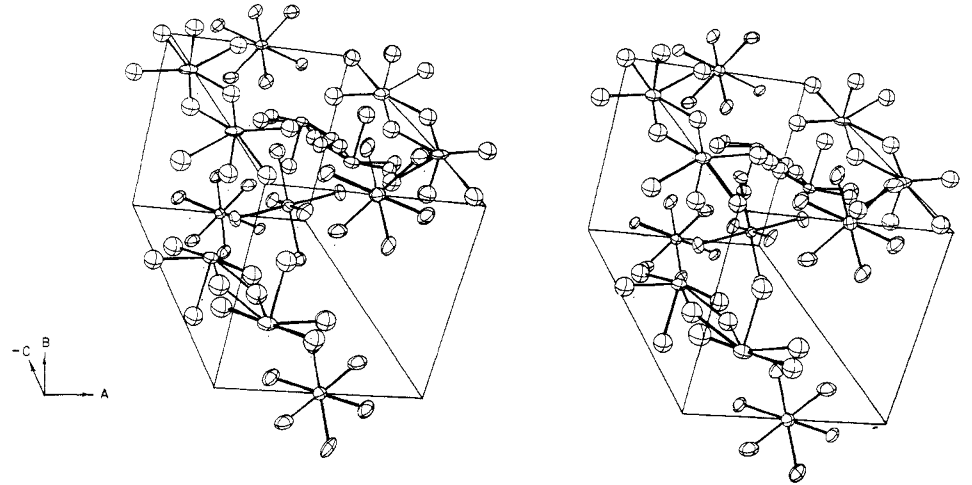

Figure 2. Stereogram of $Co(NH_3)_6Sb_2F_9$ with Co at (1/2, 0, 0).

the $Sb_2X_9^{3-}$ species, the antimony-bridging halogen distance is lengthened with respect to the terminal halogen distance. In the bromide and chloride anions this lengthening was found to be 0.37 and 0.36 Å, respectively. If the asymmetric Sb–F bridge distances are averaged in the present compound, the corresponding lengthening is 0.33 Å and is thus indicative of an effect which is essentially independent of the halogen present.

Although no hydrogen atoms were clearly indicated in the difference map, weak hydrogen bonding could well be present. The shorter nitrogen-fluorine distances range from 2.84 to 2.94 Å while the corresponding Co–N–F angles range from 97.5 to 120.2°.

Registry No. $Co(NH_3)_6Sb_2F_9$, 37871-78-6.

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Crystal and Molecular Structure of the Complex Tri-μ-methylmercapto-hexacarbonyldiiron(II) Tetrakis(*cis*-1,2-di(perfluoromethyl)ethylene-1,2-dithiolato)diiron, $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6][Fe_2(S_2C_2(CF_3)_2)_4]$

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The crystal and molecular structure of the cation-anion complex $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6][Fe_2(S_2C_2(CF_3)_2)_4]$ has been determined by single-crystal X-ray diffraction methods with data collected by the θ–2θ counter technique. The complex crystallized in space group $P\bar{1}$ of the triclinic system in a cell of dimensions a = 13.64 (1), b = 14.81 (1), c = 17.81 (1) Å; α = 124.27 (3), β = 127.19 (3), γ = 76.47 (3)°; and V = 2336 Å^3. There are two cation-anion pairs in the unit cell (ρ_{calcd} = 2.03, ρ_{exptl} = 2.02 (3) g/cm^3). The structure was solved by direct methods in the completely general space group $P1$ because of an early calculational error, and it has been refined by least-squares procedures to a conventional R factor of 0.058 for 4335 reflections above 2σ. The structure of the previously unreported cation consists of two faced-shared octahedra with methylmercapto groups occupying the bridging positions. The average Fe–S and Fe–C distances are 2.305 (2) and 1.80 (1) Å, respectively. The Fe· · ·Fe separation is 3.062 (4) Å indicating little if any direct metal–metal bonding, and, hence, the cation can be formulated as containing two discrete Fe(II) d^6 metal ions in octahedral coordination geometries. The anion $[Fe_2(S_2C_2(CF_3)_2)_4]^-$ is crystallographically required to be centrosymmetric, and it exhibits a structure characteristic of other iron and cobalt dithiolene dimers in which each metal atom has a square-pyramidal coordination geometry. Dimerization occurs through the formation of two Fe–S linkages of distance 2.311 (5) Å. The average Fe–S, C–S, and C–C bond lengths within the metal–dithiolene chelate rings are 2.190 (6), 1.721 (9) and 1.33 (1) Å, respectively. The Fe–Fe distance is 2.767 (4) Å. The anion is compared structurally with other dithiolene dimers in order to assess the effects of complex charge and the number of valence electrons on the formation of a metal–metal bond and related structural parameters.

Introduction

Everyone has at least one skeleton in his closet and in a sense, this is one of ours. During the last few years we, like many others, have been intrigued by the development and use of metal complexes as model systems for metalloenzymes and related metal-containing proteins,[1] even when these model systems are chemically far removed from the biochemical systems whose properties they are supposed to resemble. One particular area of interest in this regard has been the inorganic chemists' approach to the nonheme iron proteins and,

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[1] See, for example, *Advan. Chem. Ser.*, No. 100 (1970).

in particular, the ferredoxins which are important electron-transfer agents in biological systems and which contain Fe-S bonds.[2-5]

We were therefore interested and motivated in this direction, albeit somewhat naively, when we learned of the synthesis of a novel series of iron-sulfur complexes by Professor Jon A. McCleverty.[6] These complexes, which were assigned the general molecular formula $[Fe(XR)(CO)(S_2C_2(CF_3)_2]_n$ ($X = S$, $R = CH_3$, C_2H_5, C_6H_5; $X = Se$, $R = C_6H_5$; $n = 4$ in $CHCl_3$ and 2 in $(CH_3)_2CO$), were prepared by the reaction of $Fe_2(CO)_6(XR)_2$ with the dithietene $S_2C_2(CF_3)_2$ and were characterized by molecular weight determinations, infrared spectroscopy, and voltammetric studies.[6] Perhaps the most interesting and compelling aspect of these cluster complexes was the fact that they exhibited both one-electron and multiple-electron reduction processes, the former being reversible. We therefore undertook a single-crystal X-ray investigation of one of these complexes in order to determine the structure of the Fe-S cluster.

Through a series of trials, tribulations, and scattered soul searchings (outlined below) the structure of the complex with $X = S$ and $R = CH_3$ was eventually solved by direct methods in the completely general space group $P1$—to our knowledge only the second such structure to be solved this way[7]—whence it became apparent that the space group had been incorrectly assigned and was actually the centrosymmetric space group $P\bar{1}$. To our further dismay, the supposed tetranuclear complex turned out not to be a cluster at all but was instead the 1:1 salt of tri-μ-methylthio-hexacarbonyldiiron(II) tetrakis (*cis*-1,2-di(perfluoromethyl)ethylene-1,2-dithiolato)diiron, $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6][Fe_2(S_2C_2(CF_3)_2)_4]$.

We report herein the structure determination of this complex for several reasons: (1) the carbonyl cation has not been observed previously and there is abundant interest in mercaptide-bridged organometallics;[8-14] (2) the iron dithiolene dimer is one electron removed from the previously reported dimers $[Co_2(S_2C_2(CF_3)_2)_4]$[15] and $[Fe_2(S_2C_2(CN)_2)_4]^{2-}$ [16] and the possible effect of the additional valence electron can be assessed;[17] and (3) the saga of our structure determination may prove amusing and/or instructive to members of the reading audience doing this type of work. At any rate, after 2 painful years of working on this structure, it is a relief to pass it on for posterity.

