d–5d** in DMF solution has been examined by dc polarography, differential pulse polarography (DPP), and cyclic voltammetry (CV) at scan rates of 10–10⁴ mV/sec. DPP measurements were performed with a 25-mV pulse amplitude so that derivative pulse mode relationships⁶² valid for small pulse amplitudes apply. Half-wave potentials and related data for reductions of dimers **1** and **2d–5d** in DMF are given in Table II together with corresponding information for arylthiolate tetramers,²² which has been augmented in this work by measurement of **3t**. Electrochemical properties of dimers and tetramers show several similarities. A wide variety of [Fe₄S₄(SR)₄]²⁻ complexes, including **2t–5t**, are reducible in two one-electron steps to trianions and tetraanions with the 2–/3– reduction being reversible or nearly so.^{22,63,64} The majority of dimers show two well-defined cathodic processes by dc polarography or DPP (Figure 9) with approximately equal diffusion currents or peak areas and half-widths. Exceptions are **5d**, which evidences a poorly developed second reduction wave, and **3d**, whose diffusion current for the second reduction is peculiarly low. Diffusion currents are in reasonable agreement with those of the tetramers, whose one-electron reductions (2–/3–) have been established by coulometry and spectroscopic methods.⁶³ Slopes of log [*i*/(*i*_d – *i*)] vs. *E* plots are usually somewhat less than the value of 59 mV for a reversible one-electron reduction. Peak half-widths obtained by DPP (82–96 mV) are in adequate agreement with the theoretical value of 90.4 mV for such a process. Under the diffusion-controlled conditions prevalent in the dc and DPP methods, we conclude that the three-member electron transfer series (eq 4) is realized.



These results show that the dianion **1**, which is a synthetic analog of plant Fd_{ox} and other oxidized 2-Fe proteins, is reducible in a one-electron step as are these proteins.^{4–8} Consequently, the trianion and Fd_{red} must possess the same total oxidation level (formally involving Fe(II) + Fe(III)), but comparative electronic properties, including the important matter of trapped valence vs. delocalized electronic structure of **1**, remain to be established. No protein oxidation level corresponding to the tetraanion [2Fe(II)] has yet been detected. While **1** possesses a redox capacity requisite to its designation as a synthetic analog of the 2-Fe protein sites, its 2–/3– potential when converted to the hydrogen electrode is ca. 0.9–1 V more negative than protein potentials in water. Such a comparison of potentials is clearly inexact,²² but does serve to reveal the disparity in protein and analog potentials, which has also been encountered in tetramer 2–/3– reductions.²² Neither **1** nor simple alkylthiolate tetramers reproduce that functional property of the proteins expressed in the values of their aqueous redox potentials. Incorporation of cysteinyl-containing polypeptides

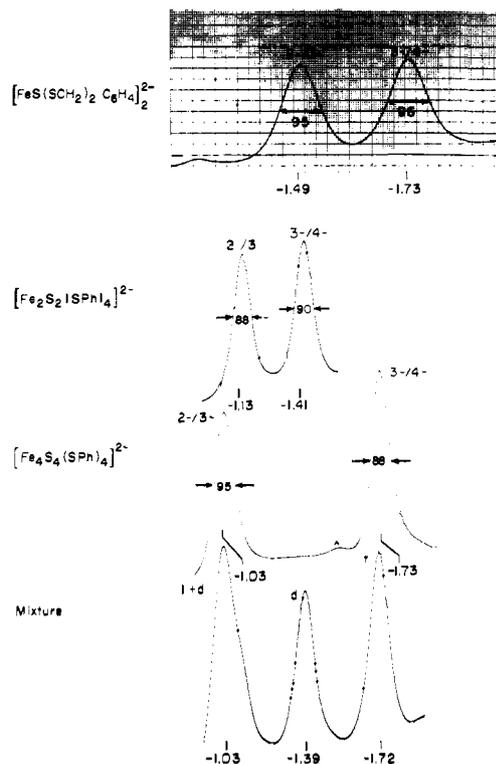


Figure 9. Differential pulse polarograms in DMF solution at 25°C: (Et₄N)₂[FeS(SCH₂)₂C₆H₄]₂, ca. 10⁻³ M; (Et₄N)₂[Fe₂S₂(SPh)₄]²⁻ (**d**), 9.00 × 10⁻⁴ M; (Me₄N)₂[Fe₄S₄(SPh)₄]²⁻ (**t**), 9.60 × 10⁻⁴ M; mixture, 9.50 × 10⁻⁴ M **d** + 9.20 × 10⁻⁴ M **t**. Peak potentials (V), half-widths (mV), and redox processes are indicated; × = impurity. All polarograms were recorded using a 25-mV pulse amplitude and within 1.5 hr after solution preparation.

around the tetramer core produces substantial anodic potential shifts.⁵⁷ Presumably a similar modification of –CH₂S ligands will be required to displace potentials of the Fe₂S₂* core redox processes toward the protein values.

