Electron-Transfer Series Involving Sulfur-Rich, Polynuclear Iron Dithiolene Complexes

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Abstract: Synthetic, polarographic, and other physicochemical studies of several polynuclear dithiolene complexes have demonstrated the ability of these systems to undergo electron-transfer reactions without a breakdown of the polynuclear unit. Treatment of $(CF_3)_2C_2S_2Fe_2(CO)_6$ or $Ph_2C_2S_2Fe_2(CO)_6$ with sulfur in boiling xylene produces the terminal oxidized member ($z = 0$) of a five-membered ($z = 0, -1, -2, -3$, and -4) electron-transfer related series based on the $[Fe_4S_4(S_2C_2R_2)_4]^z$ unit (R = Ph, CF_3). In addition the reduced members with $z = -1$ (R = CF_3, Ph) and $z = -2$ (R = CF_3) have been isolated. The conductivity, magnetic properties, and electrochemistry of these species are consistent with formulation of the fundamental unit involved in the electron-transfer reactions as a quadrimer, although it has been impossible to obtain direct molecular weight data for the neutral species. The reactions of the quadrinuclear unit with a variety of Lewis bases is described. Small amounts of $[Fe_3S_2(S_2C_2\{CF_3\}_2)_4]$ have also been isolated from the reaction of $(CF_3)_2C_2S_2Fe_2(CO)_6$ and sulfur. This trinuclear complex undergoes polarographic reduction to form $[Fe_3S_2(S_2C_2\{CF_3\}_2)_3]^z$ ($z = -1$ and -2); the monoanion has been generated but not isolated. Similarities between these synthetic, sulfur-rich complexes and the biologically important ferredoxins are pointed out. The trimers $[(CO)_3Co_3(S_2C_2\{CF_3\}_2)_3]$ and $[(NO)_3Fe_3(S_2C_2\{CF_3\}_2)_3]$, which have been previously characterized, are capable of being reduced polarographically to a monoanion and to a monoanion and a dianion, respectively.

The existence of bis- or tris-dithiolene complexes of many transition metals and the ability of these complexes to participate, intact, in electron-exchange reactions has been documented.[1] Iron and cobalt, and probably their heavy congeners as well, are differentiated from the other transition metals by their ability to form both bis and tris species. However, the propensity for forming tris species appears to be limited to the cyano-substituted complexes in the case of cobalt and iron. The three-membered series ($z = -1, -2$, and -3) based on the $[Fe(S\text{-}S,CN)_3]^z$[2] unit has been characterized electrochemically, and the members with $z = -2$ and -3 have been isolated.[3,4] Crystallographic examination of $[Ph_4As]_2[Fe(S\text{-}S,CN)_3]$ has shown that this anion has the most nearly octahedral geometry of all the tris-dithiolene complexes that have been examined to date.[5]

Dimerization is an important feature of the chemistry of the bis-dithiolene complexes of iron and cobalt.[6] The properties of these complexes are best systematized by considering the four-membered electron-transfer series **1**–**4**. X-Ray crystallographic studies of several representative complexes have revealed that the dimerization occurs in the manner shown in Figure 1. This dimeric unit, which has considerable stability, is believed to persist through the three most oxidized states **1**, **2**, and **3**. Dimerization of this sort is of considerably less importance in the chemistry of the planar bis-dithiolene complexes of nickel, copper, and their heavier congeners.

$[M_2(S\text{-}S,R)_4]$ **1** $[M_2(S\text{-}S,R)_4]^-$ **2**

$[M_2(S\text{-}S,R)_4]^{2-} \rightleftarrows 2[M(S\text{-}S,R)_2]^-$ **3** $[M(S\text{-}S,R)_2]^{2-}$ **4**

Treatment of the iron and cobalt dimers **1**–**3** with a variety of Lewis bases including phosphines, phosphites,[7-10] arsines, stibines,[7,9] pyridine, cyanide, azide,[9] and nitrous oxide[11] produces the apparently five-coordinate $[\text{base–}M(S\text{-}S,R)_2]^z$, by rapid cleavage reactions. Bidentate four-electron donors such as α,α'-bipyridyl and *o*-phenanthroline also cleave the dimers to form six-coordinate adducts.[9,10] Both the five- and the six-coordinate adducts are able to undergo electron-transfer reactions.

Schrauzer and coworkers have prepared a sulfur-rich iron dithiolene, $[FeS(S\text{-}S,Ph)]_n$, by three independent routes: (1) the reaction of an iron carbonyl or metallic iron with sulfur and diphenylacetylene; (2) the thermal degradation of $Fe(S\text{-}S,Ph)_4$; and (3) the reaction of $(S\text{-}S,Ph)Fe_2(CO)_6$ with sulfur.[8] Herein we extend the studies on sulfur-rich iron dithiolenes and examine the electron-transfer behavior of some other polynuclear dithiolene complexes. This work demonstrates the ability of these polynuclear species to undergo electron-transfer reactions without rupture of the polynuclear unit.

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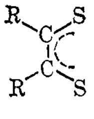
[1] Several reviews are available: G. N. Schrauzer, *Transition Metal Chem.*, 4, 299 (1968); H. B. Gray, *ibid.*, 1, 1 (1965); J. A. McCleverty, *Progr. Inorg. Chem.*, 10, 49 (1968).

[2] The symbol (S–S,R) is used to represent the dithiolene ligand



In the sulfur-rich species the additional sulfur is indicated as S.

