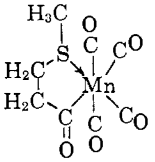
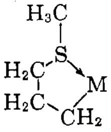
small quantities, about 1 year before any of the other metal carbonyl compounds described in this paper. The presence of a strong acyl carbonyl band at 1631 cm.$^{-1}$ and analyses for all five elements clearly indicate this manganese compound to be $CH_3SCH_2CH_2COMn(CO)_4$ of structure VI, entirely analogous to $CH_3SCH_2CH_2COFeCOC_5H_5$ (V). Unfortunately, the relative rarity of manganese carbonyl prevented studies on the manganese system as detailed as those carried out on the iron system.



VI



VII

An attempt to prepare a similar molybdenum compound ($CH_3SCH_2CH_2COMo(CO)_2C_5H_5$) from $NaMo(CO)_3C_5H_5$ and 2-chloroethyl methyl sulfide gave negative results. No reaction appeared to take place, suggesting that $NaMo(CO)_3C_5H_5$ is too unreactive[22] to react with 2-chloroethyl methyl sulfide, at least in tetrahydrofuran solution at room temperature.

The ability for the lone pair on the sulfur atom in 2-chloroethyl methyl sulfide to form more normal types of adducts with metal salts is demonstrated by the preparation by treatment of 2-chloroethyl methyl sulfide with methanolic Na