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Structure and Nature of Bonding of $[C_2H_5SFe(CO)_3]_2$[1]

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The molecular configuration of $[C_2H_5SFe(CO)_3]_2$ has been elucidated from an X-ray analysis. The compound crystallizes with four dimeric molecules in a monoclinic unit cell of symmetry $P2_1/c$ and dimensions $a = 8.98 \pm 0.02$ Å., $b = 11.68 \pm 0.02$ Å., $c = 15.65 \pm 0.02$ Å., and $\beta = 107° 15' \pm 15'$. The structure has been refined to R_1 and R_2 values of 11.6 and 11.1%, respectively, by the application of an isotropic least-squares method to the three-dimensional data. The dimeric molecule is formed by the intersection of the basal planes of two *distorted* tetragonal pyramids along the chalcogen line with a dihedral angle of 69.5°. The $[SFe(CO)_3]_2$ fragment possesses *idealized* C_{2v} symmetry; the ethyl groups are *anti* to each other. A "bent" metal–metal bond involving the overlap of octahedral-type iron orbitals is presumed to be mainly responsible for the molecular geometry with the remarkably acute bridge Fe–S–Fe angles of 68°. A comparison of the molecular features of $[C_2H_5SFe(CO)_3]_2$ with those of the corresponding isoelectronic nitrosyl compound, $[C_2H_5SFe(NO)_2]_2$, is made. On the basis of the molecular geometry of the ethylthio- compound, molecular configurations are proposed for the two isomers of $[CH_3SFe(CO)_3]_2$.

Introduction

This structural investigation of $[C_2H_5SFe(CO)_3]_2$ is an outgrowth of work in this Laboratory on metal carbonyls and their derivatives from which bent metal–metal bonding involving octahedral-type metal hybridization was proposed for dimeric compounds of the type $[XFe(CO)_3]_2$ (X = RS, RSe, where R respresents alkyl or aryl groups).[3]

The chemistry of these iron carbonyl chalcogen compounds is well known,[4-10] and their existence as diamagnetic dimers in solution has been established from magnetic susceptibility[8,9] and molecular weight measurements.[4-9] Extensive work carried out independently by Hieber and Beck[8] and Kettle and Orgel[9] has provided additional structural information. Both groups found the absence of carbonyl absorption bands in the 1800 cm.$^{-1}$ region characteristic of bridging carbonyls which strongly supported the presence of chalcogen bridges. Although Kettle and Orgel[9] showed that the infrared spectra of the phenylthio- and ethylthio- compounds are similar in the carbonyl region, they did not formulate any definite molecular models. On the basis of infrared and dipole moment studies of the series of compounds $[XFe(CO)_3]_2$ (X = S, Se, SC_2H_5, SC_6H_5, SeC_2H_5), Hieber and Beck[8] proposed a general molecular structure of C_{2v} symmetry formed by the junction of the basal planes of two tetragonal pyramids along the chalcogen line with a dihedral angle less than 180°.

The close parallelism between the properties of the isoelectronic carbonyl and nitrosyl ethylthio- compounds has been mentioned frequently.[11] Since the crystal structure of $[C_2H_5SFe(NO)_2]_2$ has been determined by Thomas, *et al.*,[12] this present investigation offered the opportunity for a detailed comparison of the molecular features of these corresponding types of compounds.

The recent preparation and isolation by King[10] of two isomers of the methyl derivative and subsequent examination by infrared and proton magnetic resonance has resulted in a need for detailed structural knowledge concerning the molecular configuration and relative orientations of the alkyl groups attached to the sulfur atoms. This structural determination of $[C_2H_5SFe(CO)_3]_2$ has yielded an explanation for the existence of the two isomeric species of $[CH_3SFe(CO)_3]_2$ consistent with their physical properties as reported by King.[10]

Experimental Procedure

Dark red crystals of $[C_2H_5SFe(CO)_3]_2$ with onion-like odor were generously supplied by Professor Dr. Hieber and Dr. Beck of Germany. An approximately cylindrical single crystal of length 0.2 mm. and of average width 0.1 mm. with the *b* axis along the cylinder axis was obtained by recrystallization from petroleum ether solution. The lattice parameters were determined from both the Weissenberg and precession photographs.

Multiple-film equi-inclination Weissenberg photographs were obtained for nine reciprocal levels, *h0l* through *h8l*, with Zr-filtered MoKα radiation, from which the intensities of 490 independent reflections were measured. Time-exposure precession photographs of *0kl*, *1kl*, and *hk0* zones obtained with MoKα radiation yielded an additional 162 independent reflections. A total of 652 independent *hkl* diffraction maxima thus was obtained from the combined Weissenberg and precession data. All intensities were judged visually by comparison with calibrated standard intensity strips made with the same crystal. The intensity data first were corrected for Lorentz-polarization effects and then merged together and correlated to place them on

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[2] Based in part on a dissertation submitted by Chin-Hsuan Wei to the Graduate School of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[10] R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

[11] *Cf.* H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1960, p. 266; C. C. Addison and J. Lewis, *Quart. Rev.* (London), **9**, 115 (1955).