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The chemical behavior of sulfur-rich iron complexes is of particular interest in view of the current studies of certain nonheme iron proteins which contain "acid-labile" or "inorganic" sulfide.[12,13] These proteins upon acidification release, along with iron, hydrogen sulfide which is not derived from the cystine residues present in the peptide chain. Reconstitution of the apoprotein requires, in addition to iron, a source of sulfide irons. At present the mode of bonding between the apoprotein and the iron and inorganic sulfide has not been elucidated. From structural studies of small, synthetic molecules, three types of coordination involving iron and free sulfur have been characterized. These include: (1) complexes with a sulfur atom bridging three iron atoms, $Cs[Fe_4S_3(NO)_7]\cdot 2H_2O$[14] and $(\pi\text{-}C_5H_5)_4Fe_4S_4$;[15] (2) complexes containing a disulfide group which bridges iron atoms, $S_2Fe_2(CO)_6$[16,17] and $S_2Fe_3(CO)_9$;[17,18] and (3) a complex containing the C–S–S–Fe group.[19]

Experimental Section

Preparation of Compounds. $(S\text{–}S,CF_3)Fe_2(CO)_6$,[20] $(S\text{–}S,CF_3)_3Co_3(CO)_3$,[21] and $(S\text{–}S,CF_3)_3Fe_3(NO)_3$[22] were prepared according to published methods.

$Fe_4S_4(S\text{–}S,CF_3)_4$. A mixture of 5.0 g of $(S\text{–}S,CF_3)Fe_2(CO)_6$, 0.8 g of sulfur, and 180 ml of xylene was refluxed for 30 min. The hot violet solution was carefully filtered to remove a black pyrophoric residue. The filtrate, protected from moisture, was allowed to stand for 12 hr at 0°. The black crystals which formed were collected by filtration, washed with dry dichloromethane, and dried under vacuum at 148° for 48 hr, yield 2.1 g.

Anal. Calcd for $C_{16}F_{24}S_{12}Fe_4$: C, 15.29; H, 0.00; F, 36.29; S, 30.62. Found: C, 15.51; H, 0.00; F, 36.01; S, 30.83.

For the preparation of $[Fe_4S_4(S\text{–}S,Ph)_4]$ an analogous procedure (which is a slight modification of the original preparation described by Schrauzer, *et al.*[8]) was used followed by recovery of the desired complex by soxhlet extraction of the xylene-insoluble residue into carbon disulfide.

$[Ph_4As]_2[Fe_4S_4(S\text{–}S,CF_3)_4]$. $[Fe_4S_4(S\text{–}S,CF_3)_4$ (1.4 g) was dissolved in 10 ml of dimethyl sulfoxide. The burgundy colored solution was diluted with 60 ml of ethanol and filtered. Addition of 1.0 g of tetraphenylarsonium chloride dissolved in 10 ml of ethanol caused the precipitation of fine black crystals. These crystals were collected by filtration, washed with ethanol and ether, recrystallized twice from acetone–isobutyl alcohol, and vacuum dried, yield 1.1 g; above 230° the complex gradually decomposes.

Anal. Calcd for $C_{64}H_{40}As_2F_{24}S_{12}Fe_4$: C, 38.00; H, 1.99; S, 19.02. Found: C, 37.89; H, 2.32; S, 19.23.

$[Bu_4N]_2[Fe_4S_4(S\text{–}S,CF_3)_4]$. This compound was prepared by the same procedure as that used for the analogous tetraphenylarsonium salt; mp 174–176°.

Anal. Calcd for $C_{48}H_{72}F_{24}N_2S_{12}Fe_4$: C, 33.11; H, 4.17; N, 1.61; S, 22.10; F, 26.19. Found: C, 33.30; H, 4.20; N, 1.61; S, 21.81; F, 26.11.

$[Ph_4As][Fe_4S_4(S\text{–}S,CF_3)_4]$. A mixture of 0.542 g (0.432 mmol) of $Fe_4S_4(S\text{–}S,CF_3)_4$ and 0.865 g (0.427 mmol) of $[Ph_4As]_2[Fe_4S_4(S\text{–}S,CF_3)_4]$ in 100 ml of dry dichloromethane was refluxed with stirring for 6 hr. After allowing the brown solution to cool, the crystalline product was collected and vacuum dried. Purification was effected by soxhlet extraction into dry dichloromethane. Above 230° for the complex gradually decomposes.

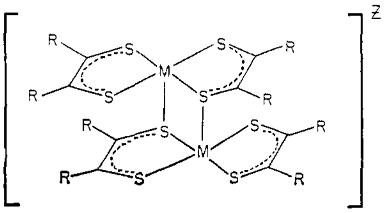

Figure 1. Idealized representation of the structure of dimeric dithiolene complexes of iron and cobalt.

Anal. Calcd for $C_{40}H_{20}AsF_{24}S_{12}Fe_4$: C, 29.30; H, 1.23; F, 27.81; S, 23.47. Found: C, 29.14; H, 1.46; F, 27.64; S, 23.24.

$Fe_3S_2(S\text{–}S,CF_3)_4$. This complex has been isolated in low yields from the xylene solution obtained from the reaction of $(S\text{–}S,CF_3)Fe_2(CO)_6$ and sulfur after the removal of the less soluble $[Fe_4S_4(S\text{–}S,CF_3)_4]$. The solvent of the remaining green xylene solutions from three preparations of $[Fe_4S_4(S\text{–}S,CF_3)_4]$ (on the scale given above) was removed at reduced pressure using a rotary evaporator. The oily solid which remained was dissolved in 40 ml of dichloromethane and filtered. Twenty milliliters of heptane was added, and the solution was boiled until its volume was *ca.* 15 ml. This solution, protected from moisture, was stored at 0° for 48 hr. The black crystalline product was collected and vacuum dried. Further purification was effected by sublimation at 145° (1 mm) for 24 hr onto an air-cooled probe. In this way 0.3–0.5 g of product was obtained.