Collection and Reduction of the X-Ray Data

Black crystals of the title complex were kindly supplied to us by Professor J. A. McCleverty of Sheffield, England. Weissenberg and precession photographs revealed the absence of any symmetry except for the inversion center required by the diffraction pattern, and a convenient primitive cell was chosen. The dimensions of this cell based on a least-squares refinement of 20 reflections centered on a Picker diffractometer are $a = 13.64$ (1), $b = 14.81$ (1), $c = 17.81$ (1) Å; $\alpha = 124.27$ (3), $\beta = 127.19$ (3), $\gamma = 76.47$ (3)°; and $V = 2336$ Å^3. A Delaunay reduction[18] supported the absence of any symmetry and yielded the following *reduced* cell: $a = 13.64$ (1), $b = 14.81$ (1), $c = 15.47$ (1) Å; $\alpha = 107.94$ (3), $\beta = 118.13$ (3), $\gamma = 103.48$ (3)°; and $V = 2341$ Å^3. All structural parameters reported below refer to the original cell chosen. The observed density of 2.02 (3) g/cm^3 obtained by the flotation method agrees with the value of 2.03 g/cm^3 calculated for two molecules of formula $[Fe_2(SCH_3)_3(CO)_6][Fe_2(S_2C_2(CF_3)_2)_4]$.

For intensity measurements, a crystal of approximate dimensions 0.42 × 0.16 × 0.24 mm was aligned accurately along the a^* axis by photographic methods and then transferred to the Picker four-circle diffractometer. Twenty reflections were then centered in the counter aperture using the left-right and top-bottom balancing features of the receiving aperture collimator. The settings for these reflections formed the basis for a least-squares refinement of the unit cell parameters and the orientation angles using our PICKLST program.[19] The mosaic spread of the crystal was estimated from open-counter, narrow-source ω scans through several strong reflections and found to have an average value of 0.20°.[20]

The intensity data were collected by the θ-2θ scan technique using Zr-filtered Mo Kα radiation. A takeoff angle of 1.5° was used for the data collection with a counter opening of 4 × 4 mm. Each reflection was scanned from −0.70 to +0.80° of the calculated 2θ value of the reflection with a scan rate of 1°/min. Allowance was made in the scan range for the separation of the Mo Kα doublet. Stationary-counter, stationary-crystal background counts of 10-sec duration were collected at both ends of the 2θ scan range for each reflection. Pulse height analysis designed to accept 90% of the diffracted radiation was employed, and attenuators were automatically inserted if the count rate exceeded approximately 10,000 counts/sec. Attenuation was found to be necessary for 43 reflections. The intensities of four standard reflections were measured after every 100 reflections and showed no significant change during the data collection.

The intensities of 5776 independent reflections were measured with 2θ angles between 5 and 50°. These were corrected for the usual Lorentz and polarization effects to yield a set of F_o^2 values, where the F_o's are the observed structure factor amplitudes. Of the 5776 reflections measured, 4335 had intensities greater than twice their estimated standard deviation (see below) and were assumed to be statistically reliable.

Solution and Refinement of the Structure

A sharpened, origin-removed Patterson function was calculated. Because of the large number of heavy atoms (8 iron atoms and 22 sulfur atoms per unit cell), the lack of Harker vectors, and the original assumption of an Fe_4S_{12} cluster, the Patterson function was never successfully solved. The superposition technique was next employed[21] and it was found that many of the superpositions yielded sets of peaks clearly assignable to fragments of an iron-sulfur cluster. However, all solutions based on the superposition results failed to refine successfully in space group $P\bar{1}$.

Our next attempt to solve the structure focussed on direct or sym-

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(19) The main programs used in this work were the PICKLST orientation refinement and setting program, a local modification of the Busing-Levy ORFLS least-squares program, the Zalkin FORDAP Fourier program, the REFINE block-diagonal least-squares program kindly supplied by Dr. J. A. Cunningham, the Dewar FAME, MAGIA, and TANG programs for direct-methods solution in the acentric case, the Busing-Martin-Levy ORFFE function and error program, the Johnson ORTEP plotting program, and local programs written for superposition methods. All computing was performed on Brown's IBM 360/67 computer.

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Table I

hkl	$\lvert E \rvert$	Initial phase calcd from ls refinement of Fe–S fragment,[a] deg	Input to Dewar's MAGIA program[b]	Final phase from acentric refinement,[c] deg	Phase shift due to change in origin,[d] deg	Phase from first centric ls refinement,[e] deg	Final phase, deg
$1\bar{3}8$	3.532	355	0	329	−148	182	182
$1,\bar{4},10$	3.165	35	$\pi/4$	20	0	2	2
$\bar{4}\bar{4}1$	2.390	3	0	41	−36	2	2
$1\bar{8}5$	2.855	334	*W*	3	−166	182	182
231	3.430	332	*X*	315	−148	181	181
$2\bar{5}3$	2.473	337	*Y*	349	+25	2	1

[a] Phase calculated from a least-squares refinement on six atoms whose positions repeatedly showed up in the superposition maps. R and R' were 0.471 and 0.549, respectively. [b] MAGIA is Dewar's symbolic addition program for acentric space groups. [c] R and R' were 0.228 and 0.248, respectively. [d] Calculated phase shift $(2\pi(hx + ky + lz))$ due to the origin shift (−0.04, −0.01, −0.30) from the acentric to the centric space group. [e] R and R' were 0.354 and 0.453, respectively, based on 16 atoms.

bolic addition methods. A statistical distribution of the normalized structure factors or $|E|$'s[22] indicated an acentric space group which, in this case, meant the completely general space group $P1$. It was not until much later when the structure was essentially solved that we realized that the Wilson plot used to determine the scale factor and the overall temperature factor had been calculated incorrectly, and a false distribution of $|E|$'s obtained. However, at the time of the error, we became quickly convinced of the correctness of the acentric space group, in part because of our notable lack of success in solving the structure from the Patterson map assuming $P\bar{1}$.

The major problems in using direct methods in the acentric case are (a) the fixing of the origin and (b) the determination of values for the symbols used in the symbolic addition step of the procedure.[23,24] With regard to the latter problem, we were able to circumvent much of the trial and error in this method by using as our approximate phases those values obtained from the refinement of part of the presumed cluster which appeared repeatedly from our superposition trials. In this structural unit, one iron atom was fixed at the origin, and the partial cluster of three iron atoms and three sulfur atoms refined to a conventional R factor $(=\Sigma||F_o| - |F_c||/\Sigma|F_o|)$ of 0.471. For fixing the origin, three reflections were chosen which had large $|E|$'s and a large number of Σ_2 interactions and which constituted a primitive, linearly independent triplet such that

$$\begin{vmatrix} h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \\ h_3 & k_3 & l_3 \end{vmatrix} = \pm 1$$

as shown by Hauptman and Karle.[23] Three additional reflections were assigned symbols, and these six reflections which formed the basis of the symbolic addition procedure are summarized in Table I. These six reflections yielded symbolic phases for 101 reflections according to the Σ_2 relationship

$$\phi_h \simeq \langle \phi_k + \phi_{h-k} \rangle_k$$

As mentioned above, the symbols were assigned initial-phase values based on the refinement of the cluster fragment and the set of phased reflections was then expanded and refined using the tangent formula[25]

$$\tan \phi_h = \frac{\sum_k |E_k E_{h-k}| \sin(\phi_k + \phi_{h-k})}{\sum_k |E_k E_{h-k}| \cos(\phi_k + \phi_{h-k})}$$

The tangent refinement yielded 457 approximately phased reflections. An E map calculated from these phased reflections revealed four iron and fourteen sulfur atoms. After two cycles of least-squares refinement of positional and isotropic thermal parameters of these atoms, the R factor was 0.441. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ where the weights w were assigned as $4F_o^2/\sigma^2(F_o^2)$ and the standard deviations were estimated from counting statistics according to the formula

$$\sigma(F^2) = \frac{1}{TLp}(C + (t_c/2t_b)^2(B_1 + B_2) + (0.03I)^2)^{1/2}$$

where Lp is the Lorentz-polarization factor, T is the transmission coefficient, C is the total integrated count obtained in time t_c, B_1 and B_2 are the background counts, each obtained in time t_b, and I is the net integrated count.[26] The neutral atom scattering factors used in this and subsequent refinements were those tabulated by Cromer and Waber.[27]

The phases of the 3565 reflections used in this initial refinement of the heavy-atom structural parameters were then refined by the tangent formula for one cycle and a second E map was calculated. The location of additional atoms from this E map was followed by a sequence of least-squares refinements and difference Fourier syntheses until all but one of the atoms in the structure were located. Because of the large number of structural parameters, least-squares refinements were carried out using the block-diagonal procedure and these refinements led to unencouraging agreement factors R and R' $(=(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2})$ of 0.228 and 0.248, respectively, assuming isotropic thermal parameters for all atoms.

