The observed results can now be explained in terms of inductive effects and the bond elongation. Although the α-carbon in *tert*-butyllithium is potentially more capable of transferring electron density to the lithium than the α-carbon in ethyl- and *sec*-butyllithium based on inductive effects, it is in actuality less capable because of the drastically increased Li–C bond distance. Ethyl- and *sec*-butyllithium, therefore, absorb at a lower energy than *tert*-butyllithium and our rationale of predicting the order of transitions within a specific aggregate unit seems justifiable.

Thus the alkyllithium aggregates have been shown to have electronic transitions observable in the ultraviolet region which may be generally associated with a charge transfer from the alkyl group to the lithium framework. Both the experimentally observed spectra and the transitions calculated using CNDO/2 procedures support these conclusions and also support the relative energies of the transitions observed.

Based on these conclusions, one may further predict that the photochemical reactions of alkyllithiums will occur primarily at high energy and involve formation of radicals by the charge transfer process. This contention is supported by Glaze[6] who postulates an interaggregate disproportionation mechanism, *e.g.*, (2),

$$(C_2H_5Li)_6{}^* \longrightarrow \cdot C_2H_5(C_2H_5Li)_5 + Li \qquad (2)$$

$$\cdot C_2H_5(C_2H_5Li)_5 \longrightarrow C_2H_6 + \cdot C_2H_4Li(C_2H_4Li)_4 \qquad (3)$$

$$\cdot C_2H_4Li(C_2H_5Li)_4 \longrightarrow C_2H_4 + (C_2H_5Li)_4 + Li \qquad (4)$$

(3), and (4) to account for the photodecomposition products of ethyllithium. The $(C_2H_5Li)_4$ may in turn equilibrate to form more hexamer or eliminate LiH and ethylene or both. This "not so free" radical-type intermediate may be common to all photolytic reactions of alkyllithiums at high energy.

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Preparation and Characterization of an Inorganic Analog for the Active Site of the Reduced 2Fe–S* Iron–Sulfur Proteins[1]

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Abstract: The reaction of $[(CF_3)_2C_2S_2]$ (ligand) with $Fe(CO)_5$ in the presence of H_2S produces a black crystalline solid, I (apparent space group $P4_332$ or $P4_132$), which, when dissolved in hydrocarbon solvents, exhibits many of the physical properties of the reduced two-iron iron–sulfur proteins. A frozen solution of I in hexane exhibits an epr spectrum which upon addition of isopropyl disulfide narrows and has an axial g tensor ($g_\perp = 1.988_0$, $g_\parallel = 2.009_8$, from computer simulation) similar to that observed in reduced adrenodoxin and putidaredoxin. The integrated intensity of the epr corresponds to one unpaired electron per two Fe. The magnetic susceptibility measured between 20 and 300°K exhibits non-Curie behavior which can be described using the antiferromagnetic interaction Hamiltonian $\mathcal{H} = -2JS_1 \cdot S_2$ with $J = -95$ cm^{-1} and $S_1 - S_2 = 1$. An endor measurement gave values for the ^{19}F hyperfine constant of $A_\parallel{}' = 1.25$ MHz and $A_\perp{}' = 0.78$ MHz, from which it was concluded that the unpaired electron resides almost exclusively on the Fe–S center. There is a hydrogen in the molecule which acts as a counterion allowing the complex to be soluble in nonpolar solvents while having the irons in different formal oxidation states. The instability of the complex to Lewis bases parallels the chemistry of hydrogen polysulfides. Spectral properties of the complex were determined from 55,000 to 200 cm^{-1}. Changes were observed following addition of isopropyl disulfide in ^{19}F nmr, Mössbauer, and epr spectra but not in the optical measurements. The near-infrared electronic and far-infrared vibrational spectra of $\{Fe[S_2C_2(CF_3)_2]_3\}_2$, $\{CO[S_2C_2(CF_3)_2]_2\}_2$, and $[(CF_3)_2C_2S_2]_2$ and the Raman spectra of I and $[(CF_3)_2C_2S_2]_2$ are reported. A convenient method for obtaining Raman spectra of highly colored solutions is described.

The iron–sulfur proteins (ferredoxins) are an intriguing and biologically significant class of compounds with the characteristic property that, when reduced, they exhibit an electron paramagnetic resonance (epr) spectrum with both g_{av} and $g_{x,y} < 2$. A subclass of this group of proteins which contain two atoms of both iron and inorganic sulfide (*e.g.*, spinach ferredoxin) has been extensively characterized by chemical and physical methods and a probable structure deduced.[2]

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

Simple chemical analogs of these proteins have been sought for several years,[3,4] in the hope of clarifying both their physical and biological properties. From the known physical data we can list a set of properties that should be exhibited by any pertinent chemical analog of the reduced 2Fe–S* proteins. The analog should have (a) two irons and no more than six ligating sulfurs,[5–7] (b) a temperature-dependent magnetic susceptibility characteristic of a system with spin $^1/_2$ ground state and antiferromagnetic coupling constant $J = -100$ to -200 cm^{-1},[8,9] (c) an epr spectrum with $g_{av} < g_e$ and g_x, $g_y < g_e < g_z$, the correct "sense" of the anisotropy,[6,10–12] (d) electron nuclear double resonance (endor) and Mössbauer spectral parameters characteristic of one high-spin ferrous and one high-spin ferric ion with hyperfine fields at the ^{57}Fe nucleus indicative of electrons localized on covalently bound iron,[13,14] and (e) electronic transitions in the visible and near-infrared region similar to those of the proteins with comparable circular dichroism properties in the near-infrared.[15] In this paper we describe the preparation and characterization of a crystalline compound which exhibits many of these properties.

Experimental Procedures

Preparative Method for the Model Compound. To 100 ml of *n*-hexane were added 7.4 g of bis(trifluoromethyl)-1,2-dithiolene, $(CF_3)_2C_2S_2$, and 2.3 g of $Fe(CO)_5$, a mole ratio of 3:1. The mixture was stirred in a closed flask, with a valve allowing pressure release,[16] for 15–24 hr at ambient temperature (~23°). During this period the solution turned magenta with some precipitated $(CO)_3Fe[(S_2C_2(CF_3)_2]$. Then with the flask opened to air and still at room temperature, the solution was saturated with H_2S passing through the solution for 3–5 min.[17] The solution was then heated, and when it began to boil, the H_2S delivery tube tip was raised to a position just below the surface of the liquid. The solvent was replenished as needed. The solution turned deep blue and then gray-green within about 20 min, and the characteristic visible spectrum of the model compounds was fully developed within 1 hr.[18] (The 830-nm peak had become maximized relative to those around 600 nm after that time.) The solvent was evaporated at about 35° to one-half the original volume over 1–2 days. Some precipitate formed. The liquid which contained the desired compound was decanted into another flask, and the solvent was allowed to evaporate to dryness at ~35° (another 3–4 days) whereupon the desired crystals and a tarry residue remained. The crystals were washed with hexane and then pentane until all the tarry substances were removed. Yields were up to 2.6 g, 45% by iron, but were highly variable.

The compound was best recrystallized from hexane or cyclohexane by dissolution at ambient temperature, evaporation to dryness, and again washing off the tarry substances. The crystals formed were air-stable, shiny black octahedra or truncated octahedra. When recrystallized from CH_2Cl_2, the crystals tended to be trigonal prisms. Compound I may be stored indefinitely at ambient temperature. Purity may be easily checked by comparing the absorbance ratios of the 830- and 630-nm bands. $A_{628}/A_{830} = 1.0$ is good. The best value achieved was $A_{628}/A_{830} = 0.9$.

The crystals melt with decomposition at 225–259° in open capillaries. The material is destroyed by solvents which are Lewis bases.

Isopropyl disulfide (Aldrich Chemical Co.), Halocarbon oil (Halocarbon Products Co., Hackensack, N. J.), and bis(trifluoromethyl)butyne-2 (Pierce Chemical Co.) were used as received. Iron pentacarbonyl (Alfa Inorganics) was filtered when necessary. Normal pentane, hexane, heptane, and octane were "pure grade" (Phillips Petroleum Co.) and used as received. For spectra, "spectroquality" (Matheson) reagents were used. Carbon tetrachloride and trichloroethylene (J. T. Baker Reagent Grade) were distilled from over Linde Type 4a molecular sieves prior to use for the molecular weight determination and spectra. Sulfur, sublimed (nonferrous), and various sulfides, thiols, and disulfides were obtained from various sources in this chemistry department. Bis(trifluoromethyl)-1,2-dithiolene, $(CF_3)_2C_2S_2$, was prepared by the method of Krespan[19] in which the fluoromethylacetylene is passed over the surface of, or even through, sulfur refluxing at about 450°. Two full-length condensers in series were necessary to condense the liquid. The material was not further purified and contained as impurities dissolved elemental sulfur and polysulfides of the fluoroethylene.

Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich. 48106. Melting points were determined on a Gallenkamp melting point apparatus in open capillaries. Densities were determined by the flotation method[20] using an aqueous $ZnBr_2$ solution with the commercial detergent "Alconox" (Alconox, Inc., New York, N. Y. 10003) used as a wetting agent. Using the same method one known compound, $[CO(S_2C_4F_6)_2]_2$, was measured to have density 2.23 compared to a literature value[21] of 2.28.

The epr spectra were obtained on a Varian V-4500-10A spectrometer with a Varian K-band (35 GHz) bridge or a special X-band (9 GHz) microwave bridge.[22] Calibration of the g values was obtained using pitch ($g = 2.0029$; Varian No. 904450-01) with the frequency determined in X-band by a Hewlett-Packard Model X532B frequency meter installed in the crystal bias arm of the bridge. The cryogenic temperature controller used down to 77°K is similar to that described by Hansen, *et al.*[23] For measurement down to 10°K, the apparatus described by Fritz[24] was used.

The powder spectra line-shapes were fit with a program described by Salmeen.[25]

Spin quantitation of a sample was done as previously described.[22] Correction was made for transition probability variation with g,[26] here a factor of 1.14. No correction was made to account for addition of reagents such as isopropyl disulfide since in the quantitation experiments they diluted the solutions less than 4%. Such a correction would lessen the Fe/spin ratio.

Endor spectra were obtained on an instrument described by Fritz.[13] ^{19}F continuous wave nmr spectra were obtained at ambient temperature on a Varian Model HA-100 spectrometer operating at 94.077 MHz locked on signal of the internal reference $CFCl_3$. The model compound sample used had been recrystallized and was dissolved in dichloromethane to saturation for the experiment. Since

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(3) *E.g.*, M. Clare, H. A. O. Hill, C. E. Johnson, and R. Richards, *Chem. Commun.*, 1376 (1970).