Anal. Calcd for $C_{16}F_{24}S_{10}Fe_3$: C, 16.91; H, 0.00; F, 40.13; S, 28.22. Found: C, 16.93; H, 0.10; F, 39.92; S, 27.85.

$[Ph_4As][Fe_4S_4(S\text{–}S,Ph)_4]$. Hydrazine hydrate (2.5 ml) was added to a stirred slurry of 1.9 g of $[Fe_4S_4(S\text{–}S,Ph)_4]$ in 50 ml of oxygen-free methanol. The solid slowly dissolved to give a violet solution characteristic of the monoanion $[Fe_4S_4(S\text{–}S,Ph)_4]^-$. Further reduction inevitably occurred with the production of red-brown color which was probably caused by the dianion. The solution was filtered under a nitrogen atmosphere and a solution of 2.5 g of tetraphenylarsonium chloride in 30 ml of oxygen-free methanol was added. The precipitated complex (largely in the form of the dianion) was collected and vacuum dried. The solid was dissolved in dichloromethane and the solution was allowed to oxidize in the air. The very slightly soluble $[Ph_4As][Fe_4S_4(S\text{–}S,Ph)_4]$ crystallized from the solution. Purification was achieved by soxhlet extraction of the salt into dichloromethane under a nitrogen atmosphere since the monoanion is susceptible to further oxidation by air to give the neutral complex.

Anal. Calcd for $C_{80}H_{60}AsS_{12}Fe_4$: C, 56.37; H, 3.55; S, 22.57; Fe, 13.11. Found: C, 56.57; H, 3.53; S, 22.45; Fe, 13.07.

Reaction of $[Fe_4S_4(S\text{–}S,Ph)_4]$ with Triphenylphosphine. A solution of 0.66 g (0.50 mmol) of $[Fe_4S_4(S\text{–}S,Ph)_4]$ and 0.55 g (2.1 mmol) of triphenylphosphine in 60 ml of benzene was heated under reflux for 9 hr. The green solution was filtered to remove a dark residue. Benzene was stripped from the filtrate, and the residual green oil was washed with six 30-ml portions of hot methanol. On concentrating the methanol washes, 0.25 g of a white crystalline solid, which was identified as triphenylphosphine sulfide (by melting point and infrared spectrum), was obtained. The green-black solid which remained after the washing was recrystallized from dichloromethane–methanol. The black crystalline material (yield 0.35 g, 87% based on the available dithiolene groups) was identified as $Ph_3PFe(S\text{–}S,Ph)_2$ by comparison (melting point, infrared spectrum, and polarography) with an authentic sample.

Reaction of $[Ph_4As]_2[Fe_4S_4(S\text{–}S,CF_3)_4]$ with Triphenylphosphine. A solution of 1.00 g (0.45 mmol) of $[Ph_4As]_2[Fe_4S_4(S\text{–}S,CF_3)_4]$ and 0.24 g (0.92 mmol) of triphenylphosphine in 60 ml of dichloromethane was heated under reflux for 3 hr. The solution was filtered to remove a small quantity of brown pyrophoric residue. The dichloromethane was stripped off and the residue was extracted with six 30-ml portions of pentane. From the pentane solutions after evaporation, 0.15 g of triphenylphosphine sulfide was recovered. The dark residue was recrystallized from acetone–isobutyl alcohol to yield 0.7 g (87%) of $[Ph_4As]_2[Fe_2(S\text{–}S,CF_3)_4]$, identified by comparison with an authentic sample.

Physical Measurements. Polarographic and magnetic susceptibility measurements (Faraday technique for solids, nmr tech-

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nique for solutions) were made as described previously.[7] Mass spectra were obtained using direct insertion techniques with source temperatures between 160 and 240° and 70 eV ionizing electrons with a Picker MS-9 spectrometer. Infrared spectra were recorded on a Perkin-Elmer 421 spectrometer. Electronic spectra were recorded on a Cary 14 spectrometer. Conductivities were measured with a Serfass conductivity bridge. A Norelco X-ray machine with Cu Kα radiation was used for measuring X-ray powder patterns. The Mössbauer spectra were obtained by Professor W. Kündig of the Department of Physics, University of California, Los Angeles, with a conventional Mössbauer spectrometer.

Results

Characterization of the $[Fe_4S_4(S-S,R)_4]^z$ Series. Treatment of $(S-S,R)Fe_2(CO)_6$ (R = Ph or CF_3) or $(S-S,CF_3)Fe(CO)_3$ with sulfur in the refluxing xylene yields, after the appropriate purification, $[Fe_4S_4(S-S,R)_4]$. Attempts to prepare analogous compounds by reacting $(4-CH_3C_6H_3S_2)Fe_2(CO)_6$ or $(C_6H_5S)_2Fe_2(CO)_6$ with sulfur have produced only intractable solids. Physical data which serve to characterize these and other new complexes are presented in Tables I–III.

