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The Molecular Structure of a Tricyclic Complex, [SFe(CO)₃]₂

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A three-dimensional single-crystal X-ray determination of $[SFe(CO)_3]_2$ has revealed the first known example of a transition metal μ-dithio complex with a disulfide group symmetrically bonded to two iron tricarbonyl fragments. The structure thereby represents a new type of transition metal carbonyl complex in which two bonding metals and two nonmetal bridging groups are fused along the bridged atoms to give a heterotricyclic system containing four three-membered rings. The compound contains two dimeric molecules in a triclinic unit cell of symmetry $P\bar{1}$ and of reduced cell parameters $a = 6.63 \pm 0.01$ Å., $b = 7.85 \pm 0.01$ Å., $c = 11.46 \pm 0.02$ Å., $\alpha = 83° 20' \pm 10'$, $\beta = 76° 09' \pm 10'$, $\gamma = 78° 25' \pm 10'$. Three-dimensional anisotropic refinement of all atoms resulted in final discrepancy factors of $R_1 = 10.3\%$ and $R_2 = 10.3\%$ for 1536 observed reflections. The dimeric molecule of idealized C_{2v} symmetry formally can be derived from the intersection of two basal planes of two distorted tetragonal pyramids along the S–S line with a sharp dihedral angle of 59.7°. A "bent" iron-iron bond involving the overlap of two iron orbitals at an angle of 130° is presumed together with the S–S bond to be responsible for the molecular geometry with the remarkably acute S–Fe–S and bridge Fe–S–Fe angles of 53.5° (av.) and 69.9° (av.), respectively. A comparison of the molecular configuration of $[SFe(CO)_3]_2$ with that of $[C_2H_5SFe(CO)_3]_2$ is made, and its structure and bonding are discussed with respect to those given for related μ-peroxo- and acetylene–dimetal complexes.

Introduction

Our interest in $[SFe(CO)_3]_2$ stemmed from previous X-ray studies of the related compounds $[C_2H_5SFe(CO)_3]_2$[2] and $X_2Fe_3(CO)_9$ (X = S, Se).[3] This dinuclear thioiron carbonyl complex and its selenium analog were first prepared and characterized by Hieber and Gruber[4] as diamagnetic solids whose infrared spectra possess only terminal carbonyl type bands. For these two compounds and the related sulfur and selenium dimeric complexes of formula $[XFe(CO)_3]_2$ (where X = SC_2H_5, SeC_2H_5, SC_6H_5), Hieber and Beck[5] later proposed from extensive infrared and dipole moment studies a general molecular configuration of C_{2v} symmetry with a nonplanar (Fe–chalcogen)₂ bridge fragment. A subsequent structural determination[2] of one of the alkyl-substituted chalcogen complexes, $[C_2H_5SFe(CO)_3]_2$, not only confirmed the *idealized* geometry suggested by Hieber and Beck[5] but also yielded detailed molecular parameters consistent with our proposal[6] of a "bent" Fe–Fe bond for these complexes. However, the structural relationship of $[SFe(CO)_3]_2$ to the ethylthio compound remained unclear; no speculation on the difference in the electronic configuration of

$[SFe(CO)_3]_2$ due to the absence of alkyl groups was made by Hieber and Beck. Besides providing an explanation for the bonding and observed diamagnetism, this present research on $[SFe(CO)_3]_2$ has afforded the opportunity for a detailed comparison of the molecular features of these corresponding types of compounds.

Experimental

The compound was prepared from iron pentacarbonyl and sodium polysulfide solution in the way described by Hieber and Gruber.[4] Reddish orange prismatic crystals were separated from the reaction products by sublimation at 40° under vacuum. A suitable single crystal of average width 0.20 mm. and length 0.43 mm. was selected for collecting Weissenberg data, while another crystal of average width 0.27 mm. and length 0.55 mm. was used for obtaining precession data. Since the absorption parameters, μR, of these two crystals are estimated to be 0.30 and 0.38, respectively, no absorption corrections were considered necessary. Both crystals were mounted in thin-walled glass capillaries such that the *a*-axis approximately corresponded to the cylinder axis for each crystal.

Since the crystal system was found to be triclinic, the lattice dimensions of the originally chosen primitive unit cell were transformed to the reduced primitive cell with acute interaxial angles.[7] The lattice parameters for both primitive cells were determined from NaCl-calibrated precession photographs.

Multiple-film equiinclination Weissenberg photographs were obtained with Zr-filtered Mo Kα radiation (λ 0.7107 Å.) for eight reciprocal layers, $0kl$ through $7kl$. In order to minimize the

(1) Fellow of the Alfred P. Sloan Foundation.
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(5) W. Hieber and W. Beck, *ibid.*, **305**, 265 (1960).
(6) L. F. Dahl, C. Martell, and D. L. Wampler, *J. Am. Chem. Soc.*, **83**, 1761 (1961).

(7) *Cf.* L. V. Azaroff and M. J. Buerger, "The Powder Method in X-Ray Crystallography," McGraw-Hill Book Company, Inc., New York, N. Y., 1958, Chapter 11; V. Balashov, *Acta Cryst.*, **9**, 319 (1956).

variations in reflection spot area which occur in upper-layer Weissenberg photographs, the reflections of an entire reciprocal lattice level were collected from only the upper half of the Weissenberg film. This procedure, which eliminates spot compaction (but not spot extension),[8] was accomplished by obtaining two different sets of multiple-film exposures for each layer. Timed-exposure $h0l$ and $hk0$ precession photographs also were obtained with Mo Kα radiation. A total of 1536 independent hkl diffraction maxima were obtained, of which 1504 were recorded from the Weissenberg data while the other 32 additional reflections were supplied only from precession data. These observed intensities were estimated by visual comparison with a set of intensity standards made with the same two crystals and then corrected for the Lorentz and polarization factors.[9] The intensities of the two different sets of multiple films for each reciprocal Weissenberg layer were merged together by comparison of common reflections which overlapped on both film sets. Finally, the corrected intensity data from different Weissenberg layers were correlated with the corrected precession data and placed on a common relative scale. Least-squares refinements of the structure by multiple scale factors (*i.e.*, for each layer the observed data are adjusted to the calculated data by a different scale factor) as well as by one over-all common scale factor were carried out for both the isotropic and anisotropic thermal models in order to assess the possible introduction of systematic error in merging the intensity data.

Results

Unit Cell and Space Group.—Crystals of $[SFe(CO)_3]_2$ are triclinic with reduced cell dimensions $a = 6.63 \pm 0.01$ Å., $b = 7.85 \pm 0.01$ Å., $c = 11.46 \pm 0.02$ Å., $\alpha = 83° 20' \pm 10'$, $\beta = 76° 9' \pm 10'$, $\gamma = 78° 25' \pm 10'$. The volume of a unit cell is 566 Å.^{3}; $\rho_{obsd} = 1.92$ g. cm.$^{-3}$ (obtained by flotation) *vs.* $\rho_{calcd} = 2.02$ g. cm.$^{-3}$ for two dimeric molecules per unit cell. A molecular weight determination carried out with a vapor pressure osmometer (Model 301 A, Mechrolab, Inc.) in chloroform solution (with benzil as a standard) gave an experimental value of 345 *vs.* a calculated value of 343.76. The total number of electrons per unit cell, $F(000) = 336$. The probable space group, P$\bar{1}$(C_i^1), was verified by the satisfactory refinement of the structure found. All atoms occupy the general twofold set of positions (2i): $\pm(x, y, z)$.[10]

Determination of the Structure.—The structural analysis involved the location of two iron, two sulfur, six oxygen, and six carbon atoms which correspond to one dimeric molecule as the asymmetric unit. The other molecule in the unit cell is related by a center of symmetry. A three-dimensional Patterson function was computed from the corrected intensities.[11] The interpretation of the resulting map revealed the positions of the iron and sulfur atoms. With the aid of a block-diagonal least-squares refinement program[12] these trial positional parameters and estimated isotropic temperature factors of 2.0 and 3.0 Å.^{2} for each iron and

sulfur atom, respectively, were refined together with ten scale factors. After two cycles, the unweighted discrepancy factor, $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100\%$, remained at 28.8%; an R_1 value of 37.7% was obtained for only the iron atoms. The phases of the calculated structure factors based on the four iron and sulfur atoms were combined with the observed structure amplitudes (derived from the Lorentz and polarization corrected intensity data by the relationship $|F(hkl)| = I(hkl)^{1/2}$) to compute a three-dimensional Fourier synthesis[11] from which initial atomic coordinates for the six carbon and six oxygen atoms were obtained. Preliminary refinement of these positional and estimated isotropic thermal parameters along with the ten scale factors was carried out again with the Sutton block-diagonal least-squares program[12]; after two cycles an R_1 value of 12.1% was obtained. Subsequent least-squares refinement of all atomic parameters was performed with the Busing–Levy full matrix least-squares program.[13] The isotropic refinement with individual temperature factors and ten scale factors yielded after two cycles final discrepancy factors of $R_1 = 11.9\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma|F_o|^2]^{1/2} \times 100\% = 12.3\%$; the final value of the error of fit function, $[w||F_o| - |F_c||^2/(m - n)]^{1/2}$, was 1.871. After the second cycle all positional parameters shifted within 16% of their individual standard deviations. A subsequent least-squares isotropic refinement with one scale factor produced $R_1 = 13.8\%$, $R_2 = 15.0\%$, and a value of 2.232 for the error of fit function. A complete three-dimensional Fourier difference analysis for the isotropic multiply-scaled data showed no residual peaks greater than 1.4 electrons/Å.^{3} or less than -2.1 electrons/Å.^{3}