(4) *E.g.*, E. Bayer, H. Eckstein, H. Hagenmaier, D. Josef, J. Koch, P. Krauss, A. Röder, and P. Schretzmann, *Eur. J. Biochem.*, 8, 33 (1969).

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

(6) J. Fee and G. Palmer, *Biochem. Biophys. Acta*, **245**, 175 (1971).

(7) T. Kimura, *Struct. Bonding (Berlin)*, **5**, 1 (1968).

(8) T. Kimura, A. Tasaki, and H. Watari, *J. Biol. Chem.*, **245**, 4450 (1971).

(9) G. Palmer, W. R. Dunham, J. A. Fee, R. H. Sands, T. Iizuka, and T. Yonetani, *Biochem. Biophys. Acta*, **245**, 201 (1971).

(10) G. Palmer and R. H. Sands, *J. Biol. Chem.*, **241**, 253 (1966).

(11) G. Palmer, H. Brintzinger, and R. W. Estabrook, *Biochemistry*, 6, 1658 (1967).

(12) J. C. M. Tsibris, R. I. Tsai, I. C. Gunsalus, W. H. Orme-Johnson, R. E. Hansen, and H. Beinert, *Proc. Nat. Acad. Sci. U. S.*, **59**, 959 (1968).

(13) J. Fritz, R. Anderson, J. Fee, G. Palmer, R. H. Sands, J. C. M. Tsibris, I. C. Gunsalus, W. Orme-Johnson, and H. Beinert, *Biochem. Biophys. Acta*, **253**, 110 (1971).

(14) W. R. Dunham, A. J. Bearden, I. T. Salmeen, G. Palmer, R. H. Sands, W. H. Orme-Johnson, and H. Beinert, *ibid.*, **253**, 134 (1971).

(15) K. A. Rubinson, Ph.D. Thesis, University of Michigan, Ann Arbor, Mich., 1972.

(16) This is easily effected using a sealed hypodermic needle resting in a fire-polished glass tube with a liberal coat of petroleum jelly.

(17) A tube with i.d. greater than 2 mm should be used to avoid clogging.

(18) If the solution becomes purple, $[Fe(S_2C_4F_6)_2]_2$, more ligand may be added; the yield will be reduced, however. Also, too much reaction time and/or H_2S results in an emerald green solution which reverts to gray-green during the prolonged solvent evaporation.

(19) C. G. Krespan, *J. Amer. Chem. Soc.*, 83, 3434 (1961).

(20) G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," Macmillan, New York, N. Y., 1968.

(21) J. H. Enemark and W. N. Lipscomb, *Inorg. Chem.*, **4**, 1729 (1965).

(22) G. Palmer in "Methods in Enzymology," Vol. X, R. W. Estabrook and M. E. Pullman, Ed., Academic Press, New York, N. Y., 1967, p 602.

(23) R. Hansen, T. T. Kalal, and H. Beinert, *Anal. Biochem.*, **20**, 40 (1967).

(24) J. W. Fritz, Ph.D. Thesis, University of Michigan, 1969.

(25) I. T. Salmeen, Ph.D. Thesis, University of Michigan, 1969.

(26) R. Äasa and T. Vänngård, *Z. Naturforsch. A*, **19**, 1425 (1964).

the lines observed were broad as expected for paramagnetic samples, no ^1H peaks could be found in a saturated solution of CCl_4 observed at the appropriate frequency.

The numerical ratio of fluorine to hydrogen was ascertained using a pulsed nmr technique. The sample used was about 2 g of crystalline solid placed in a 7-mm i.d. sample tube. Using a Brucker Model B-KR 322S, the free induction decay was observed after a 90° pulse was applied at 43.72 MHz at the magnetic field appropriate for ^{19}F and then ^1H. The free induction decays (FID) were recorded as Polaroid photographs of the oscilloscope traces. From the photographs, the signal height of the FID *vs.* time[27] was measured, plotted on a semilog graph, and extrapolated to zero time. The relative heights at zero time were corrected for amplifier attenuation differences between ^{19}F and ^1H experiments and for the difference in relative sensitivities at constant frequency for the two nuclei.

Molecular weights in solution were determined on an Hitachi Perkin-Elmer molecular weight apparatus, Model 115, calibrated with benzil. The bridge voltage was recorded on a chart recorder to obtain a continuous record of the approach to quasi-equilibrium. The data were accepted if, for three consecutive runs, the measurement voltage varied in only the second significant figure. The average weight was then used. When, in two consecutive trials, the measurement voltages differed by only a few parts in the third place, a third run was not made and the average of the two was used. Samples were weighted on a Cahn electrobalance with a regulated power supply in place of its batteries. The solvents used were weighed, and the molarities of the solutions were obtained using the solvent density determined at the temperature of the oven from the International Critical Tables.[28]

X-Ray precession photographs showed cubic O_h-$4/m\ \bar{3}\ 2/m$ Laue symmetry with systematic absences observed only for $\{h00\}$ with $h = 4n$ (h, k, l permutable). The only compatible space groups are the enantiomorphic pair $P4_332$ and $P4_132$. $P4_332$ was chosen arbitrarily. For the collection of intensity data a spherically ground crystal (diameter = 0.26 mm) was mounted on a silica fiber. The intensity data were obtained with Mo Kα radiation ($\lambda_{\alpha1}$ 0.70926 Å; $\lambda_{\alpha2}$ 0.71343 Å) on a Syntex P$\bar{1}$ autodiffractometer equipped with a graphite monochromater. Intensities for 1398 independent reflections with $\sin \theta/\lambda < 0.6$ were collected using an ω-2θ scan. The set of independent reflections corresponds to one-sixth of an octant of the reciprocal lattice. The data were corrected for Lorentz and polarization effects from monochromator-diffracted radiation[29] after which an absorption correction was applied (minimum transmission coefficient of 0.99). A least-squares analysis of the coordinates determined by a peak-maximum search gave lattice parameter averages of $a = 19.807 \pm 0.008$ Å, $\alpha = 89.99_3 \pm 0.015°$, and the unit cell volume = 7770 ± 10 Å^3 where the error values are one standard deviation in the calculation of the average value from three lengths and angles, respectively.

The temperature-dependent magnetic susceptibility of the model compound was determined in isopropyl disulfide solution on a Princeton Applied Research Model FM-1 vibrating sample magnetometer as described by Foner.[30] The instrument was calibrated with $HgCo(SCN)_4$ and run at 10.5 kG. The temperature was determined with a calibrated GaAs diode. The temperature-dependent susceptibility of a pure crystalline sample was determined on a conventional Faraday balance.

Ambient temperature absorption spectra in the range 180–2500 nm were obtained on a Zeiss Model DMR 21 spectrophotometer. Solvents used were pentane, hexane, heptane, carbon tetrachloride, dichloromethane, and Halocarbon oil. For determination of the extinction coefficients, samples were weighed on a Cahn electrobalance. All solvent volumes were determined from weight measurements made immediately prior to the spectrophotometric measurement. All solution samples were contained in stoppered cells. Liquid nitrogen temperature spectra were run on a Cary 14 spectrophotometer using a low-temperature cell designed for this instrument by Professor T. M. Dunn. In the visible region, a 1:5 isopentane–methylcyclohexane mixture was used to form the glass. For the near-infrared region, 800–2400 nm, Halocarbon oil was used.

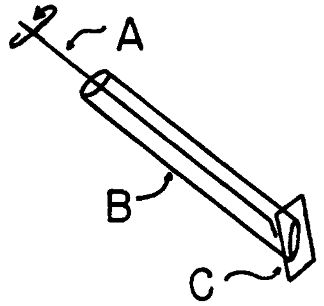

Figure 1. Raman spectrum sample cell for strongly colored solutions: (A) nichrome stirring wire; (B) tube, 5-mm i.d., 7 cm long; (C) microscope slide cover glass fastened to the sanded, beveled tube with epoxy cement.

The circular dichroism measurements in the near-infrared were made on an apparatus described by Eaton and Lovenberg.[31] The sample was an 8 m*M* solution of I in Halocarbon oil.

Infrared spectra were obtained using a Beckman IR-12 spectrometer equipped with scale expansion. The frequency was calibrated using polyethylene in its usable range and CO_2 lines in the far-ir range to 200 cm^{-1}. Three types of sampling techniques were used: (1) CCl_4 solutions contained in NaCl cells *vs.* neat solvent as reference (800–4000 cm^{-1}), (2) Nujol mulls between polyethylene plates *vs.* air (200–600 cm^{-1}), and (3) KBr disks *vs.* air (300–4000 cm^{-1}). The absorption lines of C—F and C=O vibrations were broadened considerably in the KBr disks.

Raman spectra were obtained on a Spex Ramalog system equipped with He-Ne and Ar$^+$ lasers. Clear and lightly colored solutions were held in "Kimax" melting point capillaries. Highly colored solutions were contained in cells constructed as shown in Figure 1. The solutions were stirred continuously at 600 rpm with a slightly bent nichrome wire by a motor mounted on a base separate from the cell's mounting. This stirring system prevented cavitation of the organic solvents at the focus of the laser beam while not causing any interfering vibration. The bevel angle on the tube was adjusted so that the specular reflection would not enter the monochromator when the tube itself was about 45° to the laser beam. The thin microscope slide coverglass used as a window minimized scattering from the container.

Results and Discussion

Composition and Nmr. Table I contains the elemental analyses and molecular weight data on the crystalline compound. The best empirical formula appears to be

Table I. Chemical Properties of the Model Compound (I)

Model compound, experimental results	Elemental analyses two batches, wt %		Empirical formula,[c] calculated results $Fe_3L_4S_6H_2$ $Fe_3S_{14}C_{16}F_{24}H_2$
Fe	12.99	12.39	13.23
S	35.47	35.38	35.4
C	15.32	15.44	15.2
H	0.24	0.17	0.16
F (by diff)	36.0	36.6	36.2
^{19}F:^1H ratio[a]	15 ± 1:1		12:1
Solid mol wt[b]	420/Fe		422/Fe
	In CCl_4	In C_2Cl_3H	
Solution Mol wt (2 prepn)	839 864.5	905	

[a] Determined by pulsed nmr experiment. [b] Using preliminary X-ray data and density. $V = 7770$ Å^3/unit cell, $\rho = 2.14$. [c] $L = S_2C_2(CF_3)_2$.