Table I. Infrared Spectra[a]

$[Fe_4S_4(S-S,CF_3)_4]$	1451 s, 1373 w, 1257 s, 1215 vs, 1180 sh, 1160 vs, 1080 sh, 900 s, 848 w, 728 s, 691 s
$[Ph_4As][Fe_4S_4(S-S,CF_3)_4]$	1570 w, 1472 m, 1436 s, 1258 s, 1206 vs, 1140 vs, 1072 w, 992 w, 905 w, 842 m, 740 s, 722 s, 690 s
$[Ph_4As]_2[Fe_4S_4(S-S,CF_3)_4]$	3050 vw, 1580 w, 1502 w, 1480 w, 1440 m, 1434 s, 1380 w, 1332 w, 1248 s, 1211 vs, 1180 sh, 1165 s, 1126 s, 1105 sh, 1077 w, 1018 w, 991 w, 840 w, 735 s, 718 m, 687 s
$[Bu_4N]_2[Fe_4S_4(S-S,CF_3)_4]$	2953 m, 2943 w, 2866 w, 1512 w, 1476 s, 1466 m, 1415 w, 1379 m, 1350 m, 1350 w, 1246 sh, 1208 vs, 1160 vs, 1130 vs, 873 w, 841 m, 733 w, 718 s, 688 s
$[Ph_4As][Fe_4S_4(S-S,Ph)_4]$	3050 w, 1585 w, 1565 w, 1475 w, 1441 s, 1406 s, 1168 sh, 1150 s, 1070 w, 1020 m, 990 w, 904 w, 871 s, 838 sh, 757 w, 743 s, 734 sh, 690 s, 636 w, 608 w
$[Fe_3S_2(S-S,CF_3)_4]$	1445 s, 1366 m, 1326 s, 1254 sh, 1214 vs, 1165 vs, 1110 s, 923 m, 848 s, 726 s, 701 s, 690 s, 674 s, 662 s

[a] Absorption maxima in cm^{-1}. Measured in KBr disks.

Table II. X-Ray Diffraction Data for Complexes of the $Fe_4S_4(S-S,CF_3)_4]^z$ Series

Complex	*d*-Spacings, Å, of the prominent peaks
$[Fe_4S_4(S-S,CF_3)_4]$	10.76 vs, 7.82 m, 6.75 m, 5.46 m, 5.12 s, 4.82 s, 4.59 vs, 4.41 w, 4.18 w, 4.11 w, 3.89 w, 3.81 w, 3.64 w, 3.27 w
$[Ph_4As][Fe_4S_4(S-S,CF_3)_4]$	10.51, s, 7.48 m, 5.66 w, 5.27 w, 5.12 vs, 4.71 w, 4.59 vs, 4.50 m, 4.22 w, 4.14 vw, 3.92 w, 3.80 w, 3.43 vw, 3.30 w
$[Ph_4As]_2[Fe_4S_4(S-S,CF_3)_4]$	11.84 s, 10.90 s, 9.19 m, 8.74 m, 7.07 m, 6.75 m, 6.50 s, 6.31 m, 5.50 s, 5.37 s, 5.09 m, 4.95 s, 4.64 w, 4.55 w, 4.26 w, 4.18 w, 4.08 w, 3.98 w, 3.43 m, 3.16 m, 3.05 m, 3.01 w, 2.97 m

The low solubility and low volatility of these complexes have precluded a direct determination of their molecular weights. Both complexes are diamagnetic, but this information does not aid in ascertaining the correct degree of molecular complexity of these species.

These complexes constitute the terminal oxidized members of electron-transfer related series. Investigation of the various electron-transfer related species indicates that the fundamental unit involved in the electron transfer is the quadrimer $[Fe_4S_4(S-S,R)_4]^z$. Other polymeric units may be important to the chemistry of certain of these complexes, but in all cases examined there is no evidence of more than one species contributing to the solution properties of a particular oxidation state. Consequently we adopt the simplest convention and formulate all members of the two electron-transfer series as quadrimers. The following information serves to substantiate this formulation.

Polarography of $[Fe_4S_4(S-S,CF_3)_4]$ in dichloromethane solution (Table I) reveals four successive cathodic waves with approximately equal diffusion currents. If it is assumed that each polarographic wave involves one electron, then the magnitude of the diffusion currents is consistent only with electron transfer between quadrimeric units.

Reduction of the neutral complex may be achieved by dissolution in basic solvents.[23–25] From the burgundy dimethyl sulfoxide solution the ion $[Fe_4S_4(S-S,CF_3)_4]^{2-}$ has been isolated as both the tetraphenylarsonium and the tetrabutylammonium salts. Polarography of this dianion reveals two anodic and two cathodic waves at nearly the same voltages as found for the neutral complex.[26] This information establishes the position of $[Fe_4S_4(S-S,CF_3)_4]^{2-}$ in the electron-transfer series and indicates that an intermediate complex, a quadrimeric monoanion, should exist. Reaction of $[Fe_4S_4(S-S,CF_3)_4]$ with $[Ph_4As]_2[Fe_4S_4(S-S,CF_3)_4]$ produces the anticipated $[Ph_4As][Fe_4S_4(S-S,CF_3)_4]$. The polarography of this species is entirely consistent with its formulation. The infrared data in Table I and the X-ray powder pattern data in Table II substantiates the contention that three distinct members of the electron-transfer series have been prepared and isolated. Because of their presumed oxygen sensitivity, no attempt has been made to isolate the -3 and -4 members of this electron-transfer series.