An examination of a model of the structure at this time indicated an apparent center of symmetry, and upon investigation, the error in our original calculation of the Wilson plot was discovered. A recalculated Wilson plot led to a centric distribution of the normalized structure factors, assorted mutterings, and extensive soul searching. Thankfully, the refinement of the structure from this point on was routine. A full-matrix least-squares procedure was employed but because of the large number of structural parameters, the structure was refined in sections. The Fe, S, and F atoms were assigned individual anisotropic thermal parameters in these calculations while the C and O atoms were constrained to the isotropic thermal model. The effects of anomalous scattering were included in the calculated structure factors with the values of $\Delta f'$ and $\Delta f''$ for Fe and S taken from Cromer's tabulation.[28] This refinement of positional and anisotropic thermal parameters for 70 independent atoms in space group $P\bar{1}$ converged to agreement factors R and R' of 0.058 and 0.065, respectively, for 4335 reflections above 2σ. No attempt was made to locate or refine the methyl group hydrogen atoms.

The parameters obtained from the last complete cycle of refinement are taken as the final parameters for the structure and are tabulated in Table II along with their estimated standard deviations as obtained from the appropriate inverse matrix. The final F_o and $|F_c|$ values (in electrons × 10) for the 4335 reflections used in the refinement have been tabulated and are available upon request.[29] In Table III, the root-mean-square amplitudes of vibration of the anisotropically refined atoms are presented.

There is one final point in this section of the paper. To our knowledge, only one reported structure has been solved by direct methods in space group $P1$.[7] The fact that we were able eventually to solve this structure without relying on any symmetry and little valid knowledge of the molecular structure prior to its solution indicates the power of direct methods in structure determination.

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(29) The table of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journal Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-518.

Table II

Final Positional and Thermal Parameters for $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6][Fe_2(S_2C_2(CF_3)_2)_4]$

Atom[a]	x[b]	y[b]	z[b]	B[c]	Atom[a]	x[b]	y[b]	z[b]	B[c]
Fe(1)	0.0924 (1)[d]	0.4489 (1)	−0.0117 (1)	*e*	F9(2)	1.0731 (7)	0.5058 (8)	0.3235 (7)	*e*
Fe(2)	0.5782 (1)	0.4243 (1)	0.0178 (1)	*e*	F10(2)	0.9846 (11)	0.3168 (14)	0.2824 (13)	*e*
Fe1(3)	−0.3883 (1)	−0.1840 (1)	−0.3192 (1)	*e*	F11(2)	0.8339 (9)	0.2610 (11)	0.2407 (12)	*e*
Fe2(3)	−0.6060 (1)	−0.2122 (1)	−0.3221 (1)	*e*	F12(2)	0.9230 (15)	0.4047 (10)	0.3727 (9)	*e*
S1(1)	−0.0237 (2)	0.5505 (2)	−0.0798 (2)	*e*	O1(3)	−0.1448 (8)	−0.0529 (7)	−0.1102 (7)	7.3 (2)
S2(1)	0.2377 (2)	0.5967 (2)	0.1344 (2)	*e*	O2(3)	−0.2799 (9)	−0.3711 (8)	−0.4136 (8)	9.0 (2)
S3(1)	−0.0191 (2)	0.3075 (2)	−0.1843 (2)	*e*	O3(3)	−0.4159 (7)	−0.0838 (7)	−0.4331 (7)	7.2 (2)
S4(1)	0.2396 (2)	0.3490 (2)	0.0203 (2)	*e*	O4(3)	−0.5952 (7)	−0.1048 (6)	−0.1185 (6)	5.9 (2)
S1(2)	0.5286 (2)	0.4751 (2)	−0.0947 (2)	*e*	O5(3)	−0.7208 (7)	−0.4273 (6)	−0.4150 (6)	6.3 (2)
S2(2)	0.4349 (2)	0.2750 (2)	−0.1309 (2)	*e*	O6(3)	−0.8435 (8)	−0.1409 (6)	−0.4365 (7)	7.3 (2)
S3(2)	0.7600 (2)	0.5263 (2)	0.1337 (2)	*e*	C1(1)	0.0735 (8)	0.6788 (7)	0.0110 (8)	3.6 (2)
S4(2)	0.6653 (3)	0.3285 (2)	0.0946 (2)	*e*	C2(1)	0.1843 (9)	0.6959 (7)	0.1042 (8)	3.8 (2)
S1(3)	−0.5830 (2)	−0.2895 (2)	−0.4641 (2)	*e*	C3(1)	0.0147 (11)	0.7583 (10)	−0.0259 (10)	4.9 (2)
S2(3)	−0.5006 (2)	−0.0581 (2)	−0.2609 (2)	*e*	C4(1)	0.2693 (11)	0.8050 (10)	0.1924 (10)	4.9 (2)
S3(3)	−0.4050 (2)	−0.2488 (2)	−0.2354 (2)	*e*	C5(1)	0.0622 (8)	0.2000 (7)	−0.1902 (8)	3.7 (2)
F1(1)	0.0895 (7)	0.8050 (6)	−0.0218 (7)	*e*	C6(1)	0.1799 (8)	0.2205 (7)	−0.0973 (8)	3.5 (2)
F2(1)	−0.0232 (9)	0.8364 (6)	0.0305 (7)	*e*	C7(1)	−0.0015 (12)	0.0874 (11)	−0.3084 (11)	6.1 (3)
F3(1)	−0.0847 (7)	0.7087 (6)	−0.1326 (6)	*e*	C8(1)	0.2624 (11)	0.1321 (10)	−0.0934 (10)	5.4 (3)
F4(1)	0.3563 (7)	0.8150 (6)	0.2861 (6)	*e*	C1(2)	0.4215 (8)	0.3636 (7)	−0.2311 (8)	3.6 (2)
F5(1)	0.2139 (7)	0.8901 (5)	0.2135 (8)	*e*	C2(2)	0.3840 (9)	0.2803 (8)	−0.2434 (8)	4.0 (2)
F6(1)	0.3274 (9)	0.8262 (7)	0.1668 (7)	*e*	C3(2)	0.3826 (12)	0.3791 (11)	−0.3223 (11)	5.9 (3)
F7(1)	−0.1232 (7)	0.0863 (5)	−0.3628 (6)	*e*	C4(2)	0.2893 (14)	0.1778 (13)	−0.3567 (13)	7.3 (3)
F8(1)	0.0158 (7)	0.0067 (5)	−0.2927 (6)	*e*	C5(2)	0.8545 (9)	0.4852 (8)	0.2259 (8)	4.1 (2)
F9(1)	0.0346 (9)	0.0726 (7)	−0.3629 (7)	*e*	C6(2)	0.8154 (9)	0.3977 (8)	0.2082 (8)	4.2 (2)
F10(1)	0.2625 (6)	0.0683 (5)	−0.1834 (5)	*e*	C7(2)	0.9795 (13)	0.5565 (12)	0.3247 (12)	6.6 (3)
F11(1)	0.3806 (6)	0.1793 (5)	−0.0081 (5)	*e*	C8(2)	0.8876 (14)	0.3416 (13)	0.2717 (13)	7.0 (3)
F12(1)	0.2348 (7)	0.0678 (5)	−0.0771 (6)	*e*	C1(3)	−0.2393 (11)	−0.1030 (9)	−0.1928 (10)	5.6 (3)
F1(2)	0.2674 (6)	0.3887 (7)	−0.3783 (6)	*e*	C2(3)	−0.3217 (11)	−0.2963 (10)	−0.3762 (10)	6.3 (3)
F2(2)	0.4030 (10)	0.3011 (8)	−0.3932 (7)	*e*	C3(3)	−0.3999 (10)	−0.1238 (9)	−0.3882 (9)	5.1 (2)
F3(2)	0.4417 (8)	0.4694 (8)	−0.2825 (6)	*e*	C4(3)	−0.5991 (10)	−0.1459 (9)	−0.1972 (9)	5.4 (2)
F4(2)	0.2599 (9)	0.1091 (7)	−0.3507 (6)	*e*	C5(3)	−0.6782 (10)	−0.3445 (9)	−0.3803 (9)	5.0 (2)
F5(2)	0.1917 (9)	0.1985 (6)	−0.4189 (7)	*e*	C6(3)	−0.7519 (10)	−0.1684 (9)	−0.3926 (9)	5.3 (2)
F6(2)	0.3388 (10)	0.1162 (9)	−0.4095 (8)	*e*	C7(3)	−0.6809 (10)	−0.2320 (9)	−0.5520 (9)	6.0 (3)
F7(2)	0.9930 (7)	0.6450 (8)	0.3315 (6)	*e*	C8(3)	−0.4029 (9)	0.0300 (8)	−0.1053 (8)	4.9 (2)
F8(2)	1.0057 (6)	0.5962 (7)	0.4237 (5)	*e*	C9(3)	−0.4065 (9)	−0.3998 (8)	−0.3057 (8)	4.7 (2)