Dimer and tetramer redox processes respond in a similar way to thiolate substituent variations. In both series alkylthiolate species are more difficult to reduce than their arylthiolate counterparts. The first reduction of **1** occurs at a potential 400 mV more negative than that required for **2d**; a difference of 210 mV between the 2–/3– potentials of the R = CH₂Ph and Ph tetramers has been found.²² Within the arylthiolate series **2d–5d** and **2t–5t** having para-substituents X = H, Cl, Me, and N⁺Me₃, the 2–/3– potentials can be empirically correlated with the Hammett σ_p constants by the least-squares fits expressed in eq 5 and 6. The potentials

$$\text{dimers} \quad E_{1/2}(\text{V}) = 0.328\sigma_p - 1.09 \quad (5)$$

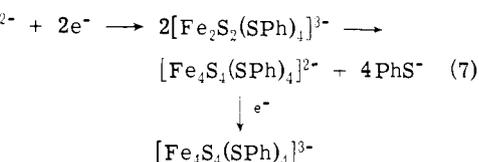
$$\text{tetramers} \quad E_{1/2}(\text{V}) = 0.298\sigma_p - 1.03 \quad (6)$$

decrease as the electron-releasing tendency of the substituent increases. The numerical similarity of the two equations is open to several interpretations. Our view is that it expresses the expected restriction of redox events to the core structures,⁶⁶ whose intrinsic affinities for the first electron addition are regulated in nearly parallel fashion by the electronic properties of substituents.

The possibility of an electrochemical assay of a dimer-tetramer mixture has been examined by DPP of DMF solutions containing **2d** and **2t**. In this method advantage is taken of the nearly constant separations of 2–/3– and 3–/4– potentials in the arylthiolate dimer and tetramer series (Table II). With the exclusion of **5d** and **5t**, whose second reductions are less than satisfactorily defined, Δ*E*_{1/2}

values are 680–710 mV for tetramers compared to 260–330 mV for dimers. Experimental conditions are specified in Figure 9, where DP polarograms of **2d** and **2t** separately and as a mixture are shown. Identical polarograms were obtained by reverse potential scan following the initial cathodic scan. The two 2–/3– processes are evident in the first peak but could not be well resolved. In DPP the observed current as a function of applied potential is proportional to the concentration of electroactive substance,⁶² with the area under a peak polarogram then being proportional to the square of this concentration. The proportionality constant will depend upon the particular electroactive substance, reduction process, solvent, and temperature. Planimetrically determined peak areas in separate dimer and tetramer polarograms normalized by squares of concentrations yielded four constants D_1 , D_2 , T_1 , and T_2 , corresponding to the first and second reductions. Areas in the mixture polarogram were determined and the equations $D_1[d] + T_1[t] = A_1$ (composite) and $D_2(d) = A_2$ solved, yielding $[d]/[t] = 0.95$. From the initial concentrations $[d]/[t] = 1.03$. The agreement is satisfactory and could be improved by refinement of the method. Conventional dc polarography could also be applied to an analysis of dimer–tetramer mixtures, but DPP was employed here because of its sensitivity in detecting lower concentrations of complexes such as might result from protein extrusion reactions.

Lastly, dimer redox processes were investigated in DMF solution by CV in order to assess the feasibility of generating reduced forms for other studies. Based on the theoretical current–potential responses for different types of charge-transfer processes,⁶⁹ the following conclusions have been drawn from the experimental results. (i) No dimer 2–/3– or 3–/4– process satisfies the diagnostic criteria for a reversible charge transfer uncomplicated by preceding or following chemical reactions. In all cases peak potential separations (ΔE_p) exceed 59 mV for a one-electron process, the current function $i_p^c/\nu^{1/2}$ is dependent on scan rate (ν), and $i_p^c/i_p^a > 1$. (ii) At a Pt electrode both reductions and corresponding reoxidations of **1** are observable, with peak resolution improved at $\nu \geq 50$ mV/sec.⁷⁰ Compared with 1 cyclic scans of both processes of arylthiolate dimers deviate further from reversible behavior. (iii) The observed dependencies of E_p , ΔE_p , i_p^c/i_p^a , and $i_p^c/\nu^{1/2}$ on scan rates for the 2–/3– processes of **1** and **2d**, do not allow unambiguous determination of any single case⁶⁹ causing deviations from responses owing to reversible charge transfer. For this reason detailed data are not presented at this time. However, we do suggest a possible interpretation of the CV results for the 2–/3– reduction of **2d**. In the interval $10 \leq \nu < 5000$ mV/sec (Pt electrode) ΔE_p increases from 97 to 220 mV, $i_p^c/\nu^{1/2}$ decreases from 1.55 to 0.85 $\mu\text{A sec}^{1/2} \text{mV}^{-1/2}$, and i_p^c/i_p^a is relatively constant at 2.5 ± 0.4 . In the reaction sequence **7**, **2d** is reduced to its trianion which then dimerizes