To provide a more realistic crystal model from which to obtain more meaningful molecular parameters, an anisotropic refinement was begun with the merged data based on one common scale factor. Individual atom temperature factors of the form

$$\exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$$

were employed. After four cycles all the parameter shifts settled down within 6% of their individual standard deviations. The discrepancy factors were $R_1 = 10.3\%$ and $R_2 = 10.3\%$; the error of fit function was 1.535. An anisotropic refinement of the multiply-scaled data (*i.e.*, ten scale factors) also was carried out and as expected yielded slightly lower discrepancy factors of $R_1 = 9.1\%$ and $R_2 = 8.8\%$ and a value of 1.312 for the error of fit function. A three-dimensional Fourier difference map based on the final anisotropic parameters for the multiply-scaled data resulted in a maximum residual peak height of 0.7 electron/Å.^{3} and a minimum height of -1.1 electrons/Å.^{3} The final positional parameters from the anisotropic refinement with the singly-scaled data are listed in Table I. The final atomic parameters for either the singly-

(8) *Cf.* M. J. Buerger, "X-Ray Crystallography," John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 227–229.

(9) D. L. Smith, "A Data Correction Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix I), University of Wisconsin, 1962.

(10) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 75.

(11) W. G. Sly and D. P. Shoemaker, "Two- and Three-dimensional Crystallographic Fourier Summation Program for the IBM 704 Computer," MIFR1 (1960).

(12) P. W. Sutton, "Acentric Block-Diagonal Least-Squares Program for the CDC 1604 Computer," University of Wisconsin, 1962.

(13) W. R. Busing and H. A. Levy, "A Crystallographic Least-Squares Refinement Program for the IBM 704," Oak Ridge National Laboratory Report 59-4-37 (1959).

TABLE I

FINAL POSITIONAL PARAMETERS AND STANDARD DEVIATIONS
FROM ANISOTROPIC LEAST-SQUARE REFINEMENT WITH ONE
SCALE FACTOR

Atom	x	y	z	σ_x	σ_y	σ_z
Fe_1	0.3614	0.4909	0.2813	0.0003	0.0002	0.0002
Fe_2	0.2113	0.8117	0.2380	0.0003	0.0002	0.0002
S_1	0.0332	0.6215	0.3566	0.0005	0.0004	0.0003
S_2	0.2622	0.6919	0.4172	0.0006	0.0005	0.0003
C_1	0.3897	0.2909	0.3695	0.0026	0.0018	0.0014
C_2	0.3371	0.4016	0.1496	0.0018	0.0017	0.0012
C_3	0.6270	0.5016	0.2261	0.0019	0.0016	0.0014
C_4	0.0470	1.0192	0.2749	0.0025	0.0018	0.0014
C_5	0.1548	0.7981	0.0978	0.0020	0.0016	0.0012
C_6	0.4523	0.8950	0.1770	0.0021	0.0017	0.0014
O_1	0.4114	0.1589	0.4262	0.0020	0.0016	0.0012
O_2	0.3146	0.3478	0.0667	0.0015	0.0014	0.0010
O_3	0.7997	0.5178	0.1860	0.0017	0.0014	0.0010
O_4	−0.0704	1.1451	0.2937	0.0021	0.0018	0.0012
O_5	0.1215	0.7823	0.0059	0.0017	0.0014	0.0009
O_6	0.6012	0.9460	0.1407	0.0020	0.0015	0.0012

and Umeda,[14] for sulfur those of Dawson,[15] and for carbon and oxygen those of Berghuis, *et al.*[16]

The interatomic distances and bond angles and their standard deviations were calculated with the Busing-Levy function and error program.[17] The intramolecular distances for the anisotropic refinement are given in Table IV and the bond angles in Table V.

In order to obtain by a least-squares method the "best" molecular planes formed by certain atoms and the distances of these and other atoms from these planes, the Smith program[18] was modified to fit the triclinic crystal system; the results are given in Table VI. Individual weights were assigned to the atoms which form the planes according to the relation $w_k = [a\sigma(x_k) \cdot b\sigma(y_k)c\sigma(z_k)]^{-2/3}$, where $\sigma(x_k)$, $\sigma(y_k)$, and $\sigma(z_k)$ are the standard deviations in fractional coordinates of the atomic coordinates x_k, y_k, and z_k, respectively. The equation of each least-squares plane is expressed in

TABLE II

FINAL ANISOTROPIC THERMAL COEFFICIENTS ($\times 10^4$) AND ROOT MEAN SQUARE RADIAL THERMAL DISPLACEMENTS

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	Radial thermal displacement, Å.
Fe_1	234 ± 5	112 ± 3	61 ± 2	−31 ± 3	−46 ± 2	7 ± 2	0.34
Fe_2	245 ± 5	94 ± 3	62 ± 2	−27 ± 3	−8 ± 2	−6 ± 2	0.35
S_1	256 ± 9	181 ± 7	65 ± 3	−60 ± 7	12 ± 4	12 ± 4	0.39
S_2	431 ± 13	221 ± 8	61 ± 3	−78 ± 8	−51 ± 5	−22 ± 4	0.43
C_1	484 ± 53	132 ± 27	97 ± 15	−73 ± 31	−85 ± 23	56 ± 17	0.44
C_2	190 ± 31	166 ± 27	86 ± 14	−35 ± 23	−8 ± 17	−0 ± 16	0.39
C_3	203 ± 36	151 ± 25	147 ± 17	−34 ± 24	−90 ± 21	−36 ± 17	0.41
C_4	409 ± 52	149 ± 28	104 ± 16	79 ± 32	−54 ± 24	−19 ± 17	0.45
C_5	319 ± 39	144 ± 26	58 ± 12	−30 ± 26	−30 ± 18	1 ± 14	0.38
C_6	242 ± 37	163 ± 28	143 ± 18	−64 ± 28	−44 ± 22	−24 ± 19	0.43
O_1	522 ± 45	265 ± 28	151 ± 15	−17 ± 29	−70 ± 21	53 ± 17	0.54
O_2	360 ± 33	234 ± 23	106 ± 11	−32 ± 21	−49 ± 16	−69 ± 14	0.45
O_3	284 ± 29	249 ± 24	138 ± 12	−46 ± 22	−56 ± 16	−9 ± 14	0.46
O_4	488 ± 47	292 ± 31	192 ± 19	145 ± 32	−28 ± 24	−20 ± 20	0.58
O_5	488 ± 38	230 ± 23	74 ± 10	−73 ± 23	−43 ± 17	−9 ± 12	0.46
O_6	431 ± 39	214 ± 24	196 ± 16	−157 ± 26	−5 ± 21	23 ± 16	0.53

scaled or multiply-scaled data were invariant within two standard deviations to change from (individual atomic) isotropic to anisotropic thermal factors. The corresponding coordinates for the singly-scaled and multiply-scaled data also did not vary by more than two isotropic standard deviations except for both the x and z coordinates of one carbon atom (C_3), which showed changes of 2–4σ. These results indicate that relatively little systematic error was introduced by merging the data. The coefficients of the anisotropic temperature factor tensors of the atoms for the singly-scaled data are given in Table II. The final observed and calculated structure factors from the last cycle of the anisotropic one-scaled refinement are given in Table III.

Throughout these least-squares refinements, the same variable weights utilized for the least-squares refinement of $[C_2H_5SFe(CO)_3]_2$ were assigned to the observed structure amplitudes as follows.

$$\sqrt{w} = 20/F_o \text{ if } I_o \geq 4I_o \text{ (min.)}$$

$$\sqrt{w} = 1.25I_o^2/F_oI_o \text{ (min.) if } I_o < 4I_o \text{ (min.)}$$

The scattering factors used for iron are those of Thomas

orthogonal coordinates (X, Y, Z) which are related to the triclinic cell coordinates (x, y, z) by the transformation $X = x \sin \gamma + z \cos \varphi$, $Y = y + z \cos \alpha + x \cos \gamma$, and $Z = z \cos \rho$ where $\cos \varphi = (\cos \beta - \cos \gamma \cos \alpha)/\sin \gamma$ and $\cos \rho = (1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)^{1/2}/\sin \gamma$. In this transformation X lies in the xy plane, Y coincides with y, and Z is perpendicular to the xy plane.