[12] J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, **11**, 599 (1958).

a common relative scale. The final scaling of the derived structure amplitudes (*i.e.*, $|F(hkl)|^2 \sim I(hkl)$) for the different layers is based on the calculated structure amplitudes for the refined structure. Since the average estimated value of the absorption parameter, μR, of 0.11 definitely indicates that absorption effects can be neglected, no such correction to the intensity data was made.

Results

Unit Cell and Space Group.—Crystals of $[C_2H_5SFe(CO)_3]_2$ (mol. wt. 402.0) are monoclinic with lattice parameters $a = 8.98 \pm 0.02$ Å., $b = 11.68 \pm 0.02$ Å., $c = 15.65 \pm 0.02$ Å., $\beta = 107° 15' \pm 15'$; volume of unit cell = 1,568 Å.^{3}; $\rho_{\text{obsd}} = 1.63$ g. cm.$^{-3}$ (obtained by flotation) *vs.* $\rho_{\text{calcd}} = 1.70$ g. cm.$^{-3}$ for four dimeric molecules per unit cell. The total number of electrons per unit cell, $F(000) = 808$. The only systematic absences observed are: $\{h0l\}$ for l odd; $\{0k0\}$ for k odd. The indicated centrosymmetric space group, $P2_1/c$ (C_{2h}^5), was confirmed by the satisfactory refinement of the structure found. All atoms are in the general fourfold set of positions (4e): $\pm(x, y, z; x, {}^1/_2 - y, {}^1/_2 + z)$.[13] Hence, the solution of the structure involves the location of two iron, two sulfur, ten carbon, and six oxygen atoms (and ideally the ten hydrogen atoms). Since the intensities of the reflections with $h + k + l$ even were observed on the films to be appreciably stronger than those with $h + k + l$ odd, it was concluded that an approximate body-centering of the iron atoms is present in the unit cell.

Determination of the Structure.—A three-dimensional Patterson function was computed from the corrected intensities. The interpretation of particularly high peaks gave a self-consistent set of coördinates for the iron atoms. The attempt to locate the sulfur vectors was not successful. Furthermore, complications were introduced by an accidental body-centering of the eight iron atoms in the unit cell. For a given iron atom (*e.g.*, Fe_1) in a molecule, it was found that a center of symmetry operation of the space group generates an iron atom in another molecule which is related to the other iron (Fe_2) in the originally chosen molecule by a *pseudo* body-centered operation. Since the resulting body-centered iron atoms make a net contribution only to the structure factors for which $h + k + l = 2n$ (for the non-body-centered reflections for which $h + k + l = 2n + 1$, the calculated structure factors based on the positions of the iron atoms alone would be zero), only the body-centered reflections were utilized for least-squares refinement of the trial positional parameters of the two asymmetric iron atoms. After three successive least-squares cycles, the discrepancy factor, $R_1 = [\Sigma \,||F_0| - |F_c||/\Sigma\, |F_0|] \times 100$, remained constant at 33%; for this refinement the arbitrarily estimated isotropic temperature factors of $B = 2.0$ Å.^{2} for the iron atoms were not varied. The resulting phases of the iron atoms, obtained from structure factor calculations, were used to compute a three-dimensional Fourier synthesis for only the body-centered reflections. The resulting synthesis consisted of a superposition of peaks for a partially correct structure and its image which is related to the partially correct one by the pseudo body-centered operation.

A careful analysis of the Fourier synthesis yielded coördinates for both sulfur atoms which were consistent with the Patterson function and with predicted bond lengths. A least-squares refinement of the assigned coördinates of the iron and sulfur atoms was carried out again for only the body-centered reflections. The presumed individual temperature factors of $B = 2.0$ and 3.0 Å.^{2} for iron and sulfur, respectively, were held constant; the R_1 value after several cycles decreased to 24.5%. Another three-dimensional Fourier then was calculated, and a trial structure involving the interpretation of six more peaks as three carbonyl groups was made. Structure factors were calculated based on the new phases which more effectively minimized the false images and magnified the true structure. A three-dimensional Fourier then was computed for all reflections. An additional four peaks considered to be a carbonyl and two ethyl carbon atoms were identified. This reiterative procedure was carried out once more for all reflections to locate the remaining two carbonyls and two ethyl carbon atoms. The subsequent least-squares refinement of all atoms (except hydrogen) including positional parameters, individual isotropic thermal parameters, and twelve scale factors resulted in final discrepancy factors of $R_1 = 11.6\%$ and $R_2 = [\Sigma\, w||F_0| - |F_c||^2/\Sigma\, w|F_0|^2]^{1/2} \times 100 = 11.1\%$ for the 652 non-zero reflections.[14] For the last cycle the coördinate shifts were all less than 10% of their individual standard deviations. Finally, the structural determination was checked by a complete three-dimensional Fourier difference analysis. No residual peaks greater than 0.9 electron/Å.^{3} or less than -1.2 electrons/Å.^{3} were found. No attempt was made to identify the positive peaks as hydrogen atoms.