Anisotropic Thermal Parameters[f]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	β_{11}	β_{12}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	59 (1)	50 (1)	48 (1)	15 (1)	32 (1)	27 (1)	F6(1)	338 (17)	191 (11)	183 (11)	−126 (11)	145 (12)	44 (9)
Fe(2)	65 (1)	65 (1)	48 (1)	8 (1)	30 (1)	30 (1)	F7(1)	142 (9)	82 (6)	117 (8)	8 (6)	9 (7)	−14 (6)
Fe(3)	99 (2)	60 (1)	54 (1)	13 (1)	41 (1)	27 (1)	F8(1)	227 (11)	69 (6)	121 (8)	−1 (6)	50 (8)	30 (6)
Fe2(3)	84 (1)	61 (1)	50 (1)	18 (1)	33 (1)	27 (1)	F9(1)	137 (12)	55 (8)	15 (6)	16 (8)	62 (8)	−5 (6)
S1(1)	73 (2)	56 (2)	53 (2)	17 (2)	36 (2)	34 (2)	F10(1)	187 (9)	119 (6)	108 (6)	90 (6)	112 (7)	68 (6)
S2(1)	66 (2)	58 (2)	60 (2)	10 (2)	34 (2)	30 (2)	F11(1)	127 (8)	128 (7)	113 (7)	72 (6)	59 (6)	68 (6)
S3(1)	75 (3)	57 (2)	45 (2)	21 (2)	32 (2)	24 (2)	F12(1)	223 (10)	110 (6)	172 (8)	78 (7)	135 (8)	107 (6)
S4(1)	66 (2)	62 (2)	60 (2)	21 (2)	32 (2)	35 (2)	F1(2)	135 (8)	273 (11)	152 (8)	73 (8)	74 (7)	172 (9)
S1(2)	71 (3)	75 (2)	54 (2)	12 (2)	38 (2)	36 (2)	F2(2)	447 (20)	267 (13)	163 (10)	205 (14)	241 (13)	151 (10)
S2(2)	98 (3)	74 (2)	62 (2)	−8 (2)	30 (2)	35 (2)	F3(2)	260 (13)	251 (12)	107 (8)	−68 (10)	43 (8)	118 (8)
S3(2)	69 (3)	93 (3)	60 (2)	3 (2)	32 (2)	43 (2)	F4(2)	315 (16)	144 (9)	91 (7)	−122 (10)	15 (9)	32 (7)
S4(2)	105 (3)	75 (2)	72 (2)	15 (2)	40 (2)	45 (2)	F5(2)	238 (13)	113 (8)	149 (9)	−37 (8)	−85 (10)	60 (7)
S1(3)	104 (3)	70 (2)	42 (2)	10 (2)	34 (2)	19 (2)	F6(2)	337 (19)	241 (13)	165 (11)	−129 (13)	166 (13)	−74 (10)
S2(3)	113 (3)	55 (2)	53 (2)	22 (2)	42 (2)	30 (2)	F7(2)	162 (10)	230 (11)	108 (7)	−97 (9)	−18 (7)	94 (8)
S3(3)	84 (3)	56 (2)	52 (2)	16 (2)	32 (2)	29 (2)	F8(2)	146 (9)	257 (11)	62 (6)	−45 (8)	32 (6)	64 (7)
F1(1)	200 (10)	162 (8)	211 (10)	52 (7)	140 (9)	144 (8)	F9(2)	99 (8)	290 (13)	151 (9)	29 (8)	67 (8)	74 (9)
F2(1)	348 (15)	156 (8)	246 (12)	171 (10)	244 (12)	161 (9)	F10(2)	335 (20)	683 (31)	532 (26)	389 (23)	357 (21)	565 (28)
F3(1)	193 (10)	128 (7)	154 (8)	0 (7)	16 (8)	112 (7)	F11(2)	197 (13)	347 (18)	395 (21)	−29 (13)	−24 (13)	341 (19)
F4(1)	223 (11)	114 (7)	103 (7)	−83 (7)	−6 (7)	55 (6)	F12(2)	604 (33)	297 (17)	186 (13)	137 (20)	201 (18)	188 (13)
F5(1)	171 (10)	62 (6)	225 (12)	−4 (6)	87 (10)	−0 (7)							

[a] In our labeling scheme, the number in parentheses refers to the particular structural entity in the unit cell; 1 and 2 are for the dithiolene dimer anions and 3 is for the mercapto-bridged cation. [b] x, y, z are in fractional coordinates. [c] Isotropic thermal parameters in Å². [d] Numbers in parentheses here and in succeeding tables are estimated standard deviations in the least significant figures. [e] Atoms refined anisotropically. [f] The form of the anisotropic thermal ellipsoid is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. The anisotropic thermal parameters given are ×10⁴.

Description of the Structure and Discussion

The structure described by the atomic parameters of Table II, the unit cell constants, and the $\bar{1}$ symmetry operation of the space group consists of the packing of discrete binuclear tri(methylmercapto)-bridged cations of formula $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+$ and centrosymmetric dithiolene dimer anions of formula $[Fe_2(S_2C_2(CF_3)_2)_4]^-$. As noted above, this result was quite unexpected. The assignment of charges to the different structural entities is based primarily on the molecular parameters discussed below. In addition, a magnetic susceptibility of 1.99 BM per $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6][Fe_2(S_2C_2(CF_3)_2)_4]$ complex is consistent with that expected for the dithiolene dimer monoanion.