Analysis of Anisotropic Thermal Motion.—The three orthogonal principal axes of the ellipsoid of thermal motion were computed[17] from the anisotropic temperature factor coefficients, B_{ij}, given in Table II according to the method described by Busing and Levy.[19] Examination of the root mean square components of thermal displacements and the orientations of the principal axes with the crystallographic axes (not given

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(16) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).
(17) W. R. Busing and H. A. Levy, "A Crystallographic Function and Error Program for the IBM 704," Oak Ridge National Laboratory Report 59-12-3 (1959).
(18) D. L. Smith, "A Least-Square Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.
(19) W. R. Busing and H. A. Levy, *Acta Cryst.*, **11**, 450 (1958).

Table III

Comparison of Observed and Calculated Structure Factors

H	K	L	F_o	F_c
0	1	0	70.3	-81.8
0	3	0	58.9	-58.4
0	4	0	20.6	19.1
0	6	0	40.5	41.9
0	7	0	25.1	-24.3
0	9	0	17.0	-14.3
0	10	0	16.0	15.1
1	0	0	11.7	-9.9
1	1	0	114.4	89.7
1	-1	0	43.8	-34.7
1	2	0	4.5	-3.7
1	-2	0	66.9	-72.2
1	3	0	27.8	-25.4
1	-3	0	51.4	53.6
1	4	0	43.1	-44.7
1	5	0	24.2	23.2
1	-5	0	49.0	52.7
1	6	0	10.8	9.5
1	-6	0	20.1	-21.8
1	7	0	14.4	14.6
1	-7	0	5.4	-6.1
1	-8	0	5.6	-6.3
1	9	0	11.7	-11.8
1	-9	0	13.0	17.3
2	0	0	43.4	-35.9
2	1	0	115.0	90.8
2	-1	0	35.5	-44.0
2	2	0	29.5	39.8
2	-2	0	16.0	17.4
2	3	0	30.8	30.7
2	-3	0	20.8	20.7
2	4	0	42.5	-46.9
2	-4	0	5.6	5.1
2	6	0	13.0	-10.1
2	-6	0	20.5	-21.8
2	7	0	17.6	17.1
2	8	0	16.9	14.2
2	-8	0	14.4	15.8
2	10	0	14.8	-14.4
3	0	0	34.2	29.3
3	1	0	94.1	-73.9
3	-1	0	22.3	-24.1
3	2	0	27.8	28.5
3	-2	0	46.2	47.8
3	3	0	34.4	34.3
3	4	0	7.2	6.1
3	5	0	27.9	-27.6
3	-5	0	17.2	-16.2
3	6	0	10.9	8.5
3	-6	0	5.4	6.6
3	7	0	26.1	-29.2
3	-7	0	12.1	10.0
3	8	0	16.3	17.3
3	-8	0	13.4	14.3
3	-9	0	7.2	-9.0
4	0	0	7.7	-8.3
4	1	0	5.7	6.0
4	-1	0	24.2	26.7
4	2	0	38.4	-47.6
4	-2	0	13.8	-14.5
4	3	0	29.5	32.3
4	-3	0	13.3	11.8
4	4	0	12.0	-9.4
4	-4	0	29.7	-28.2
4	5	0	22.5	22.7
4	-5	0	16.7	16.3
4	6	0	12.5	-10.3
4	-7	0	12.4	12.3
4	8	0	11.0	-8.0
4	9	0	13.2	11.8
5	0	0	26.2	26.0
5	1	0	14.3	14.6
5	-1	0	19.3	-18.8
5	2	0	8.5	-7.8
5	-2	0	11.1	9.5
5	3	0	12.6	-11.7
5	-3	0	24.8	-22.6
5	-4	0	6.7	8.2
5	-5	0	13.7	7.6
5	6	0	11.4	10.1
5	-6	0	6.6	8.3
5	7	0	5.5	-6.5
5	9	0	5.2	-7.0
6	-1	0	16.4	-18.4
6	2	0	9.7	9.6
6	-2	0	7.7	4.9
6	3	0	9.5	-7.7
6	4	0	8.1	-7.7
6	-4	0	11.6	8.5
6	5	0	11.6	-10.2
6	-5	0	5.2	5.6
6	6	0	16.1	15.3
6	8	0	11.4	8.5
7	0	0	13.8	-13.8
7	1	0	9.2	9.4
7	2	0	5.5	-5.3
7	3	0	18.3	19.1
7	-3	0	11.6	9.4
7	4	0	10.5	-9.7
7	6	0	5.3	-6.0
8	4	0	6.1	7.3
0	2	1	27.3	24.5
0	2	-1	12.1	-9.9
0	3	1	27.2	-24.8
0	3	-1	6.6	-4.1
0	4	1	12.7	-10.8
0	4	-1	25.6	22.0
0	5	-1	28.0	27.0
0	6	1	19.6	17.3
0	6	-1	35.0	-33.4
0	7	-1	14.3	-12.8
0	9	1	14.4	-10.3
0	9	-1	18.3	17.6
1	0	1	137.7	-101.7
1	0	-1	128.5	93.8
1	2	1	13.4	11.1
1	2	-1	27.2	25.0
1	-2	1	8.9	8.6
1	-2	-1	89.7	-111.6
1	3	1	10.6	-9.9
1	3	-1	68.9	-68.0
1	-3	1	24.0	20.8
1	-3	-1	43.2	-44.1
1	4	1	37.4	-36.5
1	4	-1	27.3	26.7
1	-4	1	42.8	43.6
1	-4	-1	30.8	30.0
1	5	1	15.1	-14.7
1	5	-1	15.1	14.7
1	-5	1	14.2	-14.0
1	6	1	10.3	-11.6
1	6	-1	28.4	30.1
1	-6	1	25.5	-26.6
1	-6	-1	27.7	28.8
1	7	1	14.5	16.5
1	7	-1	14.9	-15.5
1	-7	1	13.0	10.5
1	-7	-1	10.3	-8.4
1	-8	-1	11.3	-10.5
1	9	1	9.0	9.9
1	10	1	14.6	-17.5
1	10	-1	14.5	17.6
2	0	1	15.2	13.4
2	0	-1	44.8	-36.5
2	-1	-1	12.7	11.9
2	2	-1	6.3	-3.3
2	-2	1	48.9	60.5
2	-2	-1	53.2	-65.1
2	3	1	8.3	8.2
2	-3	1	29.7	-31.8
2	-3	-1	46.9	52.7
2	4	1	43.8	52.9
2	4	-1	26.6	-26.8
2	-4	-1	13.3	14.1
2	5	1	41.2	-46.8
2	5	-1	21.7	21.3
2	-5	1	42.6	-49.8
2	-5	-1	17.5	18.4
2	6	1	19.6	16.2
2	-6	-1	15.3	-17.7
2	7	1	19.5	-18.3
2	7	-1	27.6	30.1
2	-7	1	14.3	14.9
2	-7	-1	12.7	-10.7
2	8	-1	19.7	-19.5
2	-8	1	11.4	11.3
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3	-5	-4	25.1	-24.3
3	6	4	10.1	-10.7
3	-6	-4	18.8	19.6
3	7	4	10.6	-10.1
3	-7	4	11.9	9.9
3	8	4	18.5	19.8
4	0	4	21.2	-24.7
4	1	-4	13.0	11.5
4	-1	4	49.0	53.1
4	-1	-4	27.0	26.8
4	2	4	23.2	-27.4
4	2	-4	13.6	-13.3
4	-2	4	12.2	-11.8
4	-2	-4	12.9	-12.5
4	3	4	17.1	17.0
4	3	-4	11.3	-10.2
4	-4	4	13.8	-12.8
4	-4	-4	15.0	-13.3
4	5	4	25.0	20.9
4	5	-4	16.7	16.2
4	-5	-4	12.7	11.4
4	6	4	19.7	-20.3
4	6	-4	10.4	-9.2
4	-7	4	15.4	14.2
4	8	4	18.9	-18.6
4	9	4	13.4	16.2
5	0	4	30.4	32.3
5	1	4	11.3	-12.2
5	1	-4	7.9	2.8
5	-1	4	10.3	-9.1
5	-1	-4	10.3	7.3
5	2	4	8.2	8.7
5	2	-4	9.4	7.6
5	-2	-4	21.0	-17.4
5	3	4	34.6	-35.3
5	3	-4	13.0	-11.1
5	-3	4	24.5	-21.9
5	4	4	17.0	15.3
5	4	-4	17.5	-15.0
5	-4	4	17.6	14.6
5	5	4	15.0	-14.3
5	5	-4	23.4	19.9
5	6	4	21.6	20.0
5	-6	4	17.3	14.5
5	7	-4	13.2	10.8
5	8	-4	11.9	-8.7
6	0	4	7.9	-9.3
6	0	-4	8.8	6.2
6	1	4	14.8	19.6
6	1	-4	8.5	-6.6
6	-1	-4	11.3	-10.1
6	2	-4	21.6	23.0
6	-2	4	16.4	-16.2
6	3	4	6.2	-5.5
6	3	-4	10.1	-9.3
6	-3	4	9.5	7.8
6	-4	-4	10.8	10.0
6	5	-4	14.0	-12.7
6	-5	4	9.6	4.6
6	7	4	11.0	9.4
7	0	4	15.4	-15.6
7	0	-4	10.4	-7.9
7	1	4	5.4	5.5
7	3	4	6.3	5.7
7	3	-4	11.3	8.7
7	-3	4	9.1	7.6
7	-3	-4	10.8	9.0
7	4	4	11.8	-11.2
7	6	4	14.3	-12.9
7	6	-4	12.0	-8.6
7	7	4	12.3	11.3
0	0	5	15.4	12.1
0	1	5	31.1	27.7
0	1	-5	7.1	-4.4
0	2	5	21.9	-19.6
0	2	-5	57.3	-60.0
0	3	5	23.4	-21.1
0	3	-5	44.9	46.4
0	4	5	32.7	-30.2
0	5	5	10.0	5.7
0	5	-5	16.2	13.9
0	6	-5	11.4	-8.6
0	7	5	20.8	19.2
0	8	5	13.3	-8.1
0	8	-5	15.0	-13.8
0	9	5	13.2	-10.8
0	9	-5	15.8	15.8
1	0	5	46.1	-46.3
1	0	-5	56.0	59.3
1	-1	5	51.0	-51.6
1	-1	-5	42.7	-45.1
1	2	5	45.1	45.0
1	2	-5	31.1	-29.6
1	-2	5	7.7	5.1
1	-2	-5	29.8	28.3
1	3	-5	33.4	-34.4
1	-3	5	29.4	27.5
1	-3	-5	32.8	-33.2
1	4	-5	29.9	29.2
1	-4	-5	15.5	14.8
1	5	5	7.7	-6.6
1	-5	5	10.9	-12.3
1	6	5	23.5	-21.5
1	6	-5	27.6	28.9
1	-6	5	10.1	-8.7
1	-6	-5	18.4	19.7
1	7	5	17.0	18.8
1	7	-5	17.2	-20.0
1	-7	5	14.9	-14.9
1	-7	-5	16.7	-17.9
1	-8	5	14.9	17.1
2	0	5	10.6	-9.8
2	0	-5	19.7	-20.0