to the tetramer dianion **2t**. The potential required for this reduction is sufficient to reduce **2t** to its trianion (Table II), thereby producing an anomalously large cathodic current which will always be greater than the anodic current if the conversion (dimer)^{3–} → (tetramer)^{2–} is irreversible, as seems likely. This scheme is consistent with the values of $i_p^c/i_p^a > 1$ at all scan rates and the relative constancy of this ratio suggests that the conversion is fairly fast. The behavior of the current function further suggests that even the

highest scan rates used are not competitive with the rate of this process. The appearance of a second dimer reduction in the dc and DPP experiments presumably sets an upper limit on the dimer–tetramer conversion rate, which must be less than the rate of diffusion of the dimer to the electrode at potentials cathodic of the observed second reduction. The overall conclusions gained from the electrochemical studies are that reduced forms of **1** are somewhat more stable than those of **2d–5d**, successful generation of the latter for any appreciable time period, at least in DMF solution, is unlikely, and reduced forms of all dimers are substantially less stable than those of tetramers.

Other investigations of Fe–S dimers include magnetic and Mössbauer properties, 2-Fe protein extrusion and reconstitution reactions, and dimer–tetramer conversions, results of which will be reported subsequently.

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Supplementary Material Available. Tabular listings of calculated coordinates of hydrogen atoms (Tables VII and VIII), root-mean-square amplitudes of vibration (Tables IX and X), and structure amplitudes (Tables XI and XII) for $(\text{Et}_4\text{N})_2\text{[FeS}(\text{SCH}_2)_2\text{C}_6\text{H}_4]_2$ and $(\text{Et}_4\text{N})_2\text{[Fe}_2\text{S}_2(\text{S-}i\text{-p-tol})_4]$ will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negative) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$5.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-75-1032.

References and Notes

- (1) Part X. G. R. Dukes and R. H. Holm, *J. Amer. Chem. Soc.*, in press.
- (2) Massachusetts Institute of Technology.
- (3) Northwestern University.
- (4) W. H. Orme-Johnson, *Annu. Rev. Biochem.*, **42**, 159 (1973).
- (5) D. O. Hall, R. Cammack, and K. K. Rao, *Pure Appl. Chem.*, **34**, 553 (1973).
- (6) G. Palmer in "Iron-Sulfur Proteins," Vol. II, W. Lovenberg, Ed., Academic Press, New York, N.Y., 1973, Chapter 8.
- (7) W. R. Dunham, G. Palmer, R. H. Sands, and A. J. Bearden, *Biochim. Biophys. Acta*, **253**, 373 (1971).
- (8) T. Kimura, *Struct. Bonding (Berlin)*, **5**, 1 (1968).
- (9) L. H. Jensen, ref 6, Chapter 4.
- (10) 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.A.*, **69**, 3526 (1972).
- (11) E. T. Adman, L. C. Sieker, and L. H. Jensen, *J. Biol. Chem.*, **248**, 3987 (1973).
- (12) (a) J. F. Gibson, D. O. Hall, J. H. M. Thornley, and F. R. Whatley, *Proc. Nat. Acad. Sci. U.S.A.*, **56**, 987 (1966); (b) H. Brintzinger, G. Palmer, and R. H. Sands, *ibid.*, **55**, 397 (1966).
- (13) (a) W. C. Hamilton and I. Bernal, *Inorg. Chem.*, **6**, 2003 (1967); (b) M. R. Snow and J. A. Ibers, *ibid.*, **12**, 249 (1973); (c) W. Hu and S. J. Lippard, *J. Amer. Chem. Soc.*, **96**, 2366 (1974); (d) S. J. Lippard, *Accounts Chem. Res.*, **6**, 282 (1973); (e) A. J. Schultz and R. Eisenberg, *Inorg. Chem.*, **12**, 518 (1973).
- (14) (a) L. F. Dahl and C.-H. Wei, *Inorg. Chem.*, **2**, 328 (1963); (b) H. P. Weber and R. F. Bryan, *J. Chem. Soc. A*, 182 (1967); (c) G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Commun.*, 1165 (1968); (d) N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7472 (1970); (e) J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Crystallogr.*, **11**, 599 (1958).
- (15) D. Coucouvanis, S. J. Lippard, and J. Zubieta, *Inorg. Chem.*, **9**, 2275 (1970).
- (16) C.-H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1, 493 (1965).
- (17) G. T. Kubas, T. G. Spiro, and A. Terzis, *J. Amer. Chem. Soc.*, **95**, 273 (1973); A. Terzis and R. Rivest, *Inorg. Chem.*, **12**, 2132 (1973).
- (18) K. A. Rubinson and G. Palmer, *J. Amer. Chem. Soc.*, **94**, 8375 (1972).
- (19) C. S. Yang and F. M. Huennekens, *Biochemistry*, **9**, 2127 (1970).
- (20) Y. Sugiura and H. Tanaka, *Biochem. Biophys. Res. Commun.*, **46**, 335 (1972); Y. Sugiura, M. Kunishima, and H. Tanaka, *ibid.*, **48**, 1400, 1518 (1972).
- (21) J. J. Mayerle, R. B. Frankel, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Nat. Acad. Sci. U.S.A.*, **70**, 2429 (1973).
- (22) B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, Jr., and R. H. Holm, *J. Amer. Chem. Soc.*, **96**, 4159 (1974).
- (23) W. Autenreith and R. Hennings, *Chem. Ber.*, **34**, 1772 (1901).