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(27) The induction decay times were such that the ^{19}F signal fell to noise level within 60 μsec while the ^1H did so within 110 μsec.

(28) "International Critical Tables," Vol. III, McGraw-Hill, New York, N. Y., 1928, p 28.

(29) L. Azaroff, *Acta Crystallogr.*, 8, 701 (1955).

(30) S. Foner, *Rev. Sci. Instrum.*, 30, 548 (1959).

(31) W. A. Eaton and W. Lovenberg, *J. Amer. Chem. Soc.*, **92**, 7195 (1970).

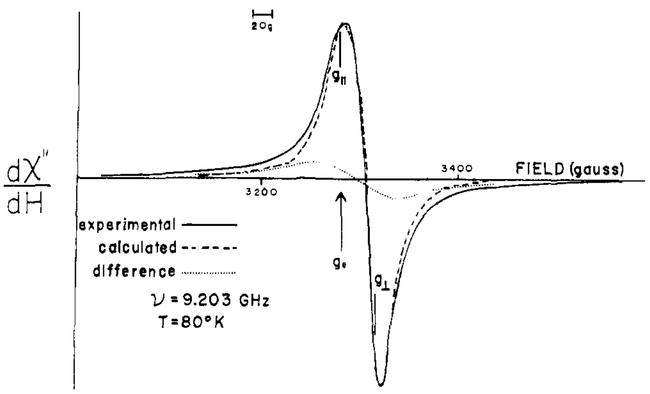

Figure 2. Epr spectrum of I in frozen hexane solution. Parameters used in the calculated spectrum are listed in Table II. All epr spectra shown were obtained under nonsaturating conditions with suitably low modulation amplitudes.

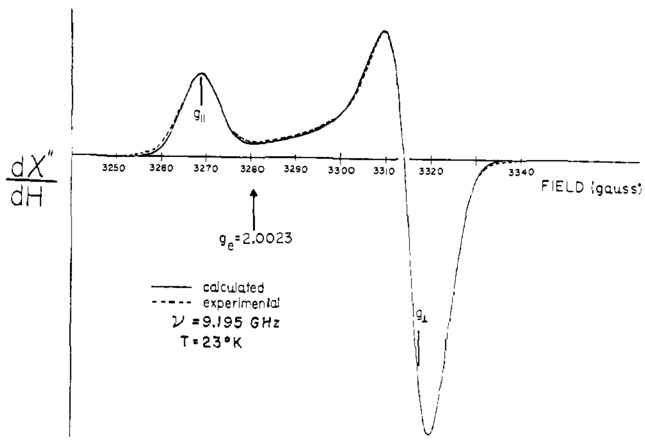

Figure 3. Epr spectrum of I in frozen hexane solution with excess isopropyl disulfide added (II). Parameters used in the calculated spectrum are listed in Table II.

Table II. Parameters for Epr Spectra of I and II[a]

Observed parameter	I (Figure 2)	II (Figure 3)
$g_\perp$	1.982	$1.980_0 \pm 0.0007$
$g_\parallel$	2.003	$2.009_8 \pm 0.0007$
$L_\perp$ (1/2 width in G)	18.5	4.80 ± 0.05
$L_\parallel$ (1/2 width in G)	18.5	4.10 ± 0.05
Line shape	Lorentzian	Gaussian
Calcd $\langle g_{av} \rangle$	1.989	$1.989_9 \pm 0.0005$
Exptl $\langle g_{av} \rangle$[b]	$1.989_3 \pm 0.0005$	$1.989_3 \pm 0.0005$
Temp, °K	80	23
Quantitation[c] (Fe/e$^-$)	4.48, 3.03, 7, 6.1	2.22, 2.06, 1.84, 1.89

[a] Error limits quoted are changes which produce a deviation from the best fit curve. [b] Determined in pentane solution at 140°K. [c] Various batches, solvents and times of running; conservatively made error estimate ±10%.

$Fe_3L_4S_6H_2$ where L = ligand $[S_2C_2(CF_3)_2]$. ^{19}F continuous wave nmr of I in CH_2Cl_2 showed three paramagnetically broadened resonances and, in addition, a single, sharp peak at 5212 cps (55.3 ppm) upfield relative to $CFCl_3$ with half-width of 1.5 cps. The narrow peak is attributable to the intermediate product in the reported synthesis, $LFe(CO)_3$, which by itself exhibits a shift of 5200 cps (55.3 ppm) at 30° relative to its solvent $CFCl_3$. The area under the sharp peak accounts for about 3% of the total fluorine intensity seen in the nmr spectrum. If all the fluorine present is observed, the relative areas would indicate that 5% of the iron is present as the diamagnetic impurity in the sample used. With sensitivity at this level no free ligand or ligand dimer appeared implying that the complex keeps its integrity upon dissolution.

To confirm the analytical hydrogen determination, the ratio of fluorine relative to hydrogen was ascertained independently by the pulsed nmr experiment; the ratio was found to be 15(±1):1 for ^{19}F:^{1}H.

The molecular weight determined in solution indicates that I exists as a diiron complex in the solvents used. At first sight these data present a paradox since the empirical formula is consistent with a triiron complex. There are two additional independent pieces of data which support the diiron formulation, *viz.*, epr quantitation and magnetic susceptibility measurements (see below).

Epr. The epr spectrum of I in frozen hexane solution is shown in Figure 2. Addition of isopropyl disulfide in large excess to this solution produces a narrower line width, higher apparent intensity relative to iron, and a different line shape for the epr spectrum (Figure 3); however, the values of the *g* tensor remain the same. The associated parameter values from the computer simulation of the two spectra are presented in Table II. For the narrow line-width species, II, the integrated intensity corresponds to one unpaired electron per two Fe; the intensity of I varied widely. When only a small excess of isopropyl disulfide (sixfold over iron) was added to a solution of I, the intensity of the spectrum increased but the line shape changed only slightly from that of Figure 2, which indicates that a relatively weak interaction with the disulfide is responsible for the conversion to II. The appearances of the respective spectra are concentration independent, and, within experimental error, they remain the same with pentane, heptane, carbon tetrachloride, dichloromethane, or carbon disulfide as solvent.

As seen in Figure 4, spectrum no. 11, adding excess ligand, 3,4-bis(trifluoromethyl)-1,2-dithietene, has the same effect as isopropyl disulfide. A wide range of sulfides and disulfides have a similar, albeit lesser, line narrowing effect. Figure 4 shows the various spectra resulting from the same starting solution after each reagent was added to its full effect and observed under the same conditions.

It has not proved possible to fit the spectrum of Figure 2 to our satisfaction, though the program gave an excellent fit to that of Figure 3. The difference between the computed and experimental spectra is a broad curve of peak-to-peak width of 80 G (Figure 2). A similar resonance was observed in microcrystals dispersed with solid KBr, suggesting that polymeric material is responsible for the broad resonance.

The broad line width displayed by the parent species I has a predominantly Lorentzian line shape *vs.* the predominantly Gaussian line shape of the disulfide-containing solution. In agreement with these characteristics the saturation behavior of the two species shows I to possess a far shorter excited state lifetime than II; I showed no signs of saturation even at 18°K with a maximum H_1 = 0.15 G, while II was easily saturated even at 77°K.

When I was dissolved in pure isopropyl disulfide, the spectrum of II appeared (Figure 3). Upon slow evaporation of the solvent, the compound recrystallized. When these crystals were dissolved in aliphatic solvents, the spectrum of I (Figure 2) appeared as from samples prepared in the usual manner. Further, these crystals had the same X-ray precession pictures as the ones prepared normally. This behavior argues that the reaction with disulfides is a weak Lewis acid–base reaction with energy so small as not to disrupt the crystallization, in accord with the disulfide titration data mentioned earlier. However, the differences in effect between the various sulfides and disulfides as seen in Figure 4 cannot be explained at this time.

The determination of the origin of the preponderately Gaussian line shape of II is more straightforward. The possible causes of a Gaussian line shape are small, statistically distributed, variations in the crystal field called "*g* strain," or electron-nuclear hyperfine interactions in which the energy of interaction is less than the lifetime-determined line width. When the spectrum of II was recorded at 34.6 GHz, no deviation from axial symmetry was seen, but the line width was approximately four times greater than at 9 GHz. This indicates that the line width is almost entirely a result of *g* strain.

Endor. The localization of the unpaired spin density in II can be inferred from an electron nuclear double resonance (endor) experiment. Present only in natural abundance (2.2%), no ^{57}Fe spectrum was observed. Large signals from ^{19}F and lesser ones from ^{1}H were seen. The peaks resulting from ^{1}H hyperfine interaction could not be resolved; this signal appeared as a single peak underlying and distorting the higher frequency peaks of the ^{19}F resonance pairs at both $g_{\parallel}$ and $g_{\perp}$.

The values for ^{19}F in the model compound in frozen solution are $A_{\perp}' = 0.78$ MHz and $A_{\parallel}' = 1.25$ MHz with all fluorines appearing equivalent; the *A* values are primed since they are expressed in the diagonalized *g* tensor coordinates. There is a sign ambiguity here which has yet to be resolved. The calculations done below are carried out assuming that the signs of the three components are the same, which implies that the interaction of the electron with the fluorine nuclei is primarily inductive, rather than dipolar, in origin. Another result of the assumption is that calculations yield the *maximum* values for the hyperfine contribution to the epr line width, and thus the maximum unpaired electron density outside the iron–sulfur center of the model compound. The value of the isotropic contribution is then $A_{\mathrm{iso}} = 0.94$ MHz. This is equivalent to a field of 0.34 G at the electron.[32] It is easy to show that 18 fluorines per electron would produce a Gaussian line with half-width about 0.86 G, while six fluorines would result in a half-width of 0.5 G.[33] These values are the order of the differences in $L_{\parallel}$ and $L_{\perp}$ used in the computer simulation of the epr spectrum of II.