here to conserve space) reveals that all the atoms have an anisotropic character. The calculated root mean square radial thermal displacements of the atoms are listed in Table II. Noteworthy is that the *average* carbon and oxygen radial thermal displacement values of 0.45 and 0.56 Å., respectively, for the two apical carbonyls (C_1 and C_4; O_1 and O_4) are greater than the corresponding *average* carbon and oxygen displacement

TABLE III (*Continued*)

The table consists of columns of structure factors, each group headed:

H	K	L	F_o	F_c

(eight such groups of columns of reflection data across the page)

values of 0.40 and 0.48 Å., respectively, for the other four equatorial carbonyl groups. As expected, the radial thermal displacement of each carbonyl oxygen is larger than that of the carbon atom to which the oxygen is bonded.

In order to visualize the thermal motions of the individual carbonyl groups with respect to the molecule, the root mean square components of thermal displacements of each carbon and oxygen atom both along and perpendicular to the Fe–C bond directions were

TABLE IV

MOLECULAR BOND DISTANCES WITH STANDARD DEVIATIONS[a]

Bond	Model A dist., Å.	Model B dist., Å.	Model C dist., Å.
Fe_1-Fe_2	2.552 ± 0.002		2.586 ± 0.002
Fe_1-S_1	2.223 ± 0.004	2.231 ± 0.004	2.262 ± 0.004
Fe_2-S_1	2.222 ± 0.003	2.229 ± 0.004	2.269 ± 0.003
Fe_1-S_2	2.238 ± 0.004	2.253 ± 0.004	2.286 ± 0.004
Fe_2-S_2	2.230 ± 0.004	2.243 ± 0.004	2.280 ± 0.004
S_1-S_2	2.007 ± 0.005		2.060 ± 0.005
Fe_1-C_1	1.768 ± 0.012	1.793 ± 0.014	1.842 ± 0.012
Fe_1-C_2	1.789 ± 0.015	1.790 ± 0.015	1.835 ± 0.014
Fe_1-C_3	1.739 ± 0.013	1.753 ± 0.014	1.793 ± 0.012
Fe_2-C_4	1.802 ± 0.014	1.825 ± 0.015	1.873 ± 0.013
Fe_2-C_5	1.754 ± 0.013	1.763 ± 0.014	1.805 ± 0.013
Fe_2-C_6	1.803 ± 0.007	1.820 ± 0.008	1.862 ± 0.008
C_1-O_1	1.160 ± 0.015	1.186 ± 0.018	1.335 ± 0.014
C_2-O_2	1.137 ± 0.015	1.170 ± 0.017	1.245 ± 0.014
C_3-O_3	1.154 ± 0.015	1.170 ± 0.017	1.272 ± 0.014
C_4-O_4	1.135 ± 0.016	1.186 ± 0.020	1.336 ± 0.015
C_5-O_5	1.152 ± 0.014	1.177 ± 0.016	1.267 ± 0.013
C_6-O_6	1.111 ± 0.013	1.150 ± 0.015	1.273 ± 0.012

[a] The values of model A are uncorrected for thermal motion; the values for models B and C are averaged over thermal motion in which either the second atom is assumed to ride on the first (model B) or the atoms are assumed to move independently (model C).

TABLE V

MOLECULAR ANGLES WITH STANDARD DEVIATIONS IN DEGREES

Angle	
$S_1-Fe_1-S_2$	53.48 ± 0.14
$S_1-Fe_2-S_2$	53.58 ± 0.14
$Fe_1-S_1-Fe_2$	70.08 ± 0.11
$Fe_1-S_2-Fe_2$	69.67 ± 0.12
$Fe_1-S_1-S_2$	63.64 ± 0.16
$Fe_1-S_2-S_1$	62.88 ± 0.15
$Fe_2-S_1-S_2$	63.42 ± 0.15
$Fe_2-S_2-S_1$	63.01 ± 0.14
$Fe_1-C_1-O_1$	178.9 ± 1.5
$Fe_1-C_2-O_2$	177.6 ± 1.1
$Fe_1-C_3-O_3$	176.0 ± 1.2
$Fe_2-C_4-O_4$	173.6 ± 1.5
$Fe_2-C_5-O_5$	177.3 ± 1.2
$Fe_2-C_6-O_6$	179.2 ± 1.5
$S_1-Fe_1-C_1$	103.9 ± 0.6
$S_2-Fe_1-C_1$	103.9 ± 0.5
$S_1-Fe_2-C_4$	103.3 ± 0.5
$S_2-Fe_2-C_4$	102.6 ± 0.5
$S_1-Fe_1-C_2$	103.0 ± 0.4
$S_2-Fe_1-C_3$	102.0 ± 0.4
$S_1-Fe_2-C_5$	102.6 ± 0.4
$S_2-Fe_2-C_6$	101.6 ± 0.5
$S_1-Fe_1-C_3$	149.8 ± 0.4
$S_2-Fe_1-C_2$	151.9 ± 0.4
$S_1-Fe_2-C_6$	151.1 ± 0.4
$S_2-Fe_2-C_5$	151.2 ± 0.4
$C_2-Fe_1-C_3$	93.9 ± 0.6
$C_5-Fe_2-C_6$	95.3 ± 0.6
$C_1-Fe_1-C_2$	96.2 ± 0.7
$C_1-Fe_1-C_3$	98.8 ± 0.7
$C_4-Fe_2-C_5$	98.6 ± 0.6
$C_4-Fe_2-C_6$	96.2 ± 0.7

computed. The values perpendicular to the Fe–C bond directions were obtained by averaging four root mean square components of thermal displacement of the atom along the neighboring two Fe–C and two Fe···O bond directions, since all the C–Fe–C angles are be-

TABLE VI

EQUATION OF MOLECULAR PLANE AND DISTANCES (Å.) OF ATOMS FROM THESE PLANES[a]