The above calculations all were performed on an IBM 704 computer with the Busing and Levy full matrix least-squares program[15] and the Sly–Shoemaker Fourier Program.[16] In the least-squares refinements variable weights were assigned to the observed structure factors according to the functions $\sqrt{w} = 20/F_0$ if $I_0 \geq 4I_0$ (min.) and $\sqrt{w} = 1.25I_0^2/F_0I_0^2$(min.) if $I_0 < 4I_0$(min.). The scattering factors reported by Thomas and Umeda[17] were utilized for iron. For sulfur the scattering factors were those of Dawson,[18] while for carbon and oxygen

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[13] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 99.

[14] Calculated and observed structure factors are deposited as Document Number 7315 with the American Documentation Institute, Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document Number and remitting $1.25 for photoprints or $1.25 for 35-mm. microfilm in advance payable to: Chief, Photoduplication Service, Library of Congress.

[15] 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).

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

[17] L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

[18] B. Dawson, *Acta Cryst.*, **13**, 403 (1960).

TABLE I

FINAL ATOMIC PARAMETERS AND STANDARD DEVIATIONS

Atom	x	y	z	B, Å.^{2}	$10^4\sigma_x$	$10^4\sigma_y$	$10^4\sigma_z$	σB, Å.^{2}
Fe_1	0.3472	0.1717	0.2300	2.83	9	4	4	0.16
Fe_2	.1517	.2884	.2817	2.93	9	4	4	.17
S_3	.1170	.2338	.1370	3.23	15	8	7	.25
S_4	.1902	.0974	.3015	2.52	15	7	6	.23
C_5	.5274	.1656	.3292	5.24	61	34	33	1.13
O_6	.6105	.1631	.3921	4.60	37	21	20	0.70
C_7	.3761	.0527	.1730	3.88	53	28	27	.95
O_8	.4093	−0.0319	.1317	5.79	37	23	19	.75
C_9	−0.0463	0.3042	.2860	4.40	57	38	28	1.20
O_{10}	−0.1642	.3185	.3032	7.34	43	29	22	0.97
C_{11}	0.2541	.3331	.3960	5.40	56	36	31	1.11
O_{12}	.3330	.3466	.4693	5.40	36	22	20	0.72
C_{13}	.2884	.0589	.4177	2.85	50	27	22	0.81
C_{14}	.1531	.0426	.4618	5.02	56	29	31	1.05
C_{15}	.4291	.2899	.1800	6.13	62	38	31	1.27
O_{16}	.4803	.3552	.1462	6.40	40	23	20	0.87
C_{17}	.1905	.4313	.2491	6.14	60	37	32	1.25
O_{18}	.2150	.5218	.2260	5.81	41	25	19	0.79
C_{19}	−0.0198	.1196	.0987	2.44	51	25	21	0.80
C_{20}	−0.1956	.1490	.0619	5.64	60	32	28	1.13

TABLE II

MOLECULAR BOND LENGTHS

Bond	Length, Å.	Std. deviation, Å.
Fe_1–Fe_2	2.537	0.010
Fe_1–S_3	2.266	.013
Fe_1–S_4	2.221	.014
Fe_2–S_3	2.284	.012
Fe_2–S_4	2.264	.011
S_3–C_{19}	1.79	.04
S_4–C_{13}	1.83	.03
C_{19}–C_{20}	1.55	.06
C_{13}–C_{14}	1.58	.05
Fe_1–C_5	1.88	.05
Fe_1–C_{15}	1.84	.05
Fe_1–C_7	1.71	.04
Fe_2–C_{11}	1.83	.05
Fe_2–C_{17}	1.81	.05
Fe_2–C_9	1.81	.05
C_5–O_6	1.04	.04
C_{15}–O_{16}	1.10	.05
C_7–O_8	1.26	.04
C_{11}–O_{12}	1.17	.04
C_{17}–O_{18}	1.16	.04
C_9–O_{10}	1.18	.05