The closest intermolecular contacts in the structure (excluding the methyl hydrogen atoms) are between fluorine and oxygen atoms and are also fluorine–fluorine contacts. The

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

Atom	Min	Intermed	Max
Fe(1)	0.175 (3)	0.185 (3)	0.203 (2)
Fe(2)	0.183 (2)	0.204 (3)	0.224 (2)
Fe1(3)	0.193 (3)	0.221 (3)	0.255 (2)
Fe2(3)	0.189 (3)	0.204 (2)	0.260 (2)
S1(1)	0.178 (4)	0.198 (4)	0.217 (4)
S2(1)	0.196 (4)	0.206 (6)	0.228 (4)
S3(1)	0.177 (4)	0.188 (4)	0.257 (4)
S4(1)	0.177 (4)	0.212 (4)	0.247 (4)
S1(2)	0.185 (4)	0.204 (4)	0.238 (4)
S2(2)	0.204 (4)	0.226 (4)	0.283 (4)
S3(2)	0.197 (3)	0.211 (4)	0.268 (4)
S4(2)	0.211 (4)	0.236 (5)	0.278 (4)
S1(3)	0.171 (4)	0.244 (4)	0.281 (4)
S2(3)	0.193 (8)	0.195 (6)	0.282 (4)
S3(3)	0.191 (3)	0.199 (4)	0.254 (4)
F1(1)	0.212 (10)	0.320 (9)	0.399 (9)
F2(1)	0.210 (10)	0.291 (10)	0.494 (11)
F3(1)	0.211 (10)	0.297 (9)	0.497 (10)
F4(1)	0.204 (10)	0.290 (9)	0.514 (11)
F5(1)	0.203 (11)	0.324 (10)	0.562 (12)
F6(1)	0.219 (12)	0.356 (11)	0.555 (13)
F7(1)	0.193 (10)	0.287 (9)	0.551 (12)
F8(1)	0.222 (10)	0.320 (9)	0.463 (10)
F9(1)[a]	0.039	0.253	0.323
F10(1)	0.192 (10)	0.266 (8)	0.387 (8)
F11(1)	0.204 (9)	0.290 (8)	0.404 (9)
F12(1)	0.210 (9)	0.311 (9)	0.378 (8)
F1(2)	0.207 (9)	0.307 (9)	0.452 (9)
F2(2)	0.182 (13)	0.339 (10)	0.587 (12)
F3(2)	0.204 (11)	0.327 (10)	0.523 (11)
F4(2)	0.211 (11)	0.341 (10)	0.559 (13)
F5(2)	0.204 (11)	0.299 (10)	0.690 (15)
F6(2)	0.240 (12)	0.384 (13)	0.670 (16)
F7(2)	0.211 (10)	0.329 (10)	0.517 (12)
F8(2)	0.202 (10)	0.302 (9)	0.477 (10)
F9(2)	0.236 (11)	0.345 (11)	0.536 (12)
F10(2)	0.225 (12)	0.314 (12)	0.764 (18)
F11(2)	0.210 (12)	0.345 (12)	0.743 (18)
F12(2)	0.239 (13)	0.452 (13)	0.648 (18)

[a] These values are approximate since the refinement led to non-positive definite thermal parameters for F9(1).

ten closest intermolecular contacts are F11(1)-O4(3) (2.859 Å), F3(2)-O5(3) (2.996 Å), F5(1)-O3(3) (3.023 Å), F2(2)-O3(3) (3.023 Å), F7(2)-O6(3) (3.083 Å), F9(1)-F4(2) (3.101 Å), F12(1)-O4(3) (3.103 Å), F3(1)-F9(2) (3.151 Å), F10(1)-O4(3) (3.157 Å), and F8(2)-O5(3) (3.137 Å). Other intermolecular contacts in the structure are greater than 3.2 Å and they are therefore not tabulated.

The $[Fe_2(S_2C_2(CF_3)_2)_4]^-$ Anion. Each of the $[Fe_2(S_2C_2(CF_3)_2)_4]^-$ anions is crystallographically required to be centrosymmetric, and, hence, there are two independent half-dimer units within each unit cell. The two dimers are structurally identical with no significant differences between them. Therefore, all chemically equivalent distances and angles within the two dimers will be averaged for discussion purposes. In Table IV, the individual bond distances and angles for the anions are presented along with a description of the labeling scheme while in Figure 1, one of the dimeric systems is shown in perspective.

The structure of $[Fe_2(S_2C_2(CF_3)_2)_4]^-$ is essentially the same as that found for other dimeric dithiolene systems such as $[Co_2(S_2C_2(CF_3)_2)_4]$,[15] $[Fe_2(S_2C_2(CN)_2)_4]^{2-}$,[16] and $[Co_2(S_2C_6Cl_4)_4]^{2-}$ [30] in which each metal atom is pentacoordinate and possesses a square-pyramidal coordination geometry. The four sulfur atoms in the basal plane are from two chelating dithiolene ligands. Dimerization occurs through the formation of two Fe-S linkages with each Fe atom displaced by 0.43 Å from the basal plane of the square pyramid toward the apical sulfur of a different dithiolene ligand. Bond parameters within each $S_2C_2(CF_3)_2$ ligand (see Table IV) agree closely with those reported in previous structural studies[31] and are taken to indicate a delocalized π structure over the ligand system. The Fe-S bonds within the chelate rings exhibit significant differences depending on whether or not the particular dithiolene ligand is involved in the dimer linkage. If so, the average Fe-S distance within the chelate ring is 2.206 (3) Å, whereas if not, the average value is 2.175 (3) Å. Both of these values are in approximate agreement with the Fe-dithiolene S distances of 2.195 (3) and 2.22 (2) Å found in $Fe(S_2C_2(CF_3)_2)(dtc)_2$[32] (dtc = *N,N*-diethyldithiocarbamate) and $[Fe(OP(C_6H_5)_3)(S_2C_2(CF_3)_2)_2]^-$,[33] respectively, and are significantly shorter than the average dimer linkage of 2.311 (3) Å and values in the range 2.29-2.34 Å reported for Fe-S complexes of 1,1-dithiolato ligands (for example, 2.310 (3) Å in $Fe(S_2C_2(CF_3)_2)(dtc)_2$,[32] 2.32 (2) Å in $Fe(S_2CAr)_2\cdot(S_3CAr)$[34] (Ar = *p*-tolyl), 2.294 (2) Å in $Fe(NO)(S_2CN(CH_3)_2)_2$,[35] and 2.287 (2) and 2.338 (2) Å in $[Fe_2(SC_2H_5)_2(S_2CSC_2H_5)_4]$[36]). The relative shortness of the observed iron-dithiolene sulfur distances in the present study is explained by the π acidity of the $S_2C_2(CF_3)_2$ ligand system and consequent metal-ligand π back-bonding.

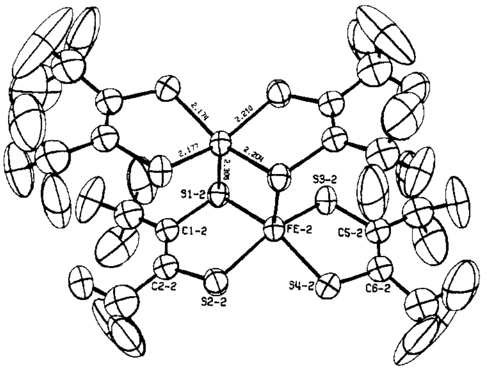

Figure 1. A perspective drawing of the $[Fe_2(S_2C_2(CF_3)_2)_4]^-$ monoanion. Dithiolene dimer 2 is shown along with its labeling scheme for the atoms in the inner coordination geometry. Dithiolene dimer 1 is identical with that shown and a completely analogous labeling scheme is employed.

One of the most interesting aspects of the structure of the $[Fe_2(S_2C_2(CF_3)_2)_4]^-$ monoanion reveals itself upon comparison with other dithiolene dimer complexes.[15,16,30] In Table V, important structural parameters for these dimeric systems are summarized. $[Fe_2(S_2C_2(CF_3)_2)_4]^-$ is at least one electron removed from the other dithiolene dimers, and hence the possible effect of the valence electron(s) occupying the highest filled orbital(s) in these systems can be assessed. Particular note is taken of the metal-metal distances reported for these systems. In the present study, the average Fe-Fe distance is 2.767 (4) Å which is well within the range of 2.5-3.0 Å suggested for metal-metal bond lengths in polynuclear iron complexes.[10-13,37,38] On the other hand, the dianionic

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Table IV. Principal Intramolecular Distances and Angles for $[Fe_2(S_2C_2(CF_3)_2)_4]^-$