(a) Plane through S_1, S_2, C_2, and C_3

$$-0.208X + 0.757Y - 0.620Z - 1.403 = 0$$

S_1	0.002	C_3	0.031	O_3	0.36
S_2	−0.003	Fe_1	−0.34	C_1	−2.10
C_2	−0.028	O_2	0.19	O_1	−3.25

(b) Plane through S_1, S_2, C_5, and C_6

$$0.583X - 0.755Y - 0.302Z + 4.621 = 0$$

S_1	−0.001	C_6	−0.016	O_6	0.17
S_2	0.002	Fe_2	−0.32	C_4	−2.09
C_5	0.014	O_5	0.29	O_4	−3.19

(c) Plane through Fe_1, Fe_2, and the midpoints of S_1-S_2

$$-0.816X - 0.471Y - 0.336Z + 5.804 = 0$$

S_1	1.02	C_2	1.32	C_5	1.29
S_2	−1.02	C_3	−1.29	C_6	−1.37
C_1	0.03	O_2	2.19	O_5	2.14
O_1	−0.06	O_3	−2.14	O_6	−2.23
C_4	−0.01				
O_4	0.11				

(d) Plane through S_1, and S_2, and the midpoint of Fe_1-Fe_2

$$-0.454X + 0.872Y - 0.182Z - 3.487 = 0$$

Fe_1	−1.26	O_1	−3.90	O_2	−1.73
Fe_2	1.26	O_4	3.87	O_5	1.67
C_1	−2.85	C_2	−1.57	C_3	−1.49
C_4	2.86	C_5	1.54	C_6	1.57
				O_3	−1.57
				O_6	1.76

[a] X, Y, and Z are orthogonal coordinates expressed in Å.

tween 90 and 100° and all the Fe–C–O angles are close to 180° (as shown in Table V). In general, the root mean square displacements of both the carbon and the oxygen atoms perpendicular to the Fe–C bond directions (*i.e.*, average perpendicular displacements are 0.25 Å. for carbon and 0.30 Å. for oxygen) are greater than those along the Fe–C bond directions (*i.e.*, average parallel displacements are 0.20 Å. for carbon and 0.23 Å. for oxygen), with the greatest observed differences in magnitude occurring for the apical carbonyl atoms (*i.e.*, average displacements are 0.29 Å. *vs.* 0.17 Å. for carbon and 0.36 Å. *vs.* 0.24 Å. for oxygen).

Although it must be emphasized that these thermal calculations at most are qualitative due to the accumulation of systematic errors in the anisotropic thermal coefficients, of interest is that the values of the root mean square components of thermal displacement and of the root mean square radial thermal displacements (Table III) compare favorably with the corresponding values reported for the carbonyl groups in $Mn_2(CO)_{10}$.[20]

Bond distances based on the singly-scaled anisotropic least-squares refinement were averaged over thermal motion as provided by the Busing–Levy function and error program.[17] For model B the second atom with the greater thermal ellipsoid is assumed to ride on the first atom, while for model C the atoms are assumed to move independently. The intramolecular bond distances for these models are listed in Table IV together with the corresponding distances obtained from the thermally uncorrected anisotropic (model A) refinement.

(20) L. F. Dahl and R. E. Rundle, *Acta Cryst.*, **16**, 419 (1963).

All bond lengths obtained from the thermally uncorrected anisotropic refinement (model A) are within two isotropic standard deviations of those calculated from the isotropic multiply-scaled refinement except for only three values (*viz.*, Fe_1-C_3, Fe_1-C_4, and C_4-O_4), each of which differs by less than 3σ. For model B the changes in bond lengths from the thermally uncorrected anisotropic values are all less than 4σ, while for model C the increases in the bond lengths are unrealistically large. These changes due to thermal motion are similar to those reported for $Mn_2(CO)_{10}$ based on the application of the same thermal models.[20] Both of these thermal models (B and C), however, are rejected for [SFe(CO)₃]₂ in favor of those with no thermal corrections for the same reasons as discussed in the case of $Mn_2(CO)_{10}$.[20] Neither of these models is believed to possess physical significance for these transition metal carbonyl complexes. The bonded atoms certainly do not move independently in the crystal, and the "piggy-back model" is not applicable for the carbonyl groups. For these reasons, the preferred values of the thermally uncorrected anisotropic model are employed hereafter in the discussion of the molecular parameters.

Discussion

Crystalline [SFe(CO)₃]₂ consists of discrete dimeric molecules of the configuration shown in Figure 1. As suggested by Hieber and Beck,[5] the over-all molecular geometries of [SFe(CO)₃]₂ and the corresponding fragment in [C₂H₅SFe(CO)₃]₂ are similar with both possessing *idealized* C_{2v} symmetry. The configuration also is compatible with our previous proposal of a bent Fe–Fe bond.[6]

In a molecular unit of [SFe(CO)₃]₂ the two irons, related to each other by an *idealized* mirror plane, are each coordinated to three carbonyl groups and two sulfurs which are located at the corners of a distorted tetragonal pyramid. The degree of distortion of these five ligands about each iron from a regular tetragonal pyramid is revealed by a calculation of the "best" basal plane (comprised of the two sulfurs and two carbonyls) as given in Table VI, (a) and (b). Both iron atoms are displaced by 0.34 and 0.32 Å. from their respective basal planes in directions toward their apical carbonyls; for [C₂H₅SFe(CO)₃]₂ the corresponding displacements are slightly greater (0.38 Å. for both irons). The dimeric molecule of [SFe(CO)₃]₂ then results from the junction of the two basal planes along the S–S line at a sharp dihedral angle of 59.7° (compared to 69.5° for [C₂H₅SFe(CO)₃]₂).

The *idealized* molecular C_{2v} symmetry of [SFe(CO)₃]₂ is verified by a calculation of the two molecular mirror planes (Table VI, (c) and (d)) which are approximately perpendicular to each other (dihedral angle 88.8°). One mirror plane (Table VI, (c)) is defined by atoms Fe_1, Fe_2, and the midpoint of S_1 and S_2, while the other mirror plane (Table VI, (d)) passes through S_1, S_2, and the midpoint of Fe_1 and Fe_2. Examination of the perpendicular distances of the
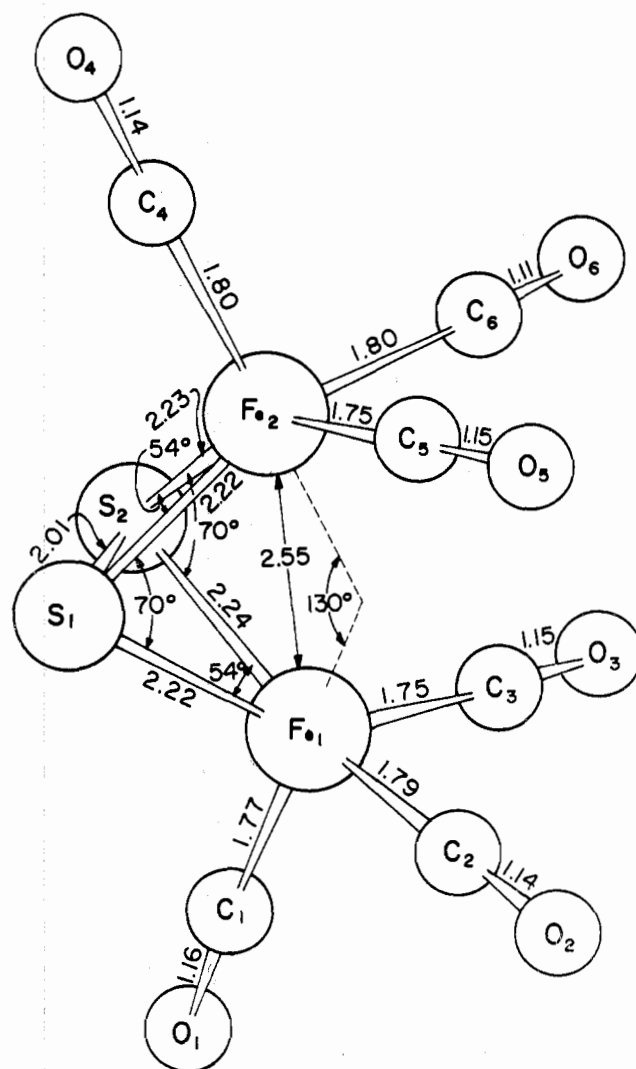

Figure 1.—The molecular structure of [SFe(CO)₃]₂.

pairs of equivalent atoms resulting from these symmetry planes establishes the corresponding atoms to be essentially equidistant on opposite sides of the mirror planes. The twofold axis in the third direction is generated from the intersection of the two perpendicular mirror planes.

Of prime significance (particularly since not predicted by Hieber and Beck) is that this structural determination revealed that the diamagnetism of [SFe(CO)₃]₂ is achieved in the absence of alkyl groups by the formation of a S–S bond in which the S–S distance has decreased from a nonbonding value of 2.932 ± 0.014 Å. for the ethylthio compound to a bonding value of 2.007 ± 0.005 Å. The resulting configuration is a new type of transition metal carbonyl complex in which the two bonding metals and two nonmetal bridging groups are fused along the bridged atoms to give a heterotricyclic system containing four three-membered rings.