The physical properties of the two anions are consistent with their formulation. The monoanion is paramagnetic and exhibits a strong, broad esr signal centered about $g = 2.02$ in the solid at 100°K. For the dianion the quadrimeric formulation $[Fe_4S_4(S-S,CF_3)_4]^{2-}$ is established in preference to the alternate dimeric formulation $[Fe_2S_2(S-S,CF_3)_2]^-$ by conductivity and magnetic measurements. The conductivity (Figure 2) of the tetrabutylammonium salt indicates that, over the concentration range 5×10^{-4}–10^{-3} M, it behaves as a 2:1 electrolyte in acetonitrite solution.[27] The salt is diamagnetic in acetone solution as well as in the solid. Whereas the dimeric formulation requires a paramagnetic anion, the quadrimeric formulation is consistent with the magnetic data.

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(23) This is not a unique reaction. Basic solvents are known to reduce neutral dithiolene complexes of the types $M(S-S,CF_3)_2$,[24] $M_2(S-S,CF_3)_4$,[24] and $M(S-S,CF_3)_3$,[25] but the fate of the reducing agents has not been ascertained.

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Table III. Polarographic Behavior of Dithiolene Complexes in Dichloromethane Solution[a]

Complex	$0 \rightleftharpoons -1$		$-1 \rightleftharpoons -2$		$-2 \rightleftharpoons -3$		$-3 \rightleftharpoons -4$	
	$E_{1/2}$, V	i_d/C[b]	$E_{1/2}$, V	i_d/C[b]	$E_{1/2}$, V	i_d/C[b]	$E_{1/2}$, V	i_d/C[b]
$[Fe_4S_4(S\text{-}S,CF_3)_4]$	+0.98	+20	+0.54	+18	−0.10		−0.7	
$[Ph_4As][Fe_4S_4(S\text{-}S,CF_3)_4]$	+1.00	−19	+0.54	+19	−0.08	+18	−0.61	+16
$[Bu_4N]_2[Fe_4S_4(S\text{-}S,CF_3)_4]$	+1.02	−18	+0.57	−17	−0.05	+16	−0.60	+16
$[Fe_4S_4(S\text{-}S,Ph)_4]$[d]	+0.13	+	−0.16	+	−0.76	+	*c*	
$[Ph_4As][Fe_4S_4(S\text{-}S,Ph)_4]$[d]	+0.15	−	−0.15	+	−0.71	+	*c*	
$[Fe_3S_2(S\text{-}S,CF_3)_4]$	+0.88	+21	+0.32	+20	*c*		*c*	
$[Fe_3(NO)_3(S\text{-}S,CF_3)_3]$	+0.45	+19	−0.40	+21	*c*		*c*	
$[Co_3(CO)_3(S\text{-}S,CF_3)_3]$	+0.54	+22						
$[Bu_4N]_2[Fe_2(S\text{-}S,CN)_4]$[e]			+1.06	−17	*f*			
$[Ph_4As]_2[Fe(S\text{-}S,CN)_3]$			+0.89	−18	−0.10	+18		
$[Bu_4N]_2[Fe_2(S\text{-}S,CF_3)_4]$[e]	+1.27	−17	+0.71	−16	*f*			

[a] Employing a rotating platinum working electrode, 0.10 *M* $(Bu_4N)_4PF_6$ as supporting electrolyte, and the modified reference electrode described in ref 7. [b] μA/m*M*. Concentrations calculated on the basis of the formulas given in the first column. [c] No further reductions observed before solvent breakdown at −1.6 V. [d] Low solubility precluded accurate determination of i_d/C; relative heights of the three waves 1:1:1. [e] Data from ref 6. [f] Further reduction leads to monomer; see ref 6.

Similar but less extensive studies have been made on $[Fe_4S_4(S\text{-}S,Ph)_4]$. In dichloromethane solution this complex undergoes three polarographic reductions with equal diffusion currents. As is usually found with dithiolene complexes, decreasing the electronegativity of R decreases the ease of reduction of a particular oxidation state. Because of the low solubility of $[Fe_4S_4(S\text{-}S,Ph)_4]$ it has been impossible to prepare solutions of known concentration of complex and hence evaluate the number of electrons involved in the reduction waves. However, it has been possible to isolate the monoanion $[Fe_4S_4(S\text{-}S,Ph)_4]^-$, establish the cation–anion stoichiometry from analytical data, and show from polarographic measurements that this complex is in fact the first reduced member of the electron-transfer series. The monoanion is paramagnetic with μ_{eff} of 2.0 BM in the solid state at 27°. In addition a broad, structureless esr signal is observed at $g = 2.03$ from the solid at room temperature. These observations indicate that the basic unit involved in the electron-transfer process of the phenyl-substituted series also consists of a quadrimeric entity.[28]

The chemical stability of the quadrinuclear unit in $[Fe_4S_4(S\text{-}S,Ph)_4]$ and $[Fe_4S_4(S\text{-}S,CF_3)_4]^z$ ($z = 0, -2$) is rather considerable. Unlike the bis-dithiolene iron dimers, these quadrimers are not cleaved by triphenylarsine and triphenylstibine, although these bases do reduce $[Fe_4S_4(S\text{-}S,CF_3)_4]$ (but not $[Fe_4S_4(S\text{-}S,Ph)_4]$) to the monoanion. Triphenylphosphine causes rupture of the quadrimeric unit with the production of $[Ph_3PFe(S\text{-}S,R)_2]$ (from the neutral complexes) or $[Fe_2(S\text{-}S,CF_3)_4]^{2-}$ (from the dianion), triphenylphosphine sulfide, and a residue of low solubility which probably consists of iron and iron sulfides. This reaction may be initiated by nucleophilic attack by the phosphine on the iron sites or at sulfur. The dianion $[Fe_4S_4(S\text{-}S,CF_3)_4]^{2-}$ dissolves intact in a variety of solvents as shown by the consistency of the electronic spectrum of this complex in solution (Table IV). However with pyridine or dimethyl sulfoxide as solvent the dianion does slowly decompose to yield $[Fe_2(S\text{-}S,CF_3)_4]^{2-}$. The presence of extra sulfur in $[Fe_4S_4(S\text{-}S,CF_3)_4]^{2-}$ is clearly demonstrated by its reactions with acid and mercuric ion. Acidification of warm solutions of $[Fe_4S_4(S\text{-}S,CF_3)_4]^{2-}$ in acetonitrile with aqueous hydrochloric acid liberates considerably more hydrogen sulfide than the trace of hydrogen sulfide which is liberated by acid from $[Fe_2(S\text{-}S,CF_3)_4]^{2-}$. Mercuric ion rapidly decolorizes acetonitrile solutions of $[Fe_4S_4(S\text{-}S,CF_3)_4]^{2-}$ and $[Fe_2(S\text{-}S,CF_3)_4]^{2-}$, but only in the former case is a black precipitate of mercuric sulfide produced.