- (24) Occasional failures in the synthesis were encountered when other than a freshly prepared solution was employed. In addition, the use of a 1:1 instead of a 2:1 mole ratio of dithiol to Fe(III) consistently resulted in little or no formation of the desired dimer.
- (25) B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Amer. Chem. Soc.*, **95**, 3523 (1973).
- (26) W. Hieber and J. Gruber, *Z. Anorg. Allg. Chem.*, **296**, 103 (1956).
- (27) L. Que, Jr., M. A. Bobrik, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, **96**, 4168 (1974).
- (28) A. Valette, *Ann. Chim. (Paris)*, **3** (12), 644 (1948).
- (29) D. J. Martin and C. C. Greco, *J. Org. Chem.*, **33**, 1275 (1968).
- (30) A. Lüttringhaus, S. Kabuss, W. Maier, and H. Friebolin, *Z. Naturforsch. B*, **16**, 761 (1961).
- (31) K. Freis and G. Brothlin, *Chem. Ber.*, **56**, 1630 (1956).
- (32) See the paragraph regarding supplementary material at the end of this article.
- (33) Although not stoichiometric multiples of each other, the generalized species $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ and $[\text{Fe}_2\text{S}_2(\text{SR})_4]^{2-}$ are referred to as tetramers (t) and dimers (d). This notation is employed in Figure 1 and in the text.
- (34) 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).
- (35) R. H. Holm, B. A. Averill, T. Herskovitz, R. B. Frankel, H. B. Gray, O. Siiman, and F. J. Grunthaler, *J. Amer. Chem. Soc.*, **96**, 2644 (1974).
- (36) T. Herskovitz, Ph.D. Thesis, M.I.T., 1973; T. Herskovitz, B. V. DePamphilis, W. O. Gillum, and R. H. Holm, *Inorg. Chem.*, in press.
- (37) J. W. Boon and C. H. MacGillivray, *Recl. Trav. Chim. Pays-Bas*, **61**, 910 (1942).
- (38) G. Johansson and W. N. Lipscomb, *Acta Crystallogr.*, **11**, 594 (1958).
- (39) M. E. Fleet, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **132**, 276 (1970).
- (40) I. E. Grey, H. Hong, and H. Steinfink, *Inorg. Chem.*, **10**, 340 (1971).
- (41) General agreement between the estimated standard deviations of individual distances and those obtained by averaging presumably equivalent distances (e.g., in the cation) suggest that the estimated standard deviations are reliable, giving credence to the idea that variations in the C-C distances arise from motional effects.
- (42) G. Palmer, H. Brintzinger, and R. W. Estabrook, *Biochemistry*, **6**, 1658 (1967).
- (43) K. Tagawa and D. I. Arnon, *Biochim. Biophys. Acta*, **153**, 602 (1968).
- (44) J. A. Fee and G. Palmer, *Biochim. Biophys. Acta*, **245**, 175 (1971).
- (45) T. Kimura and J. J. Huang, *Arch. Biochem. Biophys.*, **137**, 357 (1970).
- (46) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, **5**, 417 (1970).
- (47) T. Kimura, *Biochem. Biophys. Res. Commun.*, **43**, 1145 (1971).
- (48) D. V. DerVartanian, Y. I. Shetna, and H. Beinert, *Biochim. Biophys. Acta*, **194**, 548 (1969).
- (49) D. F. Wilson, *Arch. Biochem. Biophys.*, **122**, 254 (1967).
- (50) R. B. Frankel, W. O. Gillum, S. Foner, and R. H. Holm, work in progress.
- (51) G. Brostigen and A. Kjekshus, *Acta Chem. Scand.*, **23**, 2186 (1969); **24**, 1925 (1970).
- (52) H. Föppel, E. Busmann, and F.-K. Frorath, *Z. Anorg. Allg. Chem.*, **314**, 12 (1962).