The resemblance of the molecular configurations of [SFe(CO)₃]₂ and [C₂H₅SFe(CO)₃]₂ is clearly illustrated in Figure 2, and a comparison of their molecular parameters is summarized in Table VII. Note that the standard deviations of the molecular bond distances
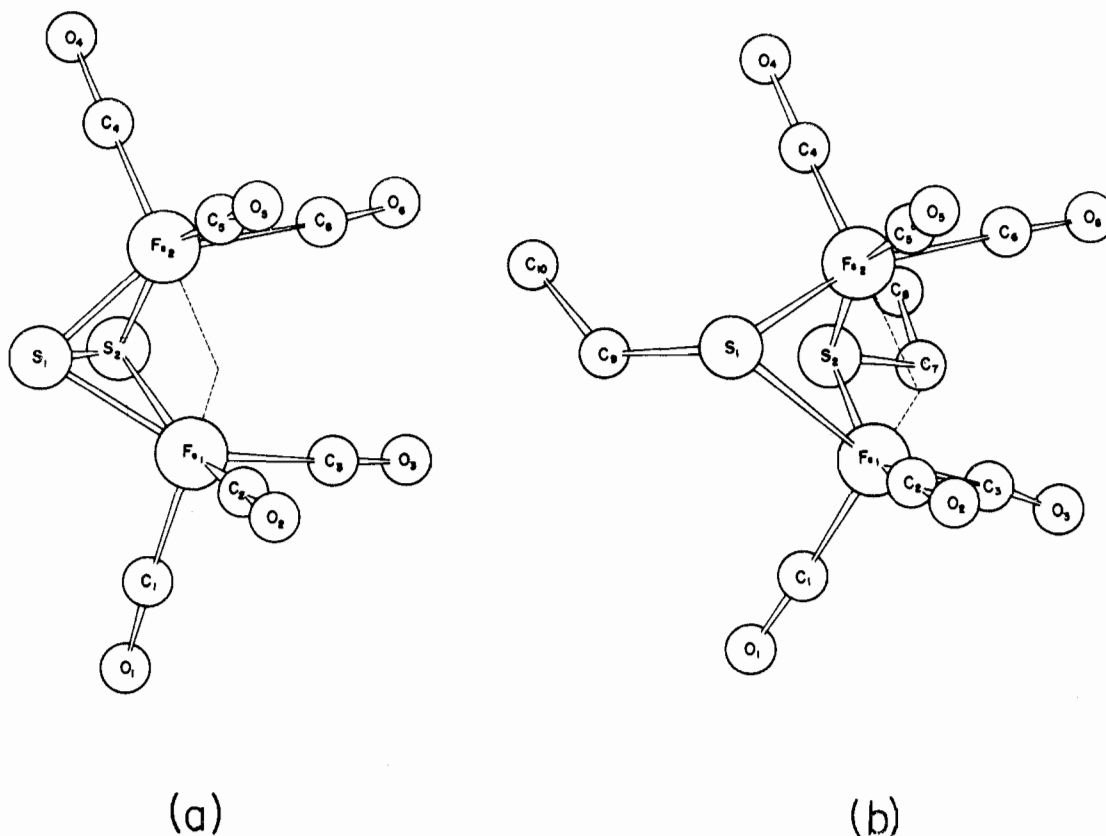
Figure 2.—Comparison of molecular configurations of [SFe(CO)₃]₂ (a) and [C₂H₅SFe(CO)₃]₂ (b).

and angles of [SFe(CO)₃]₂ are much lower than those determined for [C₂H₅SFe(CO)₃]₂. The Fe–Fe bonding distance is invariant to the conformational change of the [SFe(CO)₃]₂ moiety, being 2.552 ± 0.002 and 2.537 ± 0.010 Å. in the thio and ethylthio compounds, respectively. However, the mean Fe–S distance has decreased from 2.259 ± 0.007 Å. for the ethylthio compound to 2.228 ± 0.002 Å. for the thio compound. The sharp bridge Fe–S–Fe bond angles formed in [C₂H₅SFe(CO)₃]₂ (68.3 ± 0.3° (av.)) are retained in [SFe(CO)₃]₂ (69.9 ± 0.1° (av.)). Of theoretical importance is that with the much shorter S–S distance for [SFe(CO)₃]₂, the S–Fe–S angle has decreased from an average value of 81.0 ± 0.3° for the ethylmercapto complex to the remarkably acute average value of 53.5 ± 0.1° for the thio compound. *This angle of 53.5° is the smallest known for a metal carbonyl complex with two bridged atoms symmetrically linked to a metal atom by presumed normal electron-pair bonds (vide infra).* Another direct consequence of this large decrease (of approximately 0.9 Å.) in the S–S distance in forming the tricyclic system in [SFe(CO)₃]₂ with essentially no change in the Fe–Fe and Fe–S distances and Fe–S–Fe bridge angle is the angular deformation of the nonplanar Fe₂S₂ fragment; this distortion is such that the dihedral angle between the two planes formed by the two bridge sulfurs and one iron has decreased from 95.2 ± 0.5° in the ethylmercapto compound to 79.8 ± 0.1° in the thio compound.

A bent metal–metal bond involving the overlap of two iron orbitals at an angle of 130° is presumed (to-

TABLE VII
COMPARISON OF MOLECULAR PARAMETERS OF [SFe(CO)₃]₂ AND [C₂H₅SFe(CO)₃]₂

Bond	[SFe(CO)₃]₂ length, Å.	[C₂H₅SFe(CO)₃]₂ length, Å.
Fe–Fe	2.552 ± 0.002	2.537 ± 0.010
Fe–S	2.228 ± 0.002 (av.)	2.259 ± 0.007 (av.)
S–S	2.007 ± 0.005	2.932 ± 0.014
Fe–C	1.776 ± 0.005 (av.)	1.81 ± 0.02 (av.)
C–O	1.142 ± 0.006 (av.)	1.15 ± 0.02 (av.)
Angle	Degrees	Degrees
Fe–S–Fe	69.9 ± 0.1° (av.)	68.3 ± 0.3° (av.)
S–Fe–S	53.5 ± 0.1° (av.)	81.0 ± 0.3° (av.)
a	79.8 ± 0.1°	95.2 ± 0.5°

ᵃ Dihedral angle between two planes each formed by the two bridge sulfurs and one iron.

gether with the S–S bond) to be responsible for the molecular geometry of [SFe(CO)₃]₂. This angle of metal–metal overlap was obtained from the assumption that the participating metal orbital for each iron is collinear with the iron apical carbonyl. The value of 130°, obtained both for the presumed intersections of the Fe₁–C₁ and Fe₂–C₄ vectors and the Fe₁–O₁ and Fe₂–O₄ vectors, is significantly larger than the corresponding *average* angle of 113° for the assumed "bent" metal–metal bond in [C₂H₅SFe(CO)₃]₂, since the angular deformation of the nonplanar Fe₂S₂ fragment is greater for [SFe(CO)₃]₂ (*i.e.*, see earlier part of discussion for comparison of dihedral angles).