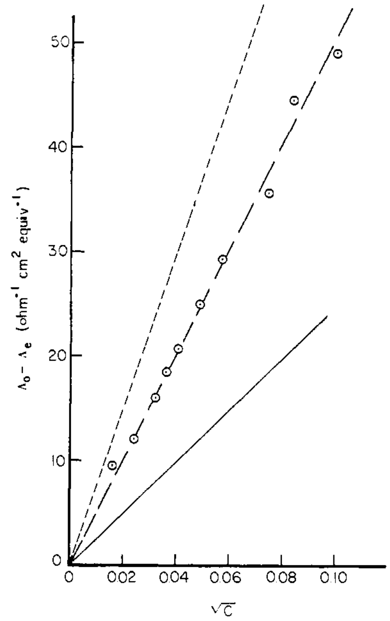

Figure 2. Conductivity data for complexes in acetonitrile solutions: - - - -, $(n\text{-}Bu_4N)_2[Ni(S\text{-}S,CN)_2]$; ——, $(n\text{-}Bu_4N)[Ni(S\text{-}S,CN)_2]$; —⊙—, $(n\text{-}Bu_4N)_2[Fe_4S_4(S\text{-}S,CF_3)_4]$.

Characterization of the $[Fe_3S_2(S\text{-}S,CF_3)_4]^z$ Series. The reaction of $(S\text{-}S,CF_3)Fe_2(CO)_6$ and sulfur also yields small quantities of $[Fe_3S_2(S\text{-}S,CF_3)_4]$ which may be separated from the more abundant $[Fe_4S_4(S\text{-}S,CF_3)_4]$ by crystallization followed by sublimation. No evidence for the existence of the analogous $[Fe_3S_2(S\text{-}S,$-

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[28] Schrauzer and coworkers have formulated the sulfur-rich species as a dimer, $Fe_2S_2(S\text{-}S,Ph)_2$.[8] The reasons for this formulation have not been specified and no evidence has been presented to substantiate it. It is reported that this species undergoes four polarographic reductions in N,N-dimethylformamide (DMF). The magnitude of the diffusion current has not been reported, but it has been implied that the diffusion currents for the four waves observed in DMF are approximately equal. The observation of an additional reduction in DMF is not unexpected since a larger cathodic potential range is available in DMF than in dichloromethane. We have been unable to measure i_d/C for this complex in DMF solution because of the low solubility. It has also been noted that the complex does decompose in this solvent.

Table IV. Electronic Spectrum of $[Fe_4S_4(S\text{–}S,CF_3)_4]^{2-}$ in Various Solvents

Solvent	Band maxima, Å (ε)			
Dichloromethane	12,100 (1,370)	7,730 (4,760)	4,950 (16,600)	4,450 (17,300)
Acetone	12,250 (1,400)	7,650 (5,030)	5,000 (16,800)	4,450 (17,500)
Acetonitrile	12,150 (1,310)	7,600 (4,360)	5,000 (15,600)	4,500 (16,000)
Dimethylformamide	12,100 (1,330)	7,750 (4,570)	5,000 (17,000)	4,500 (17,600)
Dimethyl sulfoxide	*a*	*a*	4,900 (14,500)	4,500 (15,400)
Pyridine	12,200 (1,110)	7,700 (5,100)	5,000 (16,100)	4,450 (17,200)

[a] A broad ill-defined shoulder occurs in this region.

Ph)$_4$] has been found. The composition of $[Fe_3S_2(S\text{–}S,CF_3)_4]$ has been determined by elemental analysis and observation of the parent ion in the mass spectrum (Table V). The fragmentation pattern shows features, *e.g.*, loss of F, (S–S,CF_3), and FeF_2, which are typical of complexes derived from bisperfluoromethyl-1,2-dithietene.[6,29,30] A metastable peak at *m/e* 730 may be due to overlapping of metastable peaks due to the processes $[Fe_3S_2(S\text{–}S,CF_3)_4]^+ \rightarrow [Fe_3S_2(S\text{–}S,CF_3)_3]^+ + (S\text{–}S,CF_3)$ [calcd, 729] and $[Fe_3S_2(S\text{–}S,CF_3)_3]^+ \rightarrow [Fe_2S_2(S\text{–}S,CF_3)_2(S_2C_4F_4)]^+ + FeF_2$ [calcd, 732].