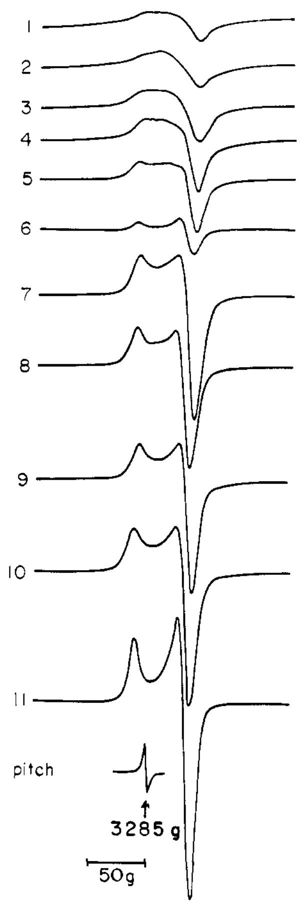

Figure 4. Results of adding various sulfur-containing reagents to samples of I in hexane solution. Each is added to its maximum effect. The spectra are of the frozen solutions at about 80°K and 9.2 GHz. Dilution effects cause less than 10% difference in amplitude. Microwave power and amplifier gain are the same for all samples. Number 1 is the starting solution. The reagents added for the other experiments are as follows: (2) S_2Cl_2; (3) $(CH_3)_2S$; (4) EtSSEt; (5) benzylthiol, $PhCH_2SH$; (6) ethylthiol; (7) benzyl disulfide, $(PhCH_2S)_2$; (8) CH_3SSCH_3; (9) Cl_3CCOOH; (10) *p*-toluyl disulfide, $(p\text{-}CH_3PhS)_2$; (11) $F_3CCS{=}CSCF_3$. For no. 5 and 6, the signal slowly disappears (minutes) when allowed to stand at room temperature. For no. 9, the amount of the effect seems to depend on the purity of the sample used, the less pure showing a larger effect from the acid. With our purest samples $[(A_{626}/A_{830}) \leq 1.0]$, the effect was similar to no. 5.

From the measured isotropic hyperfine interaction together with many assumptions, one can obtain an approximate upper limit for the electron density on the carbon and fluorine atoms of the molecule. First, by assuming a linear relationship between the isotropic hyperfine coupling constant and spin density on the fluorine,[34] the calculations of Cook and coworkers[35] can be used to obtain an approximate electron density on the fluorine. They calculated that $A_{\mathrm{iso}} = 158$ MHz corresponds to a spin density of +0.103. The measured A_{iso} for I leads to the value $\rho_{\mathrm{F}} = 6 \times 10^{-4}$.

Next we can calculate the ring carbon electron density

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[32] From the nmr line width of $[Fe(S_2C_4F_6)_2]_2^-$, Davison, *et al.*, calculated $A = +0.14$ G for the fluorines.

[33] One can determine the approximate half-width of the inhomogeneously broadened epr resonance from the value of *n*, the number of equivalent hyperfine centers, and *A*, the hyperfine coupling constant. The *n* centers give rise to $n + 1$ hyperfine lines separated from the adjacent ones by *A* and with relative intensities following the coefficients of the binomial distribution (*t*). First, calculate the height ratio, *R* between the central peak(s) [$t = n/2$ for *n* even and $t = (n \pm 1)/2$ for *n* odd]. Then, using a table of ordinates of the Gaussian (normal) distribution, find the fraction of a standard deviation, σ, associated with *R* and thus *A*. For a Gaussian curve the half-width at half-height $(\Gamma_{1/2}) = 1.18\sigma$ and from this $\Gamma_{1/2}$ as a function of *A* can be found. For example, when $n = 6$, $R = 0.75$, $A = 0.76\,\sigma$, and $\Gamma_{1/2} = (1.18/0.76)\,A = 1.55\,A$.

[34] The assumption is not too accurate but will serve for our purpose. A more correct formulation assumes separate linear relations for each fluorine orbital.[35,36] The error should not be greater than a factor of 2 which will not affect the final conclusion.

[35] R. J. Cook, J. R. Rowlands, and D. H. Whiffen, *Mol. Phys.*, 7, 31 (1964).

[36] M. Iwasaki, *Fluorine Chem. Rev.*, 5, 1 (1971).

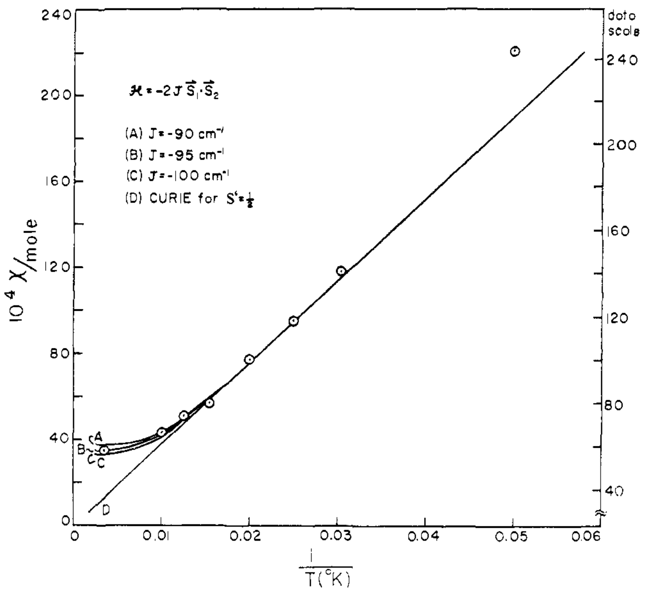

Figure 5. Plot of the molar static magnetic susceptibility *vs.* $1/T$ for the model compound. The descrepancy between experiment and theory at the lowest temperature measurement may not be significant as the deviation can be accounted for by a 1.5°K error in the measured temperature.

using a McConnell relation of the type, $A_F = Q_{CCF_3}\rho_{RC}$ where A_F and Q_{CCF_3} are assumed isotropic. This expression may be used since the dithiolene ring carbons form a planar aromatic system as required by the theory.[37] The unpaired electron density is assumed to be in the delocalized π system in such a calculation. For a freely rotating CF_3 group the value of Q_{CCF_3} is 35 ± 5,[36] and ρ_{RC} is calculated to be $0.96 \times 10^{-2} \approx 0.01$.

The electron density of the CF_3 carbon is approximated by using a value of the relative electron occupation of a carbon and its α fluorine as determined for planar radicals. The ratio ρ_F/ρ_C will tend to be larger for the planar radicals because of the greater overlapping of carbon and fluorine p orbitals. In order to obtain an upper limit of electron density on the carbons, the smallest value of ρ_F/ρ_C ($=0.11$) found was used (*cf.* Table II in ref 37). With this value for ρ_F/ρ_C and using $\rho_F = 6 \times 10^{-4}$, we find $\rho_C = 5.5 \times 10^{-3}$.

A maximum value for the unpaired electron population is obtained by assuming that all 18 fluorines on three ligands contribute to the endor signal. The total electron density on the carbons and fluorines will then be $6\rho_{RC} + 6\rho_C + 18\rho_F = 0.105$.

With one electron per diiron complex, we estimate that the electron is localized on the iron–sulfur center of I at least 85% of the time.

Magnetic Susceptibility. The temperature dependence of the magnetic susceptibility of **I** was determined in the crystalline form and in solution in isopropyl disulfide, II.

The solution susceptibility is plotted *vs.* $1/T$ in Figure 5. The straight line is the theoretically expected susceptibility of a spin-only spin $^1/_2$ system with Curie behavior—a magnetically dilute system. The experimental values are absolute, but in order to coincide with theory at low temperatures (<60°K), all the experimental susceptibility values had to be shifted down 2300×10^{-6} cgs unit and is so shown as the left scale in Figure 5. When this is done, the slope fits well when the data are interpreted as a diiron complex with molecular weight 840 per spin. This is then a third independent, albeit indirect, measurement of the molecular weight further strengthening the conclusions from vapor pressure osmometry and quantitative epr measurements. If the data were used assuming one unpaired electron per three Fe, the susceptibility graph would have a slope $^3/_2$ of that shown in Figure 5.

The value of the diamagnetic correction per diiron molecule calculated using Pascal's constants[38,39] is -333×10^{-6} cgs unit. Applying this value to the data, the downward shift needed to make the experimental and calculated values coincident becomes 1300×10^{-6} unit/Fe. This value lies at the high end of values for the second-order Zeeman effect (temperature independent paramagnetism).[36] Since no ferromagnetic impurities are expected to dissolve in the isopropyl disulfide, the most probable impurity, $LFe(CO)_3$, is diamagnetic, and no $(FeL_2)_2$ was detected in the ir, the value for the TIP should be accurate.

At temperatures greater than 60°K, there is a deviation from Curie behavior which can be well accounted for by the simple exchange Hamiltonian, $\mathcal{H} = -2JS_1 \cdot S_2$ for an antiferromagnetically coupled system of two irons with oxidation states differing by one. The possible diiron systems are: one ferric and one ferrous iron in high ($S_1 = {}^5/_2$, $S_2 = 2$) or intermediate ($S_1 = {}^3/_2$, $S_2 = 1$) spin states; one Fe(IV) and one Fe(III) in any ($S_1 = 1$, $S_2 = {}^1/_2$), ($S_1 = 2$, $S_2 = {}^3/_2$), ($S_1 = 2$, $S_2 = {}^5/_2$) spin state.

The complete high-spin-pair manifold has possible $S' = {}^1/_2, {}^3/_2, {}^5/_2, {}^7/_2, {}^9/_2$ with respective $E = 0, 3J, 8J, 15J, 24J$ above the ground state. The adjusted experimental data can be fit with a J value of -95 cm^{-1}. The first excited state ($S' = {}^3/_2$) is located 285 cm^{-1} above the ground state, and the second ($S' = {}^5/_2$) is at 760 cm^{-1}. For this value of J, at 295°K, the various spin states contribute proportionally to the total susceptibility approximately as follows: $S' = {}^1/_2$, 25%; $^3/_2$, 57%; $^5/_2$, 16%; $^7/_2$, 1%, if present.

Thus with the data at hand, a low-spin ferric–ferrous system ($S_1 = {}^1/_2$, $S_2 = 0$) can be definitely ruled out because of the large contribution to the susceptibility by states which do not exist in such system. However, it is not possible to ascertain from the data which set of formal iron states is the correct one.

For purposes of comparison with the model compound Table III[40–47] contains susceptibilities for some

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(37) H. M. McConnell and D. B. Chesnut, *J. Chem. Phys.*, 28, 107 (1958).

(38) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 6.

(39) P. Pascal, "Chemie Generale," Masson et Cie., Paris, 1949, p 409.

(40) J. F. Weiher, L. R. Melby, and R. E. Benson, *J. Amer. Chem. Soc.*, 86, 4329 (1964).

(41) A. L. Balch, I. G. Dance, and R. H. Holm, *ibid.*, 90, 1139 (1968).