The S–S bond distance of 2.007 ± 0.005 Å., which represents the first known value for a metal complex involving two bridging sulfur atoms directly bonded
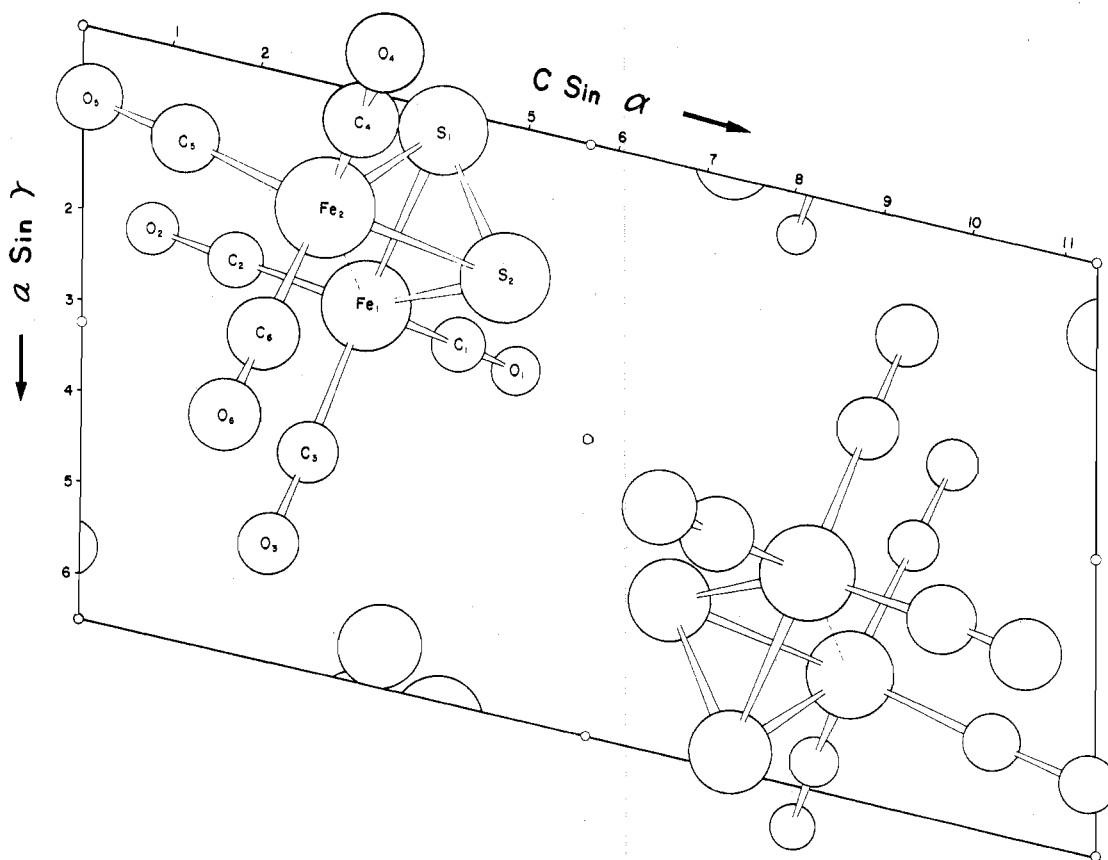
Figure 3.—[010] projection of the unit cell.

to two common metal atoms, is in general agreement with S–S distances found for S_8 (2.037 ± 0.005 Å.),[21] S_2Cl_2 (2.04 ± 0.05 Å. and 2.05 ± 0.03 Å.),[22,23] S_2H_2 (2.05 ± 0.02 Å.),[24] $(CH_3)_2S_3$ (2.04 ± 0.02 Å.),[25] $(CF_3)_2$-S_2 (2.053 ± 0.019 Å.),[26] and $(CF_3)_2S_3$ (2.065 ± 0.016 Å.).[26]

Although all Fe–C and C–O bond distances possess relatively low individual standard deviations (see Table IV), no significant differences are observed between the apical and basal carbonyl bond lengths. The *mean* Fe–C and C–O bond lengths for the six Fe–CO groups of 1.776 ± 0.005 Å. and 1.142 ± 0.006 Å., respectively, are reasonably close to the *mean* Fe–C and C–O values of 1.81 ± 0.02 Å. and 1.15 ± 0.02 Å., respectively, found for $[C_2H_5SFe(CO)_3]_2$ and compare well with other reported Fe–C and C–O values.[2] All six Fe–C–O bond angles do not deviate significantly from linearity (within the range of 6°).

Figure 3 illustrates the [010] projection of the two dimeric molecules in the unit cell and also indicates the packing as required by the space group P$\bar{1}$. The intermolecular distances less than 3.5 Å. are listed in Table VIII. These values, all of which are greater then 3.00 Å., are similar to those found for $[C_2H_5SFe(CO)_3]_2$[2] and again strongly suggest that van der Waals forces are primarily responsible for the interactions between molecules.

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(22) P. G. Ackermann and J. E. Mayer, *J. Chem. Phys.*, **4**, 377 (1936).
(23) K. J. Palmer, *J. Am. Chem. Soc.*, **60**, 2360 (1938).
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(25) J. Donohue and V. Schomaker, *J. Chem. Phys.*, **16**, 92 (1948).
(26) H. J. M. Bowen, *Trans. Faraday Soc.*, **50**, 452 (1954).

TABLE VIII

INTERMOLECULAR DISTANCES LESS THAN 3.5 Å.^{a}

Atoms	Distance, Å.	Atoms	Distance, Å.
$S_1 \cdots O_3^I$	3.04	$C_2 \cdots O_3^I$	3.43
$O_1 \cdots O_1^{III}$	3.04	$O_2 \cdots C_6^{IV}$	3.44
$O_2 \cdots O_3^{IV}$	3.18	$O_5 \cdots O_3^I$	3.44
$O_5 \cdots O_3^{IV}$	3.29	$C_5 \cdots O_3^I$	3.44
$O_2 \cdots O_6^{IV}$	3.38	$O_2 \cdots O_6^{II}$	3.47
$O_2 \cdots C_3^{IV}$	3.38	$O_5 \cdots O_6^I$	3.48
$O_2 \ldots O_3^I$	3.42		

^{a} Superscripts refer to the following positions. I: $-1 + x$, y, z; II: x, $-1 + y$, z; III: $1 - x$, $-y$, $1 - z$; IV: $1 - x$, $1 - y$, $-z$.

The structure of $[SFe(CO)_3]_2$ represents the first known example of a transition metal μ-dithio complex. Two formal representations of the σ-orbital bonding arrangement can be advanced for the compound. In one description each iron atom is assumed to be in a trigonal bipyramidal hybridized state with one sp²-hybrid directed in the trigonal plane toward the midpoint of the S–S bond. In the other formulation each iron is assumed to possess octahedral valency with two σ-type orbitals directed toward the bridged S_2 group in which the sulfur atoms assume tetrahedral character. In the past, both descriptions have been utilized for understanding the bonding in related compounds. A detailed examination of the structures and orbital descriptions for the compounds cited below can provide some insight into the nature of bonding of $[SFe(CO)_3]_2$.

From X-ray work[27] it has been reported that in the paramagnetic μ-peroxodicobalt cation, $[(NH_3)_5Co-$

(27) C. Brosset and N. Vannerberg, *Nature*, **190**, 714 (1961).

$O_2-Co(NH_3)_5]^{5+}$, the monobridged O_2 group has its axis perpendicular to a line connecting the two metals. The cation possesses *idealized* D_{2h} symmetry and can be viewed to result from the intersection of two octahedra at a common apex perpendicular to the O_2-bridged axis such that the two sets of four equatorial nitrogen ammine ligands are arranged in an eclipsed configuration with each other but in a staggered array with respect to the O–O axis. The extensive delocalization of the one unpaired electron over the entire [Co–O$_2$–Co] fragment of the cation was unambiguously established from its paramagnetic resonance absorption spectra in solution, which showed the unpaired electron to interact equally with both cobalt nuclei.[28,29] The same conclusion was previously suggested from a single-crystal ultraviolet dichroism study.[30] Of interest is that Vlček[31] predicted the foregoing structure on the basis of a qualitative molecular orbital treatment prior to the X-ray work. Vlček[31] pointed out that his LCAO–MO bonding description, which presumes localized octahedral metal valency with σ-type metal orbitals directed toward the center of the O_2 group (which thereby occupies one coordination site), is formally analogous to that given for metal–olefin complexes. However, Vlček's model, which assigns the unpaired electron to an antibonding π-type orbital extending over the cobalt atoms, more nearly approximates symmetrywise the interaction of an acetylene with two metal atoms. A coplanar monobridged system involving two metal atoms and an acetylene group is unreported to date, but nonplanar dimetal–acetylene systems are known (*vide infra*).[32–36]

Vlček[31] also considered the MO bonding of the dibridged type cation, $[(NH_3)_4Co\cdot\mu\text{-}(NH_2,O_2)\cdot Co\text{-}(NH_3)_4]^{4+}$. Here again, octahedral valency of the Co orbitals was invoked with one σ-orbital directed toward the bridging NH$_2$ group and another toward the center of the bridging peroxy group for which the O–O axis was assumed to be perpendicular to the line of the two Co atoms. The as yet unestablished structure of this binuclear cationic complex can be considered as the junction of two octahedra along a common edge with the O_2 group again symmetrically occupying one coordination site to give *idealized* C_{2v} symmetry. Its paramagnetic resonance spectrum[29] corroborates the electronic equivalence of the two cobalt atoms and hence is compatible with Vlček's proposed structure and bonding.[31] Vlček found that the group-overlap integral values calculated for the nonlinear [Co–O$_2$–Co] fragment were larger (under the same assumptions)

than those obtained for the linear monobridged complex. The fact that μ-peroxo complexes with an additional bridge are more stable with respect to splitting off the oxygen than those with the O_2 bridge only was cited by Vlček[31] as being in agreement with his rationalization of increased stability for a bent [Co–O$_2$–Co] conformation.