TABLE III

MOLECULAR ANGLES

Angle	Degrees	Angle	Degrees
S_3–Fe_1–S_4	81.62 ± 0.47	C_5–Fe_1–C_{15}	91.4 ± 2.0
S_3–Fe_2–S_4	80.30 ± 0.38	C_{11}–Fe_2–C_{17}	86.0 ± 1.9
Fe_1–S_3–Fe_2	67.78 ± 0.36	C_5–Fe_1–C_7	99.9 ± 1.8
Fe_1–S_4–Fe_2	68.88 ± 0.37	C_{15}–Fe_1–C_7	104.3 ± 1.9
Fe_1–S_3–C_{19}	112.4 ± 1.2	C_{11}–Fe_2–C_9	98.6 ± 2.0
Fe_2–S_3–C_{19}	114.6 ± 1.3	C_{17}–Fe_2–C_9	100.9 ± 2.2
Fe_1–S_4–C_{13}	114.0 ± 1.5	Fe_1–C_5–O_6	167.8 ± 5.1
Fe_2–S_4–C_{13}	112.9 ± 1.1	Fe_1–C_7–O_8	175.0 ± 3.9
S_3–C_{19}–C_{20}	118.7 ± 2.4	Fe_1–C_{15}–O_{16}	175.1 ± 4.0
S_4–C_{13}–C_{14}	105.0 ± 2.7	Fe_2–C_9–O_{10}	169.1 ± 4.2
S_3–Fe_1–C_{15}	83.7 ± 1.6	Fe_2–C_{11}–O_{12}	169.5 ± 4.1
S_3–Fe_2–C_{17}	87.6 ± 1.5	Fe_2–C_{17}–O_{18}	178.3 ± 4.2
S_4–Fe_1–C_5	95.1 ± 1.5		
S_4–Fe_2–C_{11}	97.8 ± 1.4		
S_3–Fe_1–C_7	100.1 ± 1.4		
S_4–Fe_1–C_7	99.3 ± 1.4		
S_3–Fe_2–C_9	102.6 ± 1.5		
S_4–Fe_2–C_9	102.0 ± 1.6		
S_3–Fe_1–C_5	160.0 ± 1.4		
S_4–Fe_1–C_{15}	154.0 ± 1.5		
S_3–Fe_2–C_{11}	158.6 ± 1.5		
S_4–Fe_2–C_{17}	156.0 ± 1.7		

the values used were those of Berghuis, *et al.*[19]

Table I shows the final positional parameters and isotropic temperature factors and their standard deviations obtained from the last cycle of the least-squares refinement. A function and error analysis[20] including calculation of intramolecular distances (Table II) and angles (Table III) was made with the final positional parameters. The intermolecular distances less than 3.5 Å. are given in Table IV.

The "best" molecular planes formed by certain atoms and the distances of these atoms from the planes were obtained by a least-squares method[21]; the results are given in Table V. The weighting factor, w_k, given to each atom "k" forming the plane was $w_k = [a\sigma(x_k)b\sigma(y_k)c\sigma(z_k)]^{-2/3}$, where $\sigma(x_k)$, $\sigma(y_k)$, and $\sigma(z_k)$ are the standard deviations in fractional coördinates of the final atomic coördinates x_k, y_k, and z_k, respectively. The equation of each plane is expressed in orthogonal coördinates X, Y, and Z, which are related to the monoclinic cell coördinates by the transformation $X_k = ax_k + cz_k \cos \beta$, $Y_k = by_k$, and $Z_k = cz_k \sin \beta$.

Discussion

The crystal structure of $[C_2H_5SFe(CO)_3]_2$ consists of individual molecules of the conformation depicted in Fig. 1.

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(19) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(20) 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).

(21) D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.

TABLE IV

INTERMOLECULAR DISTANCES LESS THAN 3.5 Å.

Atoms	Distance, Å.	Atoms	Distance, Å.
$O_{18}\ldots C_5^{I}$	3.18	$O_{10}\ldots C_7^{IV}$	3.42
$O_{10}\ldots O_8^{IV}$	3.20	$O_{10}\ldots C_5^{III}$	3.42
$O_{18}\ldots O_6^{I}$	3.21	$O_{10}\ldots O_{16}^{III}$	3.43
$O_{12}\ldots O_8^{II}$	3.25	$C_{14}\ldots C_{14}^{V}$	3.45
$O_{12}\ldots C_7^{II}$	3.31	$O_{12}\ldots O_8^{I}$	3.47
$O_{10}\ldots O_6^{III}$	3.32	$C_{20}\ldots O_6^{VI}$	3.49
$O_8\ldots C_{20}^{VII}$	3.36	$O_{16}\ldots C_{13}^{I}$	3.49

Superscripts refer to the following positions:

I	$1 - x$,	$^1/_2 + y$,	$^1/_2 - z$
II	x,	$^1/_2 - y$,	$^1/_2 + z$
III	$-1 + x$,	y,	z
IV	$-x$,	$^1/_2 + y$,	$^1/_2 - z$
V	$-x$,	$-y$,	$1 - z$
VI	$-1 + x$,	$^1/_2 - y$,	$-^1/_2 + z$
VII	$-x$,	$-y$,	$-z$