(42) A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *Inorg. Chem.*, 3, 814 (1964).

(43) R. Williams, E. Billig, J. H. Waters, and H. B. Gray, *J. Amer. Chem. Soc.*, 88, 43 (1966).

(44) E. Hazen in "Proceedings of the Third Symposium of Coordination Chemistry, Debrecen, Hungary, 1970," M. T. Beck, Ed., Akademiai Kiado, Budapest, 1970, p 259.

(45) J. A. McCleverty, J. Locke, E. J. Wharton, and M. Gerloch, *J. Chem. Soc. A*, 816 (1968).

(46) E. J. Wharton and J. A. McCleverty, *ibid.*, 2258 (1969).

(47) R. Beckett, G. A. Heath, B. F. Hoskins, B. P. Kelly, R. L. Martin, I. A. G. Roos, and P. L. Weickhardt, *Inorg. Nucl. Chem. Lett.*, 6, 257 (1970).

Table III. Magnetic Susceptibilities of Some Iron–Sulfur Complexes[a]

Formula	μ_{eff}, BM (molar)	Temp, °K	Ref
Model compound	1.50/2Fe	295	This work
	1.26/2Fe	87	
in isopropyl disulfide	2.88/2Fe	295	
	1.81/2Fe	80	
(a) $[Fe(S_2C_4F_6)_2]_2$	1.59/Fe	301	41
	1.13/Fe	87	
(b) $(Et_4N)[Fe(S_2C_4F_6)_2]_2$	2.08/2Fe	300	41
	1.74/2Fe	80	
(c) $(Et_4N)_2[Fe(S_2C_4F_6)_2]_2$	1.39/Fe	299	41
	0.31/Fe	87	41
	1.62/Fe	Amb	40
	1.48/Fe	298	42
in acetone solution	1.83/Fe	298	42
(c′) $(Bu_4N)_2[Fe(S_2C_4F_6)_2]_2$	1.39/Fe	299	41
	0.37/Fe	90	
(d) $(Et_4N)_2[Fe[S_2C_2(CN)_2]_2]_2$	1.67/Fe	301	41
	0.48/Fe	84	
(d′) $(Bu_4N)_2[Fe[S_2C_2(CN)_2]_2]_2$	1.55/Fe	299	41
	0.43/Fe	81	
(d″) $[Fe[S_2C_2(CN)_2]_2]^-$ in cyclohexanone	3.75/Fe	Amb	43
(e) (Et_4N) $[Fe(dmox)_2]$	2.42/Fe	224	44
(e′) $(Ph_4As)[Fe(dmox)_2]$	2.07/Fe	224	44
(f) $(Ph_4P)_2[Fe[S_2C_2(CN)_2]_3]$	2.98/Fe	305	45
	2.94/Fe	101	
(g) $(Ph_4P)_3[Fe[S_2C_2(CN)_2]_3]$	2.50/Fe	294	45
	2.28/Fe	90	
(h) $(Bu_4N)_2[Fe(tbd)_3]$	2.98/Fe	Amb	46
(i) $Fe(dtaa)_3 \cdot CHCl_3$	2.0/Fe	Amb	47
	1.75	100	

[a] All measurements were made on crystalline samples unless noted. Abbreviations: Ph = phenyl; Bu = butyl; Et = ethyl; dmox = 4,5-dimercapto-*o*-xylol; tbd = tetrachlorobenzene-1,2-dithiolate; dtaa = dithioacetylacetonato.

iron–sulfur complexes reported in the literature. Those identified as (a) through (d″) are dimers and are square pyramidally coordinated; (e) and (e′) are considered to be monomeric, square planar; and (f) through (i) are monomeric and essentially octahedral.

Note that there are only three diiron compounds in the table where both solution and crystalline susceptibilities are determined. For these the susceptibility in solution is always larger than in the crystalline form. This behavior is excellent evidence that, in addition to the intramolecular exchange, an intermolecular exchange interaction occurs in the solid. Thus only in solution are susceptibility measurements done on truly magnetically dilute systems. Nevertheless, the susceptibility values in the table can be fit reasonably well for the following dimeric crystalline compounds.

For (a), $[Fe(S_2C_4F_6)_2]_2$, assuming low-spin ferric irons, $J = -62$ cm^{-1} is derived from the 301° measurement and $J = -56$ cm^{-1} from the 87° value. The $S' = 1$ state is thus about 120 cm^{-1} above the ground ($S' = 0$) state. The susceptibility cannot be fit when allowing higher excited states in the calculation and so lead to the low-spin ferric assignment.

For (b), the monoanion of (a), the values can be fit with the first excited state ($S' = {}^3/_2$) at $3J = 690$ cm^{-1}. With such a high value of spin state of the irons cannot be ascertained.

For (c), $[Fe(S_2C_4F_6)_2]_2{}^{2-}$, the dianion of (a), the data can be fit assuming the first excited state ($S' = 1$) is at $2J = 310$ cm^{-1} only if a higher ($S' = 2$) state is allowed. Weiher and coworkers[40] found that the temperature-dependent susceptibility could be fit assuming low-spin iron(III), thus allowing only one excited state, a triplet at $2J = 300$ cm^{-1}. But they needed to use $\mu_{triplet} = 3.4$ BM *vs.* a spin-only value of 2.8 BM and questioned whether an impurity was the cause of the anomaly. However, since the upper ($S' = 2$) state contributes just the right amount of moment, a better explanation may be that the material is intermediate or high spin.

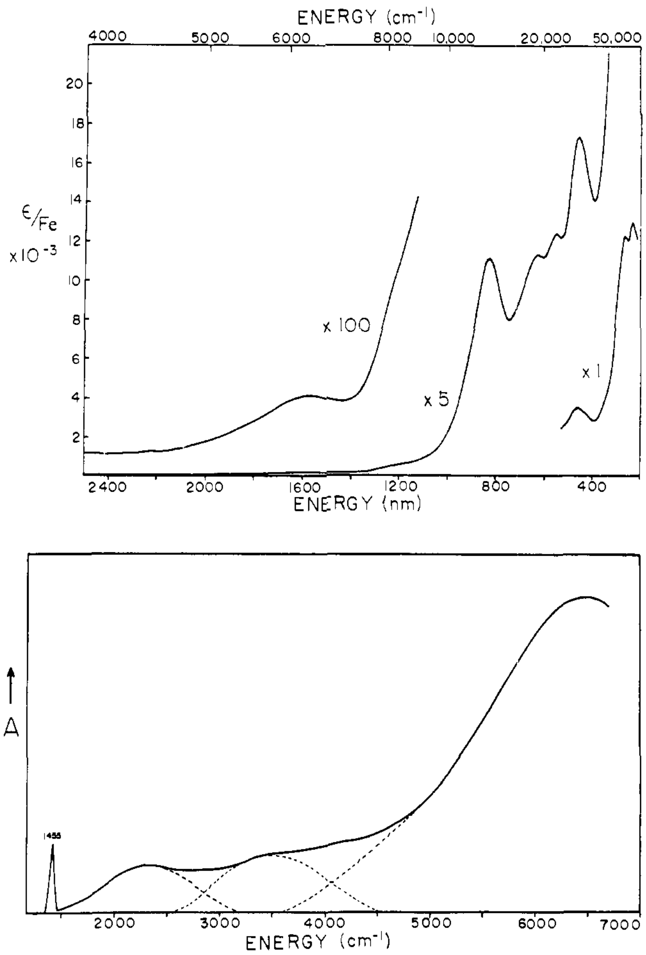

Figure 6. (Top) The uv–visible–near-infrared spectrum of the model compound in CCl_4. Numerical values are listed in Table IV. Within experimental error the addition of isopropyl disulfide has no effect on the spectrum. (Bottom) The near-infrared and infrared electronic transitions of the model compound. The solid curve shown is the combination of a spectrum of a known concentration of themod el compound dissolved in Halocarbon oil (>4000 cm^{-1}) and one taken in the infrared (<4000 cm^{-1}) in a KBr tablet with unknown concentration. Having determined a "best" base line, the data in the infrared were converted from % *T* to absorbance. This was scaled to the solution absorbance at the overlap region (4000 cm^{-1}) and plotted as a smoothed curve (there were several small, narrow vibrational lines superimposed on the broad electronic bands). The dotted curves are approximate individual band contours estimated visually and drawn freehand. Numerical values are listed in Table IV.

Electronic Spectra. The electronic transition spectrum for I is shown in Figure 6. The associated parameters are listed in Table IV. The addition of isopropyl disulfide to the solution, yielding II (*cf.* epr and nmr sections), has no effect on the spectrum within experimental error.

There appears to be little similarity between the observed electronic transitions of iron complexed with dithiolenes (unsaturated 1,2-dithiolato) and those of the

Table IV. Electronic Transitions[a]

Model compound in hexane (<55 kK)				[Fe($S_2C_4F_6$)$_2$]$_2$ in CCl_4 (55–4 kK)			(Et_4N)$_2$[Fe($S_2C_4F_6$)$_2$]$_2$ in acetone (29–4 kK)		
λ_{max}				λ_{max}			λ_{max}		
kK	nm	ε/Fe[b]	$\Gamma_{1/2}$, kK	kK	nm	ε/Fe[f]	kK	nm	ε/Fe[g]
42.0	238	13,000	5.8	42.5	235	15,500	27.8	360	6140
37.3	268	12,650		37.0	270	12,200	23.6	425	4350
*27.8 (sh)	*360 (sh)			23.1	433	4,970	22.2	450	3840
*24.4	*410			17.8	560	5,030	17.8[h]	560[h]	1260
21.8, *22.0	59, *455	3,680		16.5 (sh)	605 (sh)		10.4	955	49
18.2, *18.9	549, *530[c]	2,620		13.2 (sh)	755 (sh)		9.22	1085	45
15.9, *16.1	629, *620	2,360		11.0 (sh)	910 (sh)		5.85	1710	5
12.1, *12.2	828, *823	2,300	1.3–1.4	9.26	1080	170			
*8.55	*1170	30–40[d]		7.06	1415–20	160			
6.34, *6.50	1580, *1540	40	1.1–1.2	6.35	1575	140			
3.6[e]	2780[e]	8[e]		5.00	2000	60			
2.3[e]	4350[e]	7[e]	0.5–0.6[e]						