Atoms	Distances, Å	Av values, Å	Atoms	Distances, Å	Av values, Å
Fe(1)-Fe(1)'[a]	2.756 (4)		C5(2)-C6(2)	1.31 (1)	1.33 (1)
Fe(2)-Fe(2)'	2.777 (3)	2.767 (4)	C1(1)-C3(1)	1.50 (1)	
Fe(1)-S1(1)'	2.316 (3)		C1(2)-C3(2)	1.51 (1)	
Fe(2)-S1(2)'	2.306 (3)	2.311 (5)	C2(1)-C4(1)	1.50 (1)	
S1(1)-S1(1)'	3.585 (5)		C2(2)-C4(2)	1.54 (2)	
S1(2)-S1(2)'	3.555 (6)	3.570 (6)	C5(1)-C7(1)	1.58 (1)	
Fe(1)-S1(1)	2.204 (3)		C5(2)-C7(2)	1.50 (1)	
Fe(2)-S1(2)	2.204 (3)		C6(1)-C8(1)	1.52 (1)	
Fe(1)-S2(1)	2.205 (3)		C6(2)-C8(2)	1.51 (2)	1.52 (2)
Fe(2)-S2(2)	2.210 (4)	2.206 (3)	C3(1)-F1(1)	1.31 (1)	
Fe(1)-S3(1)	2.175 (4)		C3(1)-F2(1)	1.29 (1)	
Fe(2)-S3(2)	2.177 (4)		C3(1)-F3(1)	1.33 (1)	
Fe(1)-S4(1)	2.173 (3)		C3(2)-F1(2)	1.28 (1)	
Fe(2)-S4(2)	2.174 (3)	2.175 (3)	C3(2)-F2(2)	1.28 (1)	
S1(1)-S2(1)	3.079 (4)		C3(2)-F3(2)	1.30 (1)	
S1(2)-S2(2)	3.075 (5)	3.077 (5)	C4(1)-F4(1)	1.27 (1)	
S3(1)-S4(1)	3.008 (4)		C4(1)-F5(1)	1.29 (1)	
S3(2)-S4(2)	3.021 (5)	3.015 (5)	C4(1)-F6(1)	1.28 (1)	
S1(1)-S3(1)	2.986 (5)		C4(2)-F4(2)	1.25 (2)	
S1(2)-S3(2)	3.032 (4)	3.009 (5)	C4(2)-F5(2)	1.23 (1)	
S2(1)-S4(1)	3.034 (5)		C4(2)-F6(2)	1.30 (2)	
S2(2)-S4(2)	2.991 (5)	3.013 (5)	C7(1)-F7(1)	1.32 (1)	
S1(1)-C1(1)	1.763 (9)		C7(1)-F8(1)	1.31 (1)	
S1(2)-C1(2)	1.755 (9)	1.759 (9)	C7(1)-F9(1)	1.23 (1)	
S2(1)-C2(1)	1.701 (9)		C7(2)-F7(2)	1.29 (1)	
S2(2)-C2(2)	1.724 (10)	1.713 (10)	C7(2)-F8(2)	1.32 (1)	
S3(1)-C5(1)	1.703 (9)		C7(2)-F9(2)	1.33 (1)	
S3(2)-C5(2)	1.712 (10)		C8(1)-F10(1)	1.33 (1)	
S4(1)-C6(1)	1.687 (9)		C8(1)-F11(1)	1.33 (1)	
S4(2)-C6(2)	1.723 (10)	1.707 (10)	C8(1)-F12(1)	1.32 (1)	
C1(1)-C2(1)	1.33 (1)		C8(2)-F10(2)	1.21 (2)	
C1(2)-C2(2)	1.30 (1)		C8(2)-F11(2)	1.20 (1)	
C5(1)-C6(1)	1.36 (1)		C8(2)-F12(2)	1.27 (2)	1.29 (1)

Atoms	Angles, deg	Av values, deg	Atoms	Angles, deg	Av values, deg
Fe(1)-S1(1)-Fe(1)'	75.1 (1)		S1(2)-Fe(2)-S4(2)	155.5 (1)	
Fe(2)-S1(2)-Fe(2)'	76.0 (1)	75.6 (1)	S2(1)-Fe(1)-S3(1)	156.8 (1)	
S1(1)-Fe(1)-S1(1)'	104.9 (1)		S2(2)-Fe(2)-S3(2)	155.8 (1)	155.7 (1)
S1(2)-Fe(2)-S1(2)'	104.0 (1)	104.5 (1)	Fe(1)-S1(1)-C1(1)	105.0 (3)	
S1(1)'-Fe(1)-S2(1)	96.4 (1)		Fe(2)-S1(2)-C1(2)	105.2 (3)	
S1(2)'-Fe(2)-S2(2)	98.9 (1)	97.7 (1)	Fe(1)-S2(1)-C2(1)	105.2 (3)	
S1(1)'-Fe(1)-S3(1)	106.7 (1)		Fe(2)-S2(2)-C2(2)	104.5 (4)	105.0 (4)
S1(2)'-Fe(2)-S3(2)	105.2 (1)	106.0 (1)	Fe(1)-S3(1)-C5(1)	106.9 (3)	
S1(1)'-Fe(1)-S4(1)	100.7 (1)		Fe(2)-S3(2)-C5(2)	105.6 (4)	
S1(2)'-Fe(2)-S4(2)	100.4 (1)	100.6 (1)	Fe(1)-S4(1)-C6(1)	106.9 (3)	
S1(1)-Fe(1)-S2(1)	88.6 (1)		Fe(2)-S4(2)-C6(2)	106.0 (4)	106.4 (4)
S1(2)-Fe(2)-S2(2)	88.3 (1)	88.5 (1)	S1(1)-C1(1)-C2(1)	118.1 (7)	
S3(1)-Fe(1)-S4(1)	87.5 (1)		S1(2)-C1(2)-C2(2)	118.9 (8)	118.5 (8)
S3(2)-Fe(2)-S4(2)	87.9 (1)	87.7 (1)	S2(1)-C2(1)-C1(1)	122.5 (7)	
S1(1)-Fe(1)-S3(1)	86.0 (1)		S2(2)-C2(2)-C1(2)	122.6 (8)	122.6 (8)
S1(2)-Fe(2)-S3(2)	87.6 (1)		S3(1)-C5(1)-C6(1)	118.3 (7)	
S2(1)-Fe(1)-S4(1)	87.7 (1)		S3(2)-C5(2)-C6(2)	120.4 (8)	
S2(2)-Fe(2)-S4(2)	86.0 (1)	86.9 (1)	S4(1)-C6(1)-C5(1)	119.8 (7)	
S1(1)-Fe(1)-S4(1)	154.4 (1)		S4(2)-C6(2)-C5(2)	119.3 (8)	119.3 (8)

[a] In our labeling scheme, S1 is the bridging sulfur. S1 and S2 belong to the same dithiolene ligand and are bonded to C1 and C2, respectively. S3 and S4 are bonded to C5 and C6, respectively. C1 and C2 are bonded to C3 and C4, and C5 and C6 are bonded to C7 and C8, respectively. Primes are used to denote equivalent atoms related by symmetry.

complex $[Fe_2(S_2C_2(CN)_2)_4]^{2-}$,[16] which has one more valence electron, has an Fe· · ·Fe separation of 3.07 Å and, therefore, a significantly reduced metal-metal interaction. In the neutral $Co_2(S_2C_2(CF_3)_2)_4$ complex,[15] the metal-metal distance of 2.781 (6) Å is once again in the range suggested for discrete metal-metal bonds despite the fact that it is isoelectronic with $[Fe_2(S_2C_2(CN)_2)_4]^{2-}$ while in the dianionic system $[Co_2(S_2C_6Cl_4)_4]^{2-}$ [30] the Co· · ·Co separation increases to 3.099 (4) Å indicative of little if any metal-metal interaction. When viewed in terms of the number of valence electrons, the results for the dithiolene dimers appear to be inconsistent. However, the results can be rationalized in terms of the overall charges on the dimers. For the more oxidized neutral and monoanionic systems containing strong π-acid ligands such as $S_2C_2(CF_3)_2$, the electron density in the vicinity of the metal atoms is decreased sufficiently to make direct metal-metal interaction favored, whereas for the dianionic systems, the electron density around the metal atoms is greater and the importance of direct metal-metal bonding reduced. Further corroborative support for this notion is received from the recent structure determination of $[Fe_2(edt)_4]^{2-}$ (edt = 1,2-ethanedithiolate) in which the edt ligand is not a π acid and the Fe· · ·Fe separation increases to a nonbonding value of 3.410 (4) Å.[39]

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(38) L. F. Dahl, E. R. deGil, and R. D. Feltham, *J. Amer. Chem. Soc.*, 91, 1653 (1969).