TABLE V

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

(a) Plane through S_3, S_4, C_5, and C_{15}

$$0.309X - 0.804Y - 0.509Z + 3.110 = 0$$

S_3	0.002	C_{15}	−0.048	O_{16}	−0.21
S_4	−0.002	Fe_1	0.38	C_7	2.10
C_5	0.042	O_6	−0.27	O_8	3.35

(b) Plane through S_3, S_4, C_{11}, and C_{17}

$$-0.998X + 0.058Y - 0.006Z + 0.270 = 0$$

S_3	0.001	C_{17}	−0.017	O_{18}	−0.28
S_4	−0.001	Fe_2	0.38	C_9	2.19
C_{11}	0.014	O_{12}	−0.35	O_{10}	3.33

(c) Plane through Fe_1, Fe_2, and M (the mid-point of S_3–S_4)

$$0.055X + 0.553Y - 0.832Z + 1.637 = 0$$

Fe_1	0.000	C_9	−0.05	C_{11}	−1.11
Fe_2	0.000	O_{10}	−0.24	C_{17}	1.36
M	0.000	C_5	−1.21	O_{12}	−1.91
S_3	1.47	C_{15}	1.44	O_{18}	2.24
S_4	−1.47	O_6	−1.98	C_{13}	−3.14
C_7	−0.04	O_{16}	2.31	C_{19}	1.15
O_8	−0.03				

(d) Plane through S_3, S_4, and N (the mid-point of Fe_1–Fe_2)

$$0.802X - 0.517Y - 0.300Z + 1.694 = 0$$

S_3	0.000	O_8	3.75	C_{15}	1.55
S_4	0.000	O_{10}	−3.90	C_{17}	−1.58
N	0.000	C_5	1.79	O_{16}	1.81
Fe_1	1.27	C_{11}	−1.74	O_{18}	−1.76
Fe_2	−1.27	O_6	1.89	C_{13}	−0.01
C_7	2.66	O_{12}	−1.85	C_{19}	0.02
C_9	−2.82				

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

The *idealized* molecular geometry of the $[XFe(CO)_3]_2$ moiety suggested by Hieber and Beck[8] is confirmed and, as will be discussed later, the configuration is completely compatible with the proposal of bent metal–metal bonding involving octahedral hybridization of the iron orbitals.[3]

Each iron of similar localized environment is surrounded by three carbonyls and two sulfurs at the corners of a *distorted* tetragonal pyramid. The significantly large distortion of the five ligands about each iron from a regular tetragonal pyramid can be shown by a least-squares calculation of the "best" basal plane for each monomeric unit involving the two sulfurs and two basal carbonyl carbon atoms [Table V, (a) and (b)]. Each iron is displaced from its basal plane by 0.38 Å. in the direction of the third (*i.e.*, apical) carbonyl group. The one least-squares basal plane [Table V, (a)] passes within 0.05 Å. of the atoms S_3, S_4, C_5, and C_{15} attached to Fe_1, while the other basal plane [Table V, (b)] passes within 0.02 Å. of the atoms S_3, S_4, C_{11}, and C_{17} attached to Fe_2. The dimeric molecule then can be considered to be formed from the intersection of these two basal planes at the S–S edge with a dihedral angle of 69.5°.

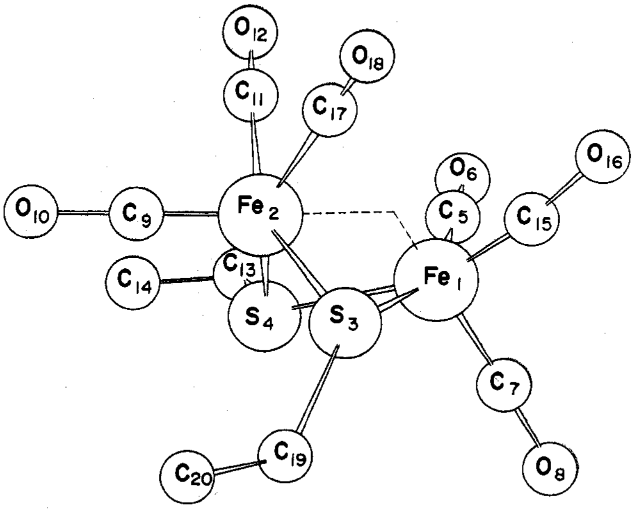

Fig. 1.—The molecular configuration of $[C_2H_5SFe(CO)_3]_2$.

Although no special molecular symmetry is demanded by the space group (*i.e.*, all atoms are in general positions), the $[SFe(CO)_3]_2$ part of the molecule possesses *idealized* C_{2v}-2mm symmetry. One mirror [Table V, (c)] comprises Fe_1, Fe_2, and the mid-point of the sulfur atoms, S_2 and S_3; the other vertical mirror [Table V, (d)] passes through S_3, S_4, and the mid-point of atoms Fe_1 and Fe_2. It can be seen (Fig. 1) that the pairs of equivalent atoms resulting from the above symmetry elements are located at roughly equal distances on opposite sides from the defined mirror planes [Table V, (c) and (d)]. Since the angle between the two vectors, Fe_1–Fe_2 and S_3–S_4, is 90° within experimental error, the two planes are perpendicular to each other. The twofold axis in the third direction with results from the intersection of the two reflection planes relates Fe_1 with Fe_2 and S_3 with S_4. The orientation of the ethyl groups linked to the sulfurs (discussed later) destroys the idealized C_{2v} symmetry for the *whole* molecule.