(CF_3)$_2C_2S_2$ in isooctane[i]			[(Fe(MNT)$_2$]$^{2-}$[j]			[Fe(MNT)$_3$]$^{3-}$[k] in CH_2Cl_2			Spinach ferredoxin: reduced form[l]			Adrenodoxin: reduced form[m]		
λ_{max}			λ_{max}			λ_{max}			λ_{max}			λ_{max}		
kK	nm	ε	kK	nm	ε	kK	nm	ε	kK	nm	ε/Fe	kK	nm	ε/Fe
42.0	238	7440	23.5	425	7200	27.9	358	16,300	37.4	267		31.2	320	
29.4	340	60	15.5	645	1000	24.4	410	8,900 (sh)	32.0	312 (sh)	(5400)	24.2	414	(2500)
			12.38	808	3300	12.5	800	2,200	25.0	400	(2700)	22.0	455	(2100)
									21.3	470	(1800)	18.0	554	
			24.4	410	7100[k]				18.7	535	(1200)	14.6	686	
			15.5	645	1000 (sh)				15.4	650		12.3	810	
			12.4	805	3100				12.6	790		11.0	910	
									11.0	910		5.99	1670	(28)
									5.81	1720	(25)	4.50	2220	(45)
									3.80	2630	(70)			

[a] An asterisk denotes value observed at 77°K in 4:1 methylcyclohexane–isopentane. Abbreviations: kK = kilokaiser = 1000 cm^{-1}. (sh) = shoulder. [b] In units of cm^{-1} M^{-1} per Fe at 23°. Estimated error limit ±2%. [c] The 530-nm band is less intense than that at 620 nm at 77°K. [d] Base line subtracted out: 120 without correction. [e] Determined in KBr = 8 ± 2 and 7 ± 2 calibrated at overlap. See comments in Figure 6. [f] In units of cm^{-1} M^{-1} per Fe at 23°. Estimated error limit ±3%. [g] In units of cm^{-1} M^{-1} per Fe at 23°. Estimated error limit ±5%. [h] In dilute solution at 25° (0.01 M). At concentration 0.05 M, the band appears at 590 nm with ε 700. [i] From ref 19. [j] Reference 52. MNT = maleonitrilodithiolato = (NC)$_2C_2S_2$. Done in chloroform to 30 kK. [k] Reference 45. Done in CH_2Cl_2. [l] References 11, 53, 54. [m] References 7, 53, 55.

iron thioxanthates and dithiocarbamates (unsaturated 1,1-dithiolato).[48, 49]

In I the 42- and 37-kK bands are assigned as intraligand transitions. Both the energy and intensity of the transition associated with the 42-kK band seem to be unaffected by coordination (Table II) and have energies similar to a $\pi-\pi^*$ transition in systems with two conjugated double bonds: 1,3-butadiene has such a band at 220 nm (45.5 kK) while the isolated double bond in ethylene has λ_{max} at 162.5 nm (61.5 kK). Apparently the "double" bond in the ligands is not localized in agreement with the vibrational spectrum (see below). The 37-kK band in I is similar in energy and intensity not only to that in (FeL_2)$_2$ (Table IV) but also to other dithiolene complexes lacking iron (*e.g.*, 50).

The band at 16 kK is estimated to have roughly 50–75% of the intensity of the rest of the bands in the region 30–12 kK,[51] and there are remarkable similarities between four of these bands and those reported for both the di- and trianionic iron tris(dicyano)-1,2-dithiolenes (tris-MNT) (Table IV[52–55]). Structurally the dianionic monomer is reported to be close to a perfect octahedron[56] and susceptibility measurements show it to be a low-spin Fe(IV) complex.[52,57] The trianionic species is said to contain low-spin Fe(III) but has a slightly anomalous magnetic susceptibility.[45] There are bands of the model compound's spectrum in this region which are not coincident with those of either of the tris-MNT complexes: those at 18.9 and 22 kK. Jørgensen notes that many high-spin $Fe^{III}S_6$ chromophores have electron transfer bands in the 17–19-kK region similar to those here.[58] Although there are many apparent regularities and difference relationships among them, we cannot assign any of the six obviously charge transfer (CT) bands to specific L → M or M → L transitions. Among those bands between 30 and 12 kK there are significant differences in energies and intensities between those of I and the square pyramidally coordinated (FeL_2)$_2$. These differences, together with the spectral similarities of I to the octahedrally coordinated iron compounds, lead to the conclusion that I has basically octahedral coordination in solution. The assignment of specific spin states to the irons is not aided since vacancies occur in the t orbital set for both high- and low-spin states; thus transition of the type L → M (t orbital set) which occur in this energy range offer no discrimination.[57] The room-temperature cir-

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(48) A. H. Ewald and E. Sinn, *Aust. J. Chem.*, **21**, 927 (1968).

(49) D. V. Coucouvanis, *J. Amer. Chem. Soc.*, **92**, 3342 (1970).

(50) G. N. Schrauzer and W. P. Mayweg, *ibid.*, 88, 3235 (1966).

(51) This estimate is made from comparison of the spectra taken at 77 and 300°K. The major part of the change becomes from a decrease of the contribution that the tails of the uv transitions make to intensities in the visible region.

(52) E. I. Steifel, L. E. Bennett, Z. Dori, T. H. Crawford, C. Simo, and H. B. Gray, *Inorg. Chem.*, **9**, 281 (1970).

(53) W. A. Eaton, G. Palmer, J. A. Fee, T. Kimura, and W. Lovenberg, *Proc. Nat. Acad. Sci. U. S.*, **68**, 3015 (1971).

(54) K. Tagawa and D. I. Arnon, *Nature (London)*, **195**, 537 (1962).

(55) D. F. Wilson, *Arch. Biochem. Biophys.*, **122**, 254 (1967).

(56) R. Eisenberg, *Progr. Inorg. Chem.*, **12**, 295 (1970).

(57) T. M. Dunn in "Physical Chemistry," Vol. 5, H. Eyring, Ed., Academic Press, New York, N. Y., 1970, Chapter 5.

(58) C. F. Jørgensen, *Inorg. Chim. Acta, Rev.*, 65 (1968).

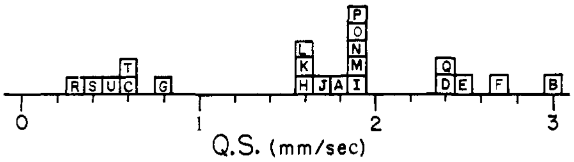

Figure 7. Mössbauer quadrupole splitting for selected iron-sulfur compounds. (A) model compound;[15] (B) spinach ferredoxin-Fe^{2+};[14] (C) spinach ferredoxin-Fe^{3+};[14] (D) $(FeL_2)_2$;[68] (E) $(Et_4N)_2(FeL_2)_2$;[68] (F) $(t\text{-}Bu_4N)_2[Fe(MNT)_2]_2$;[69] (G) $(t\text{-}Bu_4N)_2[Fe(MNT)_2]_2$ in dimethylformamide solution; (H) $(Ph_4P)_2[Fe(MNT)_3]$;[68] (I) $(Ph_4P)_3[Fe(MNT)_3]$;[68,70] (J) $(Fe_4S_4L_4)$;[71] (K) $(Ph_4As)(Fe_4S_4L_4)$;[71] (L) $(n\text{-}Bu_4N)_2(Fe_4S_4L_4)$;[71] (M) $(Fe_3S_2L_4)$;[71] (N) $Fe(ttd)_2(dtt)$;[72] (O) $Fe(dtt)_3 \cdot CHCl_3$;[72] (P) $Fe(dtaa)_3$;[47] (Q) $[Fe(Me_2dtc)_3]BF_4$;[65] (R) greigite-Fe^{2+} octahedral B site;[73] (S) greigite-Fe^{3+} octahedral B site;[73] (T) pyrite-FeS_2;[74] (U) marcasite-FeS_2.[74] Abbreviations: Ph = phenyl; Bu = butyl; Et = ethyl; MNT = maleonitrilodithiolato; ttd = trithioperoxy-*p*-toluate; dtt = dithio-*p*-toluate; dtaa = dithioacetylacetonato; dtc = dithiocarbamate; ArNC = *p*-methoxyphenyl isocyanide.

cular dichroism spectrum of the 6.34-kK band was also obtained. The Kuhn dissymmetry factor,[59] $g = (\epsilon_L - \epsilon_R)/\epsilon$, was determined to be 0.001 at the band maximum. In the equation, the ϵ's are extinction coefficients for the left and right circularly polarized light and unpolarized light, respectively. According to Mason,[60] a transition is magnetic-dipole allowed if $g > 0.01$. Because the Mössbauer data show that the compound is significantly distorted, it seems that this transition is not magnetically allowed. For d–d transitions arising from the same term we expect all transitions except $d_{xy} \rightarrow d_{z^2}$ and $d_{x^2-y^2} \rightarrow d_{z^2}$ to be magnetically allowed. Assuming basically, but not perfect octahedral symmetry around the iron, either the band is from the $d_{xy} \rightarrow d_{z^2}$ transition or from an electric-dipole forbidden charge transfer transition.

The transitions at 2.3 and 3.6 kK have half-widths that are one-half that of all the other bands as a result of smaller vibronic effects. This indicates that the transitions involve the iron d orbitals which are somewhat isolated from the bonding effects in contrast to the orbitals involved in charge transfer. Because of the low intensity, it is not possible to decide the detailed nature of these d–d transitions.

Mössbauer. The Mössbauer spectrum of the crystalline material was a simple quadrupole doublet from 300 to 4.2°K. The value of the quadrupole splitting was 1.79 mm/sec at 300°K and increased slightly to 1.85 mm/sec at 4.2°K. The value of the isomer shift is 0.12 mm (*vs.* Fe metal). The values do not change significantly when the solid is dissolved in toluene, in isopropyl disulfide, or in a mixture of the two solvents (data taken at 77 and 4.2°K). However, the linewidths of the quadrupole doublet increased by about 25% on going from the solid to a solution in toluene and by an additional 30% when the disulfide was added. The disulfide produced a small distortion of the quadrupole doublet which may be due to either hyperfine interaction or a second species of iron.