- (53) M. O. Chaney and L. K. Steinrauf *Acta Crystallogr., Sect. B*, **24**, 1564 (1968); M. M. Harding and H. A. Long, *ibid.*, **24**, 1096 (1968); B. M. Oughton and P. M. Harrison, *ibid.*, **12**, 396 (1959).
- (54) E. Bayer, H. Eckstein, H. Hagenmaier, D. Josef, J. Koch, P. Krauss, A. Röder, and P. Schretzmann, *Eur. J. Biochem.*, **8**, 33 (1969); T. Kimura, Y. Nagata, and J. Tsurugi, *J. Biol. Chem.*, **246**, 5140 (1971).
- (55) See, for example, M. C. Thompson and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 213 (1964); H. Jadamus, Q. Fernando, and H. Freiser, *ibid.*, **86**, 3056 (1964).
- (56) R. H. Holm, W. D. Phillips, B. A. Averill, J. J. Mayerle, and T. Herskovitz, *J. Amer. Chem. Soc.*, **96**, 2109 (1974).
- (57) L. Que, Jr., J. R. Anglin, M. A. Bobrik, A. Davison, and R. H. Holm, *J. Amer. Chem. Soc.*, **96**, 6042 (1974).
- (58) J. R. Bale and W. H. Orme-Johnson, unpublished results.
- (59) L. Que, Jr., R. H. Holm, and L. E. Mortenson, *J. Amer. Chem. Soc.*, in press.
- (60) Formal metal oxidation states do not appear to be reliable determinants of these differences for the approximately tetrahedral iron centers in dimers and tetramers. Based on results for $[\text{FeCl}_4]^{2-}$, $^{1-}$, $^{6+}$ Fe(III) bond distances are expected to be ca. 0.1 Å shorter than Fe(II) distances. While this trend is observed for Fe-S* distances, the reverse is true for Fe-S distances, which would be expected to reflect oxidation state effects more clearly than core bond lengths.
- (61) R. Mason, G. B. Robertson, and G. A. Rusholme, *Acta Crystallogr., Sect. B*, **30**, 894, 906 (1974); Trinh-Toan and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 2654 (1971); J. W. Lauher and J. A. Ibers, *Inorg. Chem.*, in press.
- (62) E. P. Parry and R. A. Osteryoung, *Anal. Chem.*, **37**, 1634 (1965).
- (63) R. B. Frankel, T. Herskovitz, B. A. Averill, R. H. Holm, P. J. Krusic, and W. D. Phillips, *Biochem. Biophys. Res. Commun.*, **58**, 924 (1974).
- (64) Previous measurements of 3-/4- tetramer reductions under CV conditions in DMF solution were not consistent with reversible charge transfer.²² Recent results by van Tamelen, *et al.*,⁶⁵ suggest that *N*-methylpyrrolidone may be a more satisfactory solvent for stabilization of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{4-}$.
- (65) E. E. van Tamelen, J. A. Gladysz, and C. R. Brület, *J. Amer. Chem. Soc.*, **96**, 3020 (1974).
- (66) Recent SCF X- α calculations of the electronic structure of tetramer dianions,⁶⁷ as well as more qualitative MO considerations,^{25,68} indicate that in the trianions⁶³ the unpaired electron is described by an orbital principally tetrametal in character.
- (67) J. C. Slater and K. H. Johnson, *Phys. Today*, **34** (1974); K. H. Johnson, private communication.
- (68) R. S. Gall, C. T.-W. Chu, and L. F. Dahl, *J. Amer. Chem. Soc.*, **96**, 4019 (1974).
- (69) E. R. Brown and R. F. Large in "Techniques of Chemistry," Vol. I, Part IIA, A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1971, Chapter VI.
- (70) Cf. Figure 3 of ref 21 for a cyclic voltammogram of **1** in acetonitrile at $\nu = 50$ mV/sec.