The mean value for the four Fe–S bonds, made equivalent by the idealized C_{2v} symmetry, is 2.259 Å. (e.s.d. 0.007 Å.) which is very close to the average Fe–S bond lengths found in $[C_2H_5SFe(NO)_2]_2$ (2.26 Å.),[12] $CsFe_4S_3(NO)_7 \cdot H_2O$ (2.23 Å.),[22] pyrite (2.26 Å.),[23] and marcasite (2.24 Å.).[24] The Fe–C and C–O bond lengths are not known with sufficient accuracy to determine possible differences between the apical and

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(22) G. Johansson and W. N. Lipscomb, *Acta Cryst.*, **11**, 594 (1958).
(23) H. M. Parker and W. J. Whitehouse, *Phil. Mag.*, **14**, 939 (1932).
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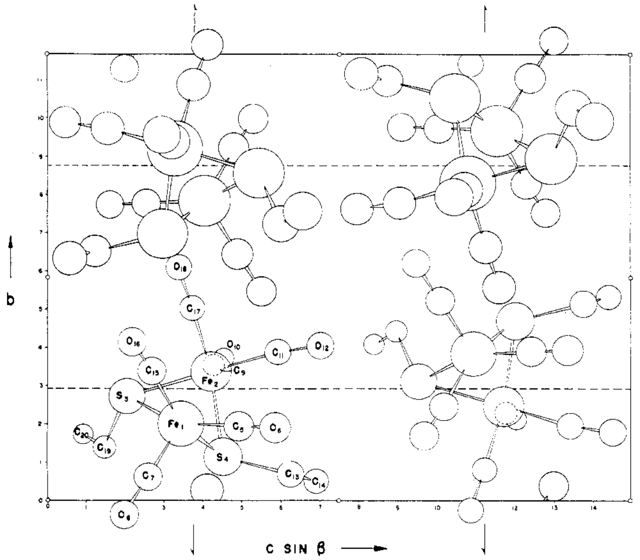

Fig. 2.—[100] projection of the unit cell.

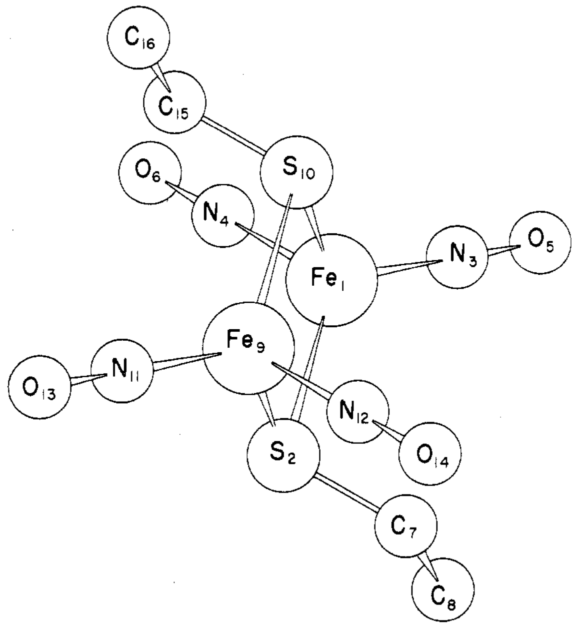

Fig. 3.—The molecular configuration of $[C_2H_5SFe(NO)_2]_2$.[12]

basal carbonyl bond lengths. The mean Fe–C and C–O distances of 1.81 ± 0.02 and 1.15 ± 0.02 Å., respectively, compare well with mean Fe–C and C–O distances reported for $(C_5H_5)_2Fe_2(CO)_4$ (1.75 and 1.12 Å.),[25] $Fe_2(CO)_6(COH)_2(CH_3C_2CH_3)$ (1.78 and 1.14 Å.),[26] $C_8H_8Fe(CO)_3$ (1.80 and 1.13 Å.),[27] $(OC)_3Fe(C_8H_8)Fe(CO)_3$ (1.76 and 1.15 Å.),[28] $Fe_2(CO)_6(C_6H_5C_2H)_3$ (1.78 and 1.15 Å.),[29] $(C_6H_3(C_6H_5)_3CO)Fe(CO)_3$ (1.77 and 1.17 Å.),[30] and $Fe_5(CO)_{15}C$ (1.75 and 1.17 Å.).[31] The individual Fe–C–O bond angles do not deviate significantly from linearity.

Figure 2 shows the [100] projection of the $[C_2H_5SFe(CO)_3]_2$ unit cell and indicates the packing of the dimeric molecules according to the symmetry requirements of $P2_1/c$. The closest intermolecular distances (Table IV) of 3.2 Å. for O. . .O contacts support the view that the molecular crystal is primarily held together by the usual van der Waals forces.