In the spectrum the solid absorption decreased to zero between the absorption peaks indicating that there was no broad underlying peak. Since the full range of possible isomer shifts for ^{57}Fe is about 1.5 mm/sec, the two peaks cannot each be from one of two inequivalent irons.[61,62]

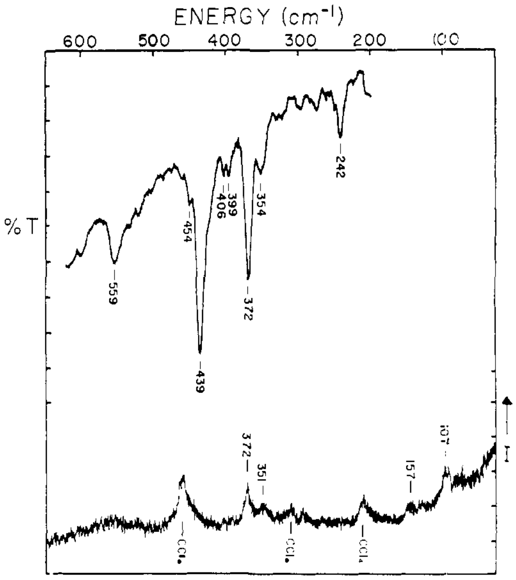

Figure 8. Far-infrared spectrum of I in Nujol (mineral oil) mull (top) and the Raman spectrum in CCl_4 solution (bottom). All the numbered Raman peaks were fully polarized.

We may ask what difference in Fe environment and oxidation states are permitted by the data. The quadrupole splitting parameter is related to the symmetry around the iron and also may contain some contributions from outside the coordination shell. The relationship between this indirect measure of distortion and actual spatial displacement is not understood. As seen in Figure 7 the absolute values of the quadrupole splitting parameter of the sulfur-coordinated compounds appear to fall into three separated ranges: <1, 1.5–1.9, and >2.3 mm/sec. The model compound falls into the middle group, the majority of which are distorted octahedrally coordinated compounds, but contains at least one compound with the irons coordinated by a distorted trigonal-bipyramidal set of sulfurs and, in addition, two full iron bonds (sample J).[63]

The half-width at half-height for each component of the quadrupole pair is about 0.33 mm/sec[64] which is comparable with other spectra of the type.[65,66] Thus we should be able to resolve differences in quadrupole splitting of about 1 mm/sec and see some skewing of the line shape if the isomer shifts differ by more than 0.3 mm/sec. If both quantities differ, the variations should be observable below the limits set for each parameter changing independently. From the variation of parameters for the differences in "oxidation states" of isomorphic complexes,[67] we conclude that some skewing of the line shapes should be observable if the irons in the model compound are in different average oxidation states. However, it is unlikely that slight differences in

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(59) W. Kuhn, *Trans. Faraday Soc.*, **46**, 293 (1950).

(60) S. F. Mason, *Proc. Chem. Soc.*, 137 (1962).

(61) N. E. Erickson in *Advan. Chem. Ser.*, **No. 68**, 86 (1967).

(62) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Int. Ed. Engl.*, **2**, 277 (1963).

(63) I. Bernal, private communication.

(64) The source half-width is about 0.025 mm/sec.

(65) E. A Pasek and D. K. Straub, *Inorg. Chem.*, **11**, 259 (1972).

(66) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *ibid.*, **2**, 153 (1963).

(67) For a discussion of the chemical shifts, see ref 15.

Table V. Vibrational Spectra[a]

Region	(1) Model	(2) $(FeL_2)_2$	(3) $(FeL_2)_2^{2-}$	(4) $(CoL_2)_2$	(5) NiL_2^-	(6) NiL_2^-	(7) NiL_2^{2-}	(8) L_2
Perturbed	1620 vw	1625 vw		(1620 vw)				1580 sh
C=C				1561 w				
stretch	(1550) vvw	1523 m	1546 s	1540 w	1529 w	1538 w	1542 sh	1561 m
1620–1300 cm^{-1}	1455 m	1433 m	(1462)	1467 m	1420 s	1485 s	1536 s	1552 m + R
			(1421)	1410 m				
		1385 vw	Obscured	1381 w				
	1373 vvw	1370 vw	Obscured	1373 w				
	1332 m							
C—F	1263 m	1256 w	1260 w[e]	1264 w				
stretch 1300–1100	1252 sh				1255 vs	1255 vs	1262 vs	1250 vs
cm^{-1} in CCl_4	1238 sh				1235 sh	1234 vs	1246 vs	
	1227 vs	1234 vs	(1225)[e]	1234 vs				
	1197 vs	1202 vs	(1190)[e]	1203 vs	1185 vs	1175 vs	1160 s	1196 s
	1176 vs	1181 vs	1157[e]	1177 vs	1170 vs			1159 s
	1123 w				1144 vvs	1135 vs	1122 vs	
1100–1000 cm^{-1} [b]	1054 vvw	1022 vw	(1038)?	1043 vvw				1004 vw + R
C=S and	935 m-w	944 m		957 w	930 sh	915 m	906 s	881 m-s
C$\cdots$S + $\nu(CCF_3)$	895 vw	895 s	899 s	916 m-s	905 s	907 sh	895 sh	874 sh + R
1000–800 cm^{-1}				892 vw				
	856 m	856 m	840 m	860 m	858 w	847 w	836 m	841 m
		842 vw		852 sh	844 vw	836 sh		834 w
	731 s	734 s		736 s	734 s	723 s	721 sh	708 s + R
CF_3 and				728 s	722 s	717 sh	716 s	696 s
CF_3 + νC$\cdots$S,	715 vvw	719 s	717 m	719 sh				
800–650 cm^{-1}	704 m			715 m				
	695 s	697 s	693 m	698 s	700 s	695 s	691 s	687 s
	680 w	686 w		686 w				
	667 m-w							
650–500 cm^{-1}	602 vw	606 vw	Obscured	604 w	600 w	600 w		600 m-w
f	557 w + R	560 w	554 w[c]	562 m	560 w	554 w	550 w	561 sh + R
								549 w, 529 R[d]
500–300 cm^{-1}			(470)	470 vw				
in KBr and mull;	454 w	455 w	455 w	456 vw				462 m
energies agree	439 s	425 m	420 w	440 m	465 m	447 w-m	424 vw	
within 3 cm^{-1} for	406 w	405 m		411 m				
both	399 w	395 vw		405 w	404 vw			388 R
	372 s + R				373 s	364 s	351 s	
	354 w + R	358 m	357 m	365 m	355 w	356 w		369 m
		326 w	330 w		326 w	329 w	328 m	328 m
		315 w		301 m				295 m
300–200 cm^{-1} [f]	242 m	246 m	249 m	246 m	245 m–s	249 m–s	248 m–s	248 m

[a] Legends: (1) The model compound; (2) $[Fe(S_2C_4F_6)_2]_2$, a dimeric complex with the same general structure as the cobalt dimer (4); (3) $(Et_4N)_2[Fe(S_2C_4F_6)_2]_2$, the dianion of 2; (4) $[Co(S_2C_4F_6)_2]_2$, which is isostructural[21] with (2) and (3) and "isoelectronic" with (3); (5) Ni$(S_2C_4F_6)_2$, a planar monomeric dithiolene complex[80] (the infrared data for (5), (6), and (7) are in ref 76); (6) Ni $(S_2C_4F_6)_2]^-$, a planar monomer,[81] the monoanion of (5); (7) $[Ni(S_2C_4F_6)_2]^{2-}$, a monomer and isostructural with (5) and (6); (8) $[S_2C_2(CF_3)_2]_2$, the dimer of the ligand which is joined through two disulfide bonds[19] (it was used in place of the ligand since it is a solid at room temperature and easier to handle and purify). Transmission minima in cm^{-1} between 4000 and 200 cm^{-1} in KBr unless otherwise stated. Abbreviations: v = very; w = weak; m = moderate; s = strong; sh = shoulder; R = seen in Raman; ( ) are less sure values—the others are reproducible ±1 cm^{-1}. [b] C=C in aromatic systems. [c] (533) in acetone solution. [d] S–S stretch. [e] In acetone solution. [f] Ligand modes.

the octahedral coordination geometry would be observable. The above conclusions still hold if the inherent line width of the sample were halved, about 0.15 mm/sec. The magnitude of the chemical shifts cannot be interpreted.[67]

Vibrational Spectra. Maxima in the vibrational spectra and their origins in the following trifluoromethyl dithiolene compounds are listed in Table V. Correlations were made by inspection with the related bands placed on the same row. The far-infrared and Raman spectra of the model compound are shown in Figure 8.[68–74]

A concentrated sample of I in KBr did not exhibit any peaks in the region typical for S–H stretching frequencies in thiols (2250–2600 cm^{-1}) even though hydrogen is present.

Among the compounds listed in Table V there are three peaks which are unique to I; they appear at 1322, 667, and 372 cm^{-1}. Similar peaks appear at approximately 1330 cm^{-1} in two octahedrally coordinated monomeric iron tris-NMT complexes[45] and in a compound characterized by Balch[71] as $[Fe_3S_2(S_2C_4F_6)_4]$ which also has a peak at 662 cm^{-1}.[75] The complexes containing MNT have normal modes and electronic structures differing from the ligands with trifluoromethyl substituents and also contain tetraphenylphos-

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(68) T. Birchall and N. N. Greenwood, *J. Chem. Soc. A*, 286 (1969).

(69) J. L. K. F. de Vries, J. M. Trooster, and E. de Boer, *Inorg. Chem.*, **10**, 81 (1971).

(70) R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Soc. A*, 797 (1971).

(71) A. L. Balch, *J. Amer. Chem. Soc.*, **91**, 6963 (1969).

(72) R. Rickards, C. E. Johnson, and H. A. O. Hill, *J. Chem. Soc. A*, 1755 (1971).

(73) D. J. Vaughan and M. S. Ridout, *J. Inorg. Nucl. Chem.*, **33**, 741 (1971).

(74) A. A. Temperley and H. W. Lefevre, *J. Phys. Chem. Solids*, **27**, 85 (1966).

(75) For the tris-MNT complexes, the lowest energy reported was 700 cm^{-1}. For Balch's the 662-cm^{-1} band was the lowest reported. Apart from the formula and infrared and Mössbauer spectrum, this triiron complex was not further characterized.

phorium cations; both of these properties lessen the clarity of the origin of apparently equivalent peaks.

The far-infrared (650–200 cm^{-1}) spectra presented in Table V seem to provide the only data in this region for iron and cobalt dithiolenes. Hopefully future workers will report far-infrared spectra of related compounds and thus increase confidence in the correlations in this range.