Table V. Principle Metal-Containing Ions with *m/e* >500 in the Mass Spectrum of $[Fe_3S_2(S\text{–}S,CF_3)_4]$

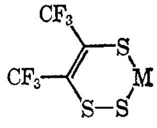
Ion	*m/e*
Parent	1136
Parent − F	1117
Parent − (S–S,CF_3)	910
Parent − (S–S,CF_3)FeF_2	816
Parent − (S–S,CF_3)FeF_3	797
Parent − S_2(S–S,CF_3)C_2F_8	734
Parent − Fe_2S_2(S–S,CF_3)F	717
Parent − (S–S,CF_3)$_2$	684
Parent − Fe(S–S,CF_3)F_{10}	664
Parent − Fe(S–S,CF_3)C_2F_{10}	640
Parent − S_2(S–S,CF_3)$_2$	620
Parent − Fe_2S_2(S–S,CF_3)$_2$	508

Polarography of $[Fe_3S_2(S\text{–}S,CF_3)_4]$ shows two cathodic waves with diffusion currents which indicate that each step involves addition of one electron to the trinuclear cluster. Because of the small quantities of $[Fe_3S_2(S\text{–}S,CF_3)_4]$ that have been isolated, we have not been able to make extensive attempts to isolate the anions whose existence is predicted by the polarography. However, it has been noted that addition of a basic solvent such as methanol to dichloromethane solutions of $[Fe_3S_2(S\text{–}S,CF_3)_4]$ results in a color change from greenish brown to a bright green; polarography of the resulting solution is identical with that of the neutral complex except that the wave at +0.88 V has become anodic rather than cathodic. It appears that the tri-iron species has undergone reduction intact and that the monoanion $[Fe_3S_2(S\text{–}S,CF_3)_4]^-$ is responsible for the polarographic behavior of the methanol-treated solution.[23]

Attempts to develop better synthetic routes to $[Fe_3S_2(S\text{–}S,CF_3)_4]$ have been unsuccessful. Refluxing an equimolar mixture of $[Fe_4S_4(S\text{–}S,CF_3)_4]$ and $[Fe_2(S\text{–}S,CF_3)_4]$ in xylene for 2 days produced only traces of $[Fe_3S_2(S\text{–}S,CF_3)_4]$. Reduction of $[Fe_4S_4(S\text{–}S,CF_3)_4]$ with $[Fe_2(S\text{–}S,CF_3)_4]^{2-}$ proceeds without exchange to give $[Fe_4S_4(S\text{–}S,CF_3)_4]^-$ and $[Fe_2(S\text{–}S,CF_3)_4]^-$.

Discussion

Speculation concerning the structure of these new sulfur-rich complexes has produced several proposals. The extra sulfur probably acts to bridge iron atoms, although incorporation of this sulfur into an expanded chelate ring such as **5** is a possibility. Oxidative sulfur-addition reactions which produce chelate ring expansion have been described for several 1,1-dithiolate complexes and dithioaryl acid complexes[31] but no comparable reactions have been reported for 1,2-dithiolate complexes. The existence of an expanded chelate ring in the new species reported herein is unlikely since formation of such units would drastically reduce the number of atoms available for coordination about iron.



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For the quadrimer $[Fe_4S_4(S\text{–}S,R)_4]^z$ two reasonable arrangements involving bridging sulfur are shown in Figures 3 and 4. The structure in Figure 3 consists of a cube with iron and sulfur atoms occupying alternate vertices. The four dithiolene ligands are attached individually to each iron atom. The results produces acceptable coordination about both iron and sulfur. A less symmetrical form of the Fe_4S_4 core of this proposed structure is found to exist in $(\pi\text{-}C_5H_5)_4Fe_4S_4$.[14] The second possible structure (Figure 4) involves bridging by dithiolene units as well as by the "free" sulfur. This structure is obviously closely related to the bisdithiolene dimers (Figure 1). This structure also results in pentacoordination about iron, but two different types of sulfur result; one pair of sulfur atoms is two coordinate while the other pair is three coordinate. The iron atoms are also divided into two sets each; the iron atoms of one set are each coordinated by three dithiolene sulfurs and two "free" sulfurs, while each iron atom of the other pair is coordinated by two dithiolene sulfurs and three "free" sulfurs. In contrast the structure shown in Figure 3 has identical coordination about each iron.

In an endeavor to probe the symmetry of these complexes ^{19}F nmr and Mössbauer measurements have been made. The only species which has suitable solubility properties for nmr measurements is $[Bu_4N]_2[Fe_4S_4(S\text{–}S,CF_3)_4]$. In acetone solution only a single ^{19}F resonance at 570 cps downfield of internal benzotrifluoride is observed. The Mössbauer data for the complexes are set out in Table VI. For the quadrimeric series the spectra

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(29) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **6**, 469 (1967).

(30) R. B. King, *J. Amer. Chem. Soc.*, **89**, 6368 (1967).

(31) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *ibid.*, **90**, 2784 (1968), and references therein.

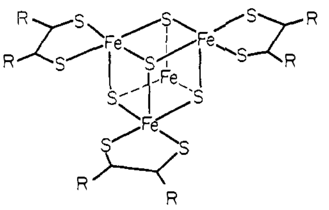

Figure 3. A possible structure for the $[Fe_4S_4(S\text{-}S,R)_4]^z$ unit. The dithiolene group on the rear iron atom has been omitted for clarity.