Table VI

Comparison of Bond Lengths and Angles

	$[C_2H_5SFe(CO)_3]_2$	$[C_2H_5SFe(NO)_2]_2$
Fe. . .Fe	2.537 ± 0.010 Å.	2.720 ± 0.003 Å.
Fe–S	2.259 ± 0.007 Å. (av.)	2.270 ± 0.004 Å. (av.)
S. . .S	2.932 ± 0.014 Å.	3.633 ± 0.004 Å.
$S–CH_2$	1.81 ± 0.03 Å. (av.)	1.84 ± 0.02 Å.
$CH_2–CH_3$	1.56 ± 0.04 Å. (av.)	1.50 ± 0.02 Å.
Fe–S–Fe	68.3 ± 0.3° (av.)	73.7 ± 0.1°
S–Fe–S	81.0 ± 0.3° (av.)	106.3 ± 0.1°
$Fe–S–CH_2$	113.5 ± 0.7° (av.)	106.6 ± 0.5° (av.)
$S–CH_2–CH_3$	118.7 ± 2.4° 105.0 ± 2.7°	111.9 ± 0.8°

A comparison of the structural features of $[C_2H_5SFe(CO)_3]_2$ with those of the corresponding isoelectronic nitrosyl complex of formula $[C_2H_5SFe(NO)_2]_2$, the so-called Roussin's red ethyl ester, is informative. An X-ray structural determination of the nitrosyl compound by Thomas, *et al.*,[12] conclusively shows that the two $Fe(NO)_2$ fragments are linked together by the two bridged ethyl mercaptide groups such that the sulfur and the iron atoms form a planar rhombus. The two terminal NO groups and two S atoms form an approximate tetrahedral configuration about each iron. Since the molecular configuration for $[C_2H_5SFe(NO)_2]_2$ is required by the space group $P2_1/a$ to possess a center of symmetry, the ethyl groups are *anti* to one another. The approximate point symmetry of the $[SFe(NO)_2]_2$ moiety (without the ethyl groups) is D_{2h}. An interaction between the iron atoms was proposed to account for the diamagnetism of the compound.

The molecular configuration of $[C_2H_5SFe(NO)_2]_2$ is shown in Fig. 3, and selected bond lengths and angles for $[C_2H_5SFe(CO)_3]_2$ and $[C_2H_5SFe(NO)_2]_2$ are given in Table VI. Unlike the planar Fe_2S_2 rhombus in $[C_2H_5SFe(NO)_2]_2$, the Fe_2S_2 fragment in $[C_2H_5SFe(CO)_3]_2$ possesses a "butterfly" form such that the dihedral angle between the two planes each formed by the two bridge sulfurs and one iron is 95.2 ± 0.5°. As expected, the mean Fe–S, CH_2–CH_3, and S–CH_2 distances for each of the two compounds are in agreement within the limits of their standard deviations.

A qualitative description of the iron–iron bond in $[C_2H_5SFe(NO)_2]_2$ can be given. Assume that each iron atom is under an approximately tetrahedral environment and that only the two NO ligands are strongly π-bonding. (Possible d_π–d_π bonding between the iron and sulfur atoms is neglected.) The formation of a *direct* iron–iron bond coupling the otherwise unpaired electrons can occur by the overlap of two equivalent s-p-d hybrid iron orbitals made up primarily of the d_{z^2}, p_z, and s atomic orbitals. A suitable linear combination of these atomic orbitals possesses favorable directional properties for bonding. The degree of the s-, p-, and d-character in the hybrid orbital is not known. To the extent that the d_{z^2} and p_z orbitals are not involved in

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π-bonding and the s and p_z orbitals are free from σ-bonding with the other ligands, these atomic orbitals are available for the metal–metal bonding. Since the two strongly π-bonding d_{z^2} and $d_{x^2-y^2}$ iron orbitals are assumed to form molecular orbitals with the appropriate symmetry orbitals for only the two NO ligands, the d_{z^2} orbital is presumed to make a large contribution to the hybrid orbital utilized for the iron–iron bond. The tendency for each iron to possess an approximate tetrahedral angle (106°) leads to an acute bridge Fe–S–Fe angle of 74°. This sharp bridge angle may be partly due to the metal–metal bond which pulls the iron atoms closer together than normal.

A "bent" metal–metal bond arising from the use of octahedral-type iron orbitals which overlap at an angle of approximately 113° is presumed to be mainly responsible for the molecular geometry of $[C_2H_5SFe(CO)_3]_2$ with the remarkably acute symmetrical bridging Fe–S–Fe angles of 68.3°. The angle of metal–metal overlap was obtained from the assumption that the sixth octahedral metal orbital is collinear with the iron-apical carbonyl group. The 113° angle represents an average of the 110° 15′ angle obtained for the presumed intersection of the Fe_1–C_7 and Fe_2–C_9 vectors and the 115° 32′ angle obtained for the presumed intersection of the Fe_1–O_8 and Fe_2–O_{10} vectors. It seems reasonable to assume that the acute Fe–S–Fe angles and the orientation of the mean basal pyramid planes is due primarily to the energy gained from attainment of better overlap of the two iron orbitals with each other.