A trigonal bipyramidal model with an sp^2 hybrid orbital of each metal directed in a trigonal plane toward the midpoint of a bridged acetylene group was preferably adopted over the octahedral valency model for each metal by Brown[37] in his MO description of the structure of the binuclear metal acetylene complex, $(C_6H_5C_2C_6H_5)Co_2(CO)_6$. The molecular configuration[33] of $(C_6H_5C_2C_6H_5)Co_2(CO)_6$ also possesses *idealized* C_{2v} symmetry and is essentially identical with that for [SFe(CO)$_3$]$_2$ with the substitution of a $C_6H_5C_2C_6H_5$ group for the S$_2$ fragment. Brown[37] rejected the octahedrally hybridized metal model, in which two σ-type lobes are directed from each cobalt toward the two acetylene carbon atoms, since he concluded that the molecular parameters from the X-ray data[33] do not conform to tetrahedral hybridization of the carbon atoms.

Of consequence to the discussion of bonding in these two isoelectronic carbonyl complexes is that in order for each metal to achieve the so-called "inert gas" configuration, the S$_2$ group in [SFe(CO)$_3$]$_2$ functions as a three-electron donor to each iron atom as contrasted to the acetylene moiety in $(C_6H_5C_2C_6H_5)Co_2(CO)_6$[32,33] and $(RC_2R)Ni_2(C_5H_5)_2$[34–36] which in both these compounds effectively donates two electrons to each metal atom.

We do not question the MO treatments of either Vlček[31] or Brown,[37] each of whom assumed σ-type metal orbitals directed toward the center of the bridged X$_2$ group. However, we feel that the electron-density distribution of [SFe(CO)$_3$]$_2$ obtained from a *rigorous* MO calculation (which at present is not feasible), without the assumption of hybridized orbitals to constrain the weighting coefficients of the AO's, will more nearly conform to that of the octahedral metal valency.[38]

This conceptual octahedral model is essentially identical with that given for [C$_2$H$_5$SFe(CO)$_3$]$_2$ with each bridging sulfur atom again possessing an approximately tetrahedral arrangement of three bonding pairs and one lone pair of electrons, which, of course, are directed differently from those of the corresponding ethylmercaptoiron complex. Although our choice is based mainly on intuitive grounds, it does not seem unreasonable for the following reasons. The average

(28) I. Bernal, E. A. V. Ebsworth, and J. A. Weil, *Proc. Chem. Soc.*, 57 (1959).

(29) E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959); G. L. Goodman, H. G. Hecht, and J. A. Weil, "Free Radicals in Inorganic Chemistry," Advances in Chemistry Series, No. 36, American Chemical Society, Washington, D. C., 1962, pp. 90–97.

(30) S. Yamada, Y. Shimura, and R. Tsuchida, *Bull. Chem. Soc. Japan*, **26**, 72 (1953).

(31) A. A. Vlček, *Trans. Faraday Soc.*, **56**, 1137 (1960).

(32) H. Greenfield, H. W. Sternberg, R. A. Friedel, J. H. Wotiz, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **78**, 120 (1956).

(33) W. G. Sly, *ibid.*, **81**, 18 (1959).

(34) J. F. Tilney-Bassett and O. S. Mills, *ibid.*, **81**, 4757 (1959).

(35) M. Dubeck, *ibid.*, **82**, 502 (1960).

(36) J. F. Tilney-Basset, *J. Chem. Soc.*, 577 (1961).

(37) D. A. Brown, *J. Chem. Phys.*, **33**, 1037 (1960).

(38) If the electronic configuration of the S$_2$ fragment is considered as analogous to that of O$_2$ such that the relative energies of the presumably zerovalent iron d-orbitals are closer to the half-filled S$_2$-antibonding π-orbitals (possible mixing with the unfilled 3d sulfur orbitals is neglected) than to the filled S$_2$-bonding orbitals, greater delocalization of the electrons would occur from the antibonding sulfur orbitals to the appropriate iron orbitals. One then can rationalize that the bond order of the S–S bond should increase with a resulting decrease in S–S bond length. Noteworthy is that the S–S distance of 2.007 ± 0.005 Å. in [SFe(CO)$_3$]$_2$ is slightly shorter than other reported S–S bond lengths (given in the earlier part of the discussion).

value of 94.6° for the two equatorial C–Fe–C bond angles in [SFe(CO)$_3$]$_2$, which is somewhat larger than the corresponding average value of 88.7° in [C$_2$H$_5$-SFe(CO)$_3$]$_2$,[2] is much nearer the *idealized* magnitude of 90° expected for octahedral metal valency rather than the *idealized* value of 120° based on the trigonal bipyramidal metal valency. The similarly sharp Fe–S–Fe angles (Table VII) of approximately 69° for both the thio- and ethylthioiron carbonyl complexes suggest a similar Fe–S electronic interaction. Both these angles and the more acute S–Fe–S angles of average value 53.5 ± 0.1° for [SFe(CO)$_3$]$_2$ necessitate "bent" Fe–S bonds in order for each of the iron and sulfur atoms to utilize *two equivalent* orbitals in forming electron-pair bonds with one another. It should be emphasized that both theoretical models are only approximations. This discussion has neglected all refinements of these two extreme bonding representations, but nevertheless its purpose is to give some idea of the structural relationships of these type compounds.

Other isoelectronic dimeric carbonyl complexes with presumably similar configurations to that of [SFe(CO)$_3$]$_2$ include the recently prepared [HNFe(CO)$_3$]$_2$[39]

(39) W. Hieber and H. Beutner, *Z. Naturforsch.*, **15b**, 324 (1960).

and the as yet unreported [RPFe(CO)$_3$]$_2$ (R = H, alkyl, aryl group). This structural investigation certainly suggests that S$_2$ groups can be incorporated into other metal complexes as bridging groups (with a three-electron donor capacity per metal) to produce a number of new type compounds (*e.g.*, [SCoC$_5$H$_5$]$_2$ and [SFe(NO)$_2$]$_2$ with metal-metal bonds and the corresponding analogs [SNiC$_5$H$_5$]$_2$ and [SCo(NO)$_2$]$_2$ without metal-metal bonds). Finally, it is tempting to speculate that under appropriate conditions it may be possible to prepare nonbridging dithio complexes.

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Transition Metal Ion Complexes of Tetramethylguanidine

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Tetramethylguanidine (TMG), HNC[N(CH$_3$)$_2$]$_2$, complexes of Co(II), Cu(II), Zn(II), Pd(II), Ni(II), and Cr(III) are described. The assignment of the C=N stretching frequency of TMG in the infrared region is discussed and evidence is presented to indicate that the imine nitrogen is the donor site in the compounds reported. The conductance of each complex is evaluated. Spectral and magnetic data obtained for [Co(TMG)$_4$](ClO$_4$)$_2$ suggest that this complex is tetrahedral. Spectroscopic studies leading to the evaluation of the ligand field parameters Δ, β, and B' were carried out. A very large Δ value, 4454 cm.$^{-1}$, is obtained. The similarity in the X-ray powder diffraction patterns of [Cu(TMG)$_4$](ClO$_4$)$_2$ and [Zn(TMG)$_4$](ClO$_4$)$_2$, the latter being a tetrahedral complex, indicates that these compounds have similar configurations. Distortions are expected in the copper complex. Magnetic and spectroscopic data are presented for the copper(II) compound.

Introduction

In earlier articles,[2–5] the geometry and coordination number of complexes formed by several nonaqueous solvents were investigated and the positions of these solvents in the spectrochemical series were determined. Because of the multiplicity of coordination positions and the strongly basic character of tetramethylguanidine, HN=C[N(CH$_3$)$_2$]$_2$, this material is an interesting nonaqueous solvent. Consequently, it was of interest to prepare some complexes of this material, to determine their structure, and to locate tetramethylguanidine in the spectrochemical series. Transition metal

ion complexes of TMG have not been previously reported.

Experimental

Chemicals and Purification of Materials.—All of the chemicals used in this research are commercially available. Some of the less common were obtained from the following sources: Metal perchlorates, G. F. Smith Chemical Co., Columbus, Ohio; anhydrous nickel(II) iodide and anhydrous nickel(II) bromide, Amend Drug and Chemical Co., New York, N. Y.; tetramethylguanidine, American Cyanamid Co., New York, N. Y.; and 2,2-dimethoxypropane, Dow Chemical Company, Midland, Mich.

Diethyl ether and hydrocarbon solvents were dried over sodium wire prior to use, but the 2,2-dimethoxypropane was used as received. Tetramethylguanidine was dried over anhydrous barium oxide and distilled from fresh BaO prior to use. Solvents were distilled from anhydrous barium oxide and kept dry during their storage and handling.

(1) Abstracted in part from the Ph.D. thesis of Raymond Longhi, University of Illinois, 1962.

(2) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962).

(3) J. T. Donoghue and R. S. Drago, *ibid.*, **1**, 866 (1962).

(4) R. S. Drago, *et al.*, *ibid.*, **2**, 124 (1963).

(5) R. S. Drago, *et al.*, *ibid.*, **2**, 1056 (1963).