Because of improved data on ligand modes and the Raman activity of the 708-cm^{-1} band of the ligand, the assignments of Adams and Cornell[76] have been slightly modified and extended. The full normal coordinate analysis of the bis(dimethyldithiolene)nickel compound[77] and that on F_3CSF_5[78] (*cf.* ref 79) were of value in preparing Table V.[80,81] Carbon–sulfur single bond frequencies usually have been assigned between 750 and about 600 cm^{-1} but may be lower as in F_3CSF_5 (324 cm^{-1}); double bonded C=S vibrations are expected in the range 1050–1200. Since full double bonding does not occur because of the metal coordination, "unperturbed" carbon–sulfur vibrations and mixed modes involving CF_3 motions can be expected to appear below about 1000 cm^{-1}. The region between 300 and 500 cm^{-1} contains the iron–sulfur stretching modes. Among the vibrational modes of the compounds reported here, the only band in this region that seems to be sensitive to changes in the electronic structure is that corresponding to the 439-cm^{-1} peak in the spectrum of I. Its position is similar to that in the cobalt complex.

A correspondence may be drawn between the band at 372 cm^{-1} in the spectrum of I and similar bands of the nickel complexes. There is no corresponding band in the square-pyramidal dimeric complexes. A similar relationship occurs in the C–F stretching region. An important difference in localization of the π electrons occurs between the planar monomeric complexes and the dimers. As is well documented,[82] the planarity of the nickel complexes allows the π cloud to be delocalized over the ligands and the metal. In contrast, the metal atoms in the dimers lie about 0.4 Å out of the ligand plane[56] precluding delocalization onto the metal to any great extent. From these factors it appears that the ligands are not identical, and one of them may form a planar iron–ligand moiety.

A fully double bonded carbon–carbon vibration frequency is usually assigned to be about 1600 cm^{-1}, and fluorine substitution nearby raises this value. Thus, with the carbon–carbon vibrations averaging around 1500 cm^{-1} in I, there is not a full double bond in the carbon–carbon system in agreement with the conclusion drawn from the ligand electronic transition energies.

The single most valuable piece of information that the infrared spectrum of I can give is the confirmation of the presence or absence of a structure Fe-S-Fe. Since only frequencies for iron atoms singly bridged by oxygen have been reported previously in the literature, the behavior of the possible sulfur bridged system must be extrapolated from that body of data.

The vibration which would be observed in the infrared is the antisymmetric stretch analogous to that exhibited by a linear system such as CO_2. In such linear triatomic systems this is designated the ν_3 mode, and this notation persists into the metal systems. The relation between the masses and force constants for ν_3 of the simple triatomic system is given by

$$\nu_3 = \frac{1}{2\pi}\left[\frac{2M + m}{mM}k\right]^{1/2}$$

where M is the metal mass, m is the central atom mass, and k is the force constant. This expression is accepted as valid for the bridged metal system assuming that the M–A–M group is not coupled to the rest of the molecule at its ν_3 frequency. From analyses of metal acetylacetonates and dithioacetylacetonates the ratios of force constants for M–S and M–O stretches ($k_{\mathrm{M-S}}/k_{\mathrm{M-O}}$) are found to vary from about 0.95 to 0.60.[83] It follows that the extrapolated M–S frequencies will be the upper limit assuming constant k in the above expression. More probably the frequencies will be 10–20% lower.

The simplified expression for the ratios of the ν_3 vibration between oxygen and sulfur bridges is given by

$$\frac{\nu_3(\text{oxygen})}{\nu_3(\text{sulfur})} = \left[\frac{2M + m_{\mathrm{ox}}m_{\mathrm{s}}}{2M + m_{\mathrm{s}}m_{\mathrm{ox}}}\right]^{1/2}$$

Khedekar and coworkers[84] found that a number of linear iron–oxygen–iron 1,10-phenanthroline complexes exhibited infrared spectra with a "strong broad band" in the range 820–840 cm^{-1} which they attributed to the ν_3 stretch. The compound $K_4[Ru_2OCl_{10}]\cdot H_2O$ has a similar band at 888 cm^{-1} which was substantiated by ^{18}O substitution.[85] This system has "considerable" double bond character as deduced from the X-ray structure data.[86] Griffith found bands between 845 and 860 cm^{-1} for six compounds similar to the ruthenium one above which contain ruthenium, rhenium, osmium, and molybdenum.[87] There is no appreciable difference in the ν_3 frequencies even though rhenium and osmium have about twice the masses of molybdenum and ruthenium. Using the masses for the appropriate metals in the expression for the ratios of ν_3's, the range for ν_3 of Fe–S–Fe extrapolated from the iron–oxygen data is 615–630 cm^{-1}. Since different metals do not seem to cause large changes in frequency, the conclusion from these data is that the ν_3 vibration for a linear Fe–S–Fe system will occur in the range 600–650 cm^{-1}. With 15% reduction in the force constant, the above values become 565–580 cm^{-1}.

For singly bonded iron–sulfur minerals, the values of the force constants, range from 1.54 to 1.87 mdyn/Å.[88] From these values, ν_3 is calculated to be in the range 457–505 cm^{-1}. The full possible range for the ν_3 vibration can be taken as 450–640 cm^{-1}. Comparing the data for $(FeL_2)_2$ and the cobalt analog with those of the model compound, we see that there are no new bands in the region 450–650 cm^{-1} which would be from

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(76) D. M. Adams and J. B. Cornell, *J. Chem. Soc. A*, 1299 (1968).

(77) O. Siimann and J. Fresco, *Inorg. Chem.*, **10**, 297 (1971).

(78) J. E. Griffiths, *Spectrochim. Acta, Part A*, **23**, 2145 (1967).

(79) P. R. McGee, F. F. Cleveland, A. G. Meister, and C. E. Decker, *J. Chem. Phys.*, **21**, 242 (1953).

(80) R. D. Schmitt, R. M. Wing, and A. H. Maki, *J. Amer. Chem. Soc.*, **91**, 4394 (1969).

(81) R. Wing and R. C. Schlupp, *Inorg. Chem.*, in press.

(82) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).

(83) O. Siimann and J. Fresco, *Inorg. Chem.*, 8, 1846 (1969).

(84) A. V. Khedekar, J. Lewis, F. E. Mabbs, and H. Weigold, *J. Chem. Soc. A*, 1561 (1967).

(85) A. H. Gillieson in "XV Colloquium Spectroscopicum Internationale," Adam Hilger, Ltd., London, 1969, p 193 ff.

(86) J. C. Morrow, *Acta Crystallogr.*, **15**, 851 (1962).

(87) W. P. Griffith, *J. Chem. Soc. A*, 211 (1969).

(88) This compares with k = 1.40–1.65 mdyn/Å for Ni-S bonds in the planar nickel dithiolenes.

the ν_3 vibration of a linear Fe–S–Fe system. Here the required iron–iron distance would be about 4.4 Å[89,90] necessitating an approximately single-bonded iron–sulfur system which would have the ν_3 vibration in the lower part of the 450–650-cm^{-1} range. Not only are there no new bands in the spectrum of the model compound, but the equivalent bands in the region do not change frequency. This is good evidence that there is no mixing of vibrations in this range which might alter the frequencies expected from calculations assuming an "isolated" chromophore.

Conclusions

In this section we shall review briefly the picture of the analog compound thus far ascertained. Each characteristic is followed by the experimental method(s) from which it was inferred. In the solid state I is a triiron compound (elementary analysis) which, in disulfide containing solution, is converted, reversibly, into a diiron species (epr, susceptibility, solution molecular weight). The iron atoms appear to be equivalent in both solid and solution (Mössbauer) with octahedral coordination in both states (Mössbauer, electronic spectrum). The irons are doubly bridged by sulfur forming an approximately square-planar heterocyclic system (vibrational spectrum). The magnetic properties of the diiron complex require that the irons differ by one in formal oxidation number (susceptibility, epr). The interaction between the irons can be characterized by a number of sets of possible spin states with coupling that can be described using the interaction Hamiltonian $\mathcal{H} = -2JS_1 \cdot S_2$ with $J = -95$ cm^{-1} (susceptibility). This coupling may arise from an interaction either predominately through the bridging sulfurs or predominately through the weak inter-iron bond which is inferred from the iron–iron intramolecular distance (preliminary X-ray analysis). From this coupling, the ground state of the complex appears as a spin $^1/_2$ system (epr, solution susceptibility). This ground state exhibits epr g values of $g_\perp = 1.98$ and $g_\parallel = 2.01$. The unpaired electron resides almost exclusively on the iron–sulfur center of the molecule (endor, epr); the carbon–fluorine part of the dithiolene ligands is apparently isolated from it. There is a hydrogen in the molecule which acts as an anion allowing the complex to be soluble in nonpolar solvents while having irons in different formal oxidation states (empirical formula, pulsed nmr). The instability of the complex to Lewis bases parallels the chemistry of hydrogen polysulfides.[89]

In closing, we shall briefly summarize the properties of the model compared with those of the 2Fe–S* proteins. First, of course, is the similarity in epr spectra; the spectrum which results from a spin $^1/_2$ system containing two irons has $g_{av} > g_e$ with the anisotropy in the correct "sense." It is the only analog for adrenodoxin and putidaredoxin which have essentially axial spectra. The chromophores for all appear to be located on an iron–sulfur site. The antiferromagnetic interaction is within the same range as the spinach protein, but is much smaller than that of adrenodoxin to which the g values seem to be more closely related. In addition the visible and near-infrared spectra are in exceptional agreement. There is less correspondence in other aspects. In the model compound there are more than nine sulfurs coordinated to the two irons in contrast to six or seven believed for the proteins. The spin state and formal oxidation numbers of the irons probably differ from those of the proteins. Further, the circular dichroism properties and Mössbauer parameters of the model compound differ significantly from those of the proteins. The conclusion that must be reached is that even though the model compound exhibits many chemical and physical properties which match those of the proteins, fundamental differences do exist, and while the chemistry of this compound is interesting in its own right, the value as a model compound for the iron–sulfur proteins is limited.

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(89) J. H. Walton and L. B. Parsons, *J. Amer. Chem. Soc.*, 43, 2539 (1921).

(90) As indicated in the Experimental Section the model compound appears to crystallize in one of the enantiomorphic space groups $P4_332$ or $P4_132$ and the lattice parameters have been determined. The preliminary analysis has shown that the iron–iron separation is 2.9–3.0 Å which is at the long end of bonding distances. The Fe–S distance are about 2.2 Å, typical of singly bonded FeS. Because there is no evidence of the Fe–S–Fe linear structure in the infrared spectra, we conclude that the iron atoms are doubly bridged by two sulfurs forming a square-planar system.