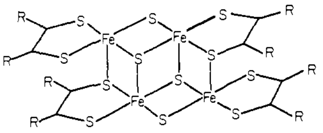

Figure 4. A possible structure for the $[Fe_4S_4(S\text{-}S,R)_4]^z$ unit.

consist of a pair of sharp lines. The splitting must be due to quadripole interaction since the iron atoms are not expected to have cubic symmetry. There is no evidence of asymmetry or further splitting of the Mössbauer lines. Both the nmr and the Mössbauer observations indicate only that any environment differences for the CF_3 groups or for the iron atoms are not great enough to produce effects detected by these forms of spectroscopy. Although the structure in Figure 3 is entirely consistent with the observed data and appears most reasonable, the alternate proposal for the quadrimeric unit cannot be excluded by the available data.[32,33] This point is emphasized when the $[Fe_3S_2(S\text{-}S,CF_3)_4]$ unit is considered. The Mössbauer spectrum of this compound also consists of only two lines. Again there is no detectable difference between iron sites, but in this case we have not been able to devise a structure in which all three iron atoms are equivalent. Two reasonable structures may be derived from the structures proposed for the quadrimers by removing an $S_2Fe(S\text{-}S,R)$ unit and replacing it with a dithiolene unit. The result of performing such an operation on the structure in Figure 4 is shown in Figure 5. The same operation performed on the structure in Figure 3 produces a similar structure except that the lower $Fe(S\text{-}S,R)_2$ unit is rotated in its plane by 90° so that one dithiolene group is terminal and the other bridges all three iron atoms. In either of these possible structures, all of the iron atoms do not reside in identical environments although each iron atom is coordinated by five sulfur atoms. Clearly the structural problem posed by these complexes must await X-ray crystallographic study before definite conclusions can be made.

Table VI. Parameters from Mössbauer Spectra of Polynuclear Iron Complexes

Compound	Isomer shift,[a,b] mm/sec	Quadripole splitting,[a] mm/sec	Line width,[a,c] mm/sec
$[Fe_4S_4(S\text{-}S,CF_3)_4]$	0.32	1.68	0.30, 0.28
$[Ph_4As][Fe_4S_4(S\text{-}S,CF_3)_4]$	0.35	1.62	0.26, 0.26
$[Bu_4]N_2[Fe_4S_4(S\text{-}S,CF_3)_4]$	0.39	1.64	0.29, 0.25
$[Fe_4S_4(S\text{-}S,Ph)_4]$	0.36	1.68	0.31, 0.30
$[Fe_3S_2(S\text{-}S,CF_3)_4]$	0.46[d]	1.85[d]	0.49, 0.49[d,e]

[a] At *ca.* 25°, unless noted otherwise, error is less than 0.01 mm/sec. [b] Relative to sodium nitroprusside. [c] Full width at half-height; the first number refers to the component with a negative shift with respect to the center of the standard spectrum. [d] Measured at 77°K; insufficient sample for room temperature observation. [e] Increased line width due at least in part to mechanics of low-temperature operation.

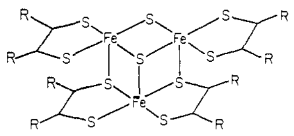

Figure 5. A possible structure for $[Fe_3S_2(S\text{-}S, CF_3)_4]$.

Other features of the Mössbauer spectra are also of interest. The isomer shift is expected to respond to changes in the iron oxidation states with lower oxidation states predicted to give larger positive isomer shifts. In the $[Fe_4S_4(S\text{-}S,CF_3)_4]^z$ series, as electrons are added to the cluster the isomer shift is observed to increase in agreement with theory. However, the effect is very small and it is evident that the added electrons are delocalized throughout the cluster. This is interesting in light of Mössbauer studies on spinach ferredoxin which suggest that the two iron atoms of this ferredoxin are nearly equivalent in the oxidized form but that upon reduction they become detectiably different.[34] The quadripole splitting in $[Fe_4S_4(S\text{-}S,R_4)]^z$ is smaller than that reported for the bis-dithiolene iron dimers but it is within the range reported for some other five-coordinate iron-dithiolene complexes.[1,35]

Electron-transfer capabilities of polynuclear iron-dithiolene complexes are now well established. In addition to the species already described, a polynuclear iron-dithiolene nitrosyl, $[Fe_2(NO)_2(S\text{-}S,Ph)_3]^z$, has been reported to exist in a three-membered series ($z = 0, -1, -2$).[36] We have examined polarographically the two isoelectronic trimers, $[Fe_3(NO)_3(S\text{-}S,CF_3)_3]$ and $[Co_3(CO)_3\text{-}(S\text{-}S,CF_3)_3]$, that have been characterized previously by King.[20,21,37] The polarographic data set out in Table III indicate that the iron complex undergoes two successive reductions; the diffusion current indicates that the processes involve one electron. Similarly the cobalt complex can undergo a one-electron reduction. Presumably these reductions leave the trimeric unit structurally intact.

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(32) In two related situations either ^{19}F nmr spectroscopy or Mössbauer spectroscopy has failed to detect the true molecular symmetry. Initial ^{19}F nmr observations[24] on $[Co_2(S\text{-}S,CF_3)_4]^{2-}$ and $[Fe_2(S\text{-}S,CF_3)_4]^{2-}$ did not reveal any nonequivalence of the CF_3 groups although these two species probably have (under the conditions of the nmr experiments) the dimeric structure shown in Figure 1. However, in these cases rapid monomer-dimer equilibrium[6] may average the CF_3 environments and so produce a single resonance. The Mössbauer spectrum of $Na[Fe_4S_3(NO)_7]$ was reported to exhibit only two equally intense lives[33] although an X-ray study has shown that one of the four iron atoms resides in a location quite different from that of the other three. Despite the rather narrow Mössbauer line widths that were reported, no evidence of further splitting was observed. In this case it is clear that the Mössbauer spectrum in its present state of resolution does not reflect the true structure.

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