The sharp bridge angles of 68.3 and 73.7° for $[C_2H_5SFe(CO)_3]_2$ and $[C_2H_5SFe(NO)_2]_2$, respectively, necessarily require "bent" Fe–S bonds for both molecules, since each bridging sulfur atom must use *two equivalent* orbitals to form normal electron-pair bonds to the two like iron atoms, and equivalent orthogonal hybrids which point at an angle less than 90° from each other cannot be constructed from the s,p atomic orbitals. In both compounds the sulfur atoms no doubt have an approximately tetrahedral arrangement of three bonding pairs and one lone pair of electrons. This tetrahedral (or trigonal pyramidal) configuration is symmetrically oriented between the iron atoms such that the two nonequivalent sp^3 hybrid orbitals of sulfur used for the bond to the ethyl group and the unshared pair of electrons lie in a plane which passes through the sulfur atoms and the mid-point of the iron atoms (corresponding to an *idealized* mirror plane for each of the molecules). For $[C_2H_5SFe(CO)_3]_2$ the methylene carbon atoms C_{13} and C_{19} are within 0.02 Å. of this plane [Table V, (d)]. The mean of the resulting equivalent Fe–S–CH_2 angles is 113.5 ± 0.5° for $[C_2H_5SFe(NO)_2]_2$. These bridge angles are the smallest known for two symmetrical bridging groups linked to two metal atoms by normal electron-pair bridge bonds.

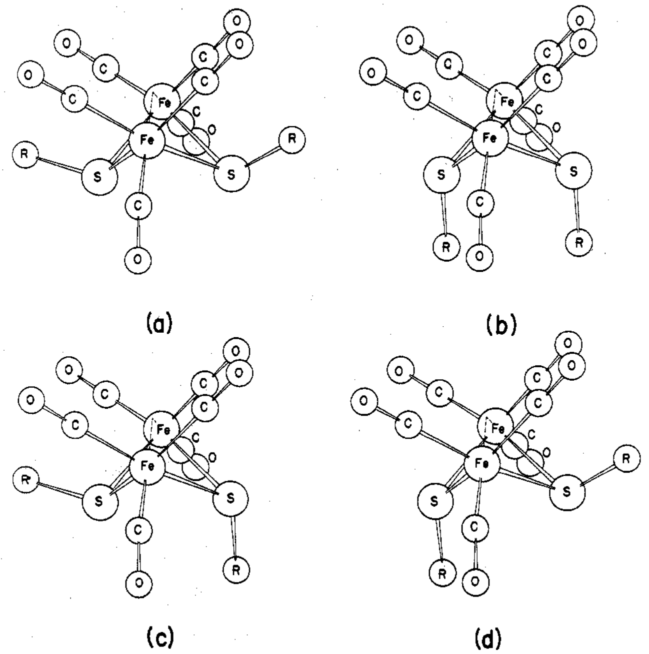
(a) (b) (c) (d)

Fig. 4.—Possible stereoisomers of $[RSFe(CO)_3]_2$.

The molecular geometry of $[C_2H_5SFe(CO)_3]_2$ provides an explanation for the existence of two isomers of $[CH_3SFe(CO)_3]_2$. Figure 4 shows the four possible orientations of the alkyl groups attached to the sulfur atoms in the molecule $[RSFe(CO)_3]_2$ (R = alkyl group). The molecular configuration of $[C_2H_5SFe(CO)_3]_2$ corresponds to model (c); the ethyl groups are *anti* to each other. Since the $[SFe(CO)_3]_2$ fragment possesses *idealized* C_{2v} symmetry, for similar R groups models (c) and (d) are virtually identical. In models (a) and (b) the two R groups are related by the *idealized* vertical mirror plane formed by the two iron atoms and the mid-point of the sulfur atoms. The approximate separation of the two R groups (in general corresponding to the carbon atoms directly bonded to the sulfur groups) in models (a) and (b) can be estimated from the orientation of the ethyl groups in the $[C_2H_5SFe(CO)_3]_2$ molecule by calculation of the perpendicular distances of the methylene carbon atoms C_{13} (3.14 Å.) and C_{19} (1.15 Å.) from this *idealized* mirror plane [Table V, (c)]. For model (a) the separation then is 6.28 Å., for model (b) 2.30 Å. Since the van der Waals *radius* of the methyl group is 2.0 Å., the *syn*-isomer (b) can be precluded by steric considerations as being energetically unfavorable.

This leaves two possible isomers, models (a) and (c), for $[CH_3SFe(CO)_3]_2$. From n.m.r. work King[10] reported that the two methyl groups of one isomer (King's isomer A) are in different chemical environments while for the other isomer (King's isomer B) the methyl groups are in identical positions. Hence, isomer A must possess the configuration (c) (Fig. 4) with the methyl groups *anti* to each other, while isomer B must correspond to model (a) (Fig. 4) with the methyl groups *syn* to one another.

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