(39) M. R. Snow, personal communication; M. R. Snow and J. A. Ibers, to be submitted for publication.

Table V. A Comparison of the Dimensions of the Dimeric Bis(1,2-dithiolene) Complexes of Co and Fe

	$[Fe_2(S_2C_2(CF_3)_2)_4]^-$	$[Fe_2(S_2C_2(CN)_2)_4]^{2-}$ [a]	$Co_2(S_2C_2(CF_3)_2)_4$ [b]	$[Co_2(S_2C_6Cl_4)_4]^{2-}$ [c]
		Bond distances, Å		
M-S	2.190 (6)	2.23 (1)	2.161 (4)	2.185 (7)
M-S′ [d]	2.311 (3)	2.46 (1)	2.382 (4)	2.404 (7)
M-M′ [e]	2.767 (4)	3.068	2.781 (6)	3.099 (4)
S-C	1.721 (9)	1.73 (3)	1.694 (4)	1.76 (2)
C-C (chelate ring)	1.33 (1)	1.39 (3)	1.39 (1)	1.41 (3)
		Bond angles, Deg		
S-M-S (intra)	88.1 (2)	90.0 (3)	89.8 (2)	90.6 (2)
M-S-C	105.7 (3)	103 (2)	105.5 (2)	104.9 (7)
S-C-C	120.0 (6)	121 (2)	119.3 (2)	119 (2)

[a] Reference 16. [b] Reference 15. [c] Reference 30. [d] Metal-sulfur dimer linkage. [e] Metal-metal distance in the dimeric structure.

Table VI. Principal Intramolecular Distances (Å) and Angles (deg) for $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+$

	Distances		
Fe1(3)-Fe2(3)	3.062 (4)	Fe2(3)-C5(3)	1.81 (1)
Fe1(3)-S1(3)	2.295 (4)	Fe2(3)-C6(3)	1.80 (1)
Fe1(3)-S2(3)	2.305 (3)	S1(3)-C7(3)	1.84 (1)
Fe1(3)-S3(3)	2.310 (3)	S2(3)-C8(3)	1.85 (1)
Fe2(3)-S1(3)	2.310 (4)	S3(3)-C9(3)	1.85 (1)
Fe2(3)-S2(3)	2.303 (4)	C1(3)-O1(3)	1.14 (1)
Fe2(3)-S3(3)	2.307 (4)	C2(3)-O2(3)	1.15 (1)
Fe1(3)-C1(3)	1.79 (1)	C3(3)-O3(3)	1.14 (1)
Fe1(3)-C2(3)	1.77 (1)	C4(3)-O4(3)	1.14 (1)
Fe1(3)-C3(3)	1.80 (1)	C5(3)-O5(3)	1.13 (1)
Fe2(3)-C4(3)	1.80 (1)	C6(3)-O6(3)	1.13 (1)
	Angles		
Fe1(3)-S1(3)-Fe2(3)	83.3 (1)	S1(3)-Fe2(3)-C6(3)	94.1 (4)
Fe1(3)-S2(3)-Fe2(3)	83.3 (1)	S2(3)-Fe1(3)-C1(3)	94.7 (4)
Fe1(3)-S3(3)-Fe2(3)	83.1 (1)	S2(3)-Fe1(3)-C2(3)	171.1 (4)
S1(3)-Fe1(3)-S2(3)	81.5 (1)	S2(3)-Fe1(3)-C3(3)	90.4 (4)
S1(3)-Fe1(3)-S3(3)	80.2 (1)	S2(3)-Fe2(3)-C4(3)	93.8 (3)
S2(3)-Fe1(3)-S3(3)	80.5 (1)	S2(3)-Fe2(3)-C5(3)	171.8 (4)
S1(3)-Fe2(3)-S2(3)	81.2 (1)	S2(3)-Fe2(3)-C6(3)	89.6 (4)
S1(3)-Fe2(3)-S3(3)	80.0 (1)	S3(3)-Fe1(3)-C1(3)	91.2 (4)
S2(3)-Fe2(3)-S3(3)	80.6 (1)	S3(3)-Fe1(3)-C2(3)	94.9 (4)
Fe1(3)-S1(3)-C7(3)	110.4 (4)	S3(3)-Fe1(3)-C3(3)	170.0 (3)
Fe2(3)-S1(3)-C7(3)	109.8 (4)	S3(3)-Fe2(3)-C4(3)	92.4 (4)
Fe1(3)-S2(3)-C8(3)	109.7 (3)	S3(3)-Fe2(3)-C5(3)	94.7 (3)
Fe2(3)-S2(3)-C8(3)	109.3 (3)	S3(3)-Fe2(3)-C6(3)	169.2 (4)
Fe1(3)-S3(3)-C9(3)	110.0 (3)	C1(3)-Fe1(3)-C2(3)	93.0 (5)
Fe2(3)-S3(3)-C9(3)	109.9 (3)	C1(3)-Fe1(3)-C3(3)	93.8 (5)
S1(3)-Fe1(3)-C1(3)	171.1 (4)	C2(3)-Fe1(2)-C3(3)	93.5 (5)
S1(3)-Fe1(3)-C2(3)	90.2 (4)	C4(3)-Fe2(3)-C5(3)	93.2 (5)
S1(3)-Fe1(3)-C3(3)	94.2 (3)	C4(3)-Fe2(3)-C6(3)	92.8 (5)
S1(3)-Fe2(3)-C4(3)	171.5 (4)	C5(3)-Fe2(3)-C6(3)	94.4 (5)
S1(3)-Fe2(3)-C5(3)	91.3 (4)		

The $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+$ Cation. The species $[Fe_2(SCH_3)_3(CO)_6]^+$ has not been reported previously. Its structure is essentially that of two face-shared octahedra in which methylmercapto groups occupy the bridging positions. In Table VI, all of the important intramolecular distances and angles for the cation are tabulated, and in Figure 2, a perspective drawing of the cation is presented. While each iron atom has an essentially octahedral coordination geometry, the symmetry of the entire cation is only C_{3h} by virtue of the orientation of the methyl groups bonded to the bridging sulfur atoms. The average Fe-S distance in the cation is 2.305 (2) Å which agrees with the bridging Fe-S distance of 2.311 (5) Å found in the dithiolene dimer anion and with Fe-S distances reported for 1,1-dithiolato structures[32,34-36] and binuclear μ-mercapto systems.[10-13] Other important bond parameters for the structure are the average Fe-C distance of 1.80 (1) Å, the average C-O distance of 1.14 (1) Å, and the Fe-C-O bond angle of 178.0 (7)° which is not significantly different from the expected value of 180°.

In Table VII, the important structural parameters for a series of mercapto-bridged binuclear iron complexes are summarized. The most important difference between the present structure and others presented in the table involves the much longer Fe-Fe distance of 3.062 (4) Å which we find in the former. This value reflects a considerably reduced metal-metal interaction and leads to our formulation of the cation as containing two Fe(II) d^6 ions in octahedral geometries with essentially no direct metal-metal bond between them. In the way of offering alternative comments, we note that approximately this value has been proposed for an Fe-Fe single bond in $[Fe_2(\mu\text{-}I)_2(NO)_4]$[38] and that 2.925 (4) Å has been proposed by Connelly and Dahl for a *one-electron* metal-metal bond in $[(\pi\text{-}C_5H_5)Fe(\mu\text{-}SCH_3)(CO)]_2{}^+$.[14] If we were to assume the existence of significant metal-metal interaction in the present case, then the cation formulation of this species based on Fe(II) ions is no longer necessary and it is possible to reformulate the entire complex as composed of the two neutral species $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^0$ and $[Fe_2(S_2C_2(CF_3)_2)_4]^0$. We believe, however, that this formulation is unreasonable and we reject it in favor of the cation-anion formulation presented throughout this paper on the following chemical and structural grounds: (1) neutral $Fe_2(S_2C_2(CF_3)_2)_4$ is a good oxidant and one would expect it to oxidize the binuclear system $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]$ which would be one electron over the number needed to satisfy the EAN rule; (2) the complex as reported by Jones, *et al.*,[6] exhibits both reduction and oxidation potentials polarographically—a situation compatible with the monoanionic dithiolene dimer as reported by Balch, *et al.*,[40] but not with the neutral dithiolene dimer; and (3) the energetic reasonableness of two low-spin d^6 metal ions octahedrally coordinated in the cation and separated by over 3 Å with no apparent need for the for-

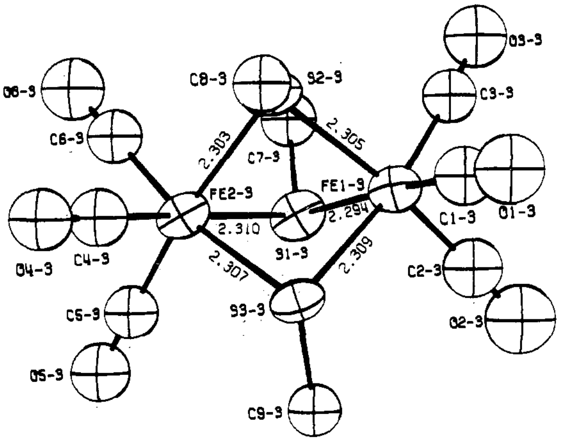

Figure 2. A perspective drawing of the $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+$ cation with its labeling scheme.

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[40] A. Balch, I. G. Dance, and R. H. Holm, *J. Amer. Chem. Soc.*, 90, 1139 (1968).

Table VII. Dimension of Binuclear Mercapto-Bridged Iron Complexes

	Fe–Fe, Å	Fe–S, Å	Fe–S–Fe, deg	S–Fe–S, deg
$[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+$	3.062 (4)	2.305 (2)	83.2 (1)	80.7 (2)
$[C_2H_5SFe(CO)_3]_2$[a]	2.54 (1)	2.259 (7)	68.3 (3)	81.0 (3)
$[Fe(h^5\text{-}C_5H_5)(CO)(SC_6H_5)]_2$[b]	3.39	2.262 (6)	98	81
$[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2^+$[c]	2.925 (4)	2.234 (4)	81.8 (1)	95.4 (1)
$[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$[d]	2.618 (2)	2.218 (2)	72.35 (7)	107.65 (7)

[a] L. F. Dahl and C. H. Wei, *Inorg. Chem.*, 2, 328 (1963). [b] G. Ferguson, C. Hannaway, and K. M. S. Islam, *Chem. Commun.*, 1165 (1968). [c] N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7472 (1970). [d] D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, 9, 2775 (1970).

mation of a metal-metal bond. Finally, at the urging of a merciless referee, we measured the conductivity of the complex.[41] The value of $\Lambda = 50.3$ cm^2 ohm^{-1} M^{-1} which we obtained is in excellent agreement with values reported for known 1:1 electrolytes such as $[AsPh_4][Au(S_2C_2(CF_3)_2)_2]$ and $[(n\text{-}C_4H_9)N][Ni(S_2C_2(CF_3)_2)_2]$ in CH_2Cl_2 solution.[42] The cation-anion formulation of $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+\cdot[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]^+\cdot$ thus established. The referee, though merciless, was correct in his urging.

In closing, it is worthwhile once again pointing out the utility of X-ray structure determination in the characterization of new and complex systems—even if it sometimes takes over 2 years for such studies.

Registry No. $[Fe_2(\mu\text{-}SCH_3)_3(CO)_6]\{Fe_2[S_2C_2(CF_3)_2]_4\}$, 37448-73-0.

Acknowledgments. The research was supported by the National Science Foundation (Grant GP-23139) and by the Advanced Research Projects Agency to which we express our gratitude. We also wish to thank Professor Jon A. McCleverty for a sample of the complex, Dr. Gary Christoph for his help with the direct-methods solution of the structure, and Professor Gene B. Carpenter for his helpful comments.

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[41] The conductivity was measured using a Radiometer CDM2e conductivity meter with a Type CDC104 cell calibrated with 0.10 M KCl solution. The solvent used was CH_2Cl_2 and the concentration was approximately 2×10^{-4} M.

[42] A. Davison, D. V. Howe, and E. T. Shawl, *Inorg. Chem.*, 6, 458 (1967).

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Crystal and Molecular Structure of 1,6,7,8-*Tetrahapto*heptafulveneiron Tricarbonyl, a Heptafulvene Complex of Iron(0) Containing a Trimethylenemethane-Iron Linkage

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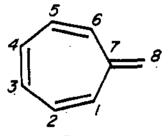
1,6,7,8-*Tetrahapto*heptafulveneiron tricarbonyl, $(C_7H_6CH_2)Fe(CO)_3$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with $a = 6.119$ (2), $b = 6.979$ (2), $c = 24.954$ (7) Å; $\beta = 90.46$ (2)°; $\rho_{\text{obsd}} = 1.514 \pm 0.010$ and $\rho_{\text{calcd}} = 1.521$ g cm^{-3} for $M = 244.03$ and $Z = 4$. X-Ray diffraction data complete to $2\theta = 50°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer and the structure was solved using conventional Patterson, Fourier, and least-squares refinement techniques. All atoms, including hydrogens, were located, the final discrepancy indices being $R_F = 3.41\%$ and $R_{wF} = 4.29\%$ for 1886 independent reflections. The heptafulvene and $Fe(CO)_3$ moieties interact *via* a trimethylenemethane-metal linkage in which Fe–C(central) = 1.946 (2) and Fe–C(peripheral) = 2.120 (3), 2.175 (3), and 2.192 (3) Å.

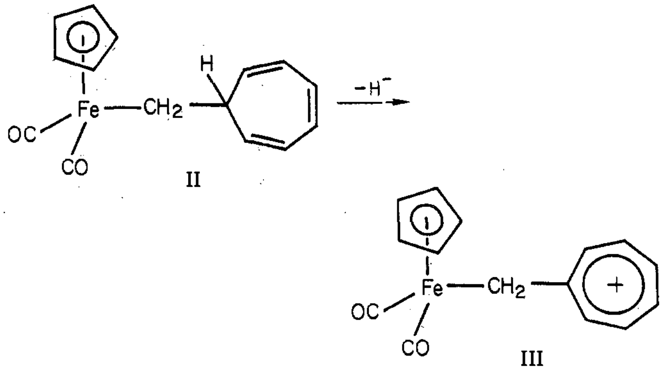
Introduction

Heptafulvene (I) is a conjugated nonbenzenoid hydrocarbon which is stable only in dilute solution at −170°. Attempts to concentrate a solution in propane by evaporation at −60° *in vacuo* resulted only in polymeric products.[1]



I

Kerber and coworkers[2] showed that a cationic heptafulvene derivative of iron(II) could be obtained by β-hydride abstraction from $\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}CH_2C_7H_7)$ (II) using $[(C_6H_5)_3C^+][SbF_6^-]$; a subsequent crystallographic study[3] revealed that the product, $[\pi\text{-}C_5H_5Fe(CO)_2(C_8H_8)^+][SbF_6^-]$, contained a *monohapto* (or σ-bonded) heptafulvene fragment (III).



II

III

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[1] W. von E. Doering and D. W. Wiley, *Tetrahedron*, 11, 183 (1960).

[2] D. J. Ehntholt, G. F. Emerson, and R. C. Kerber, *J. Amer. Chem. Soc.*, 91, 7547 (1969).

[3] M. R. Churchill and J. P. Fennessey, *Chem. Commun.*, 1056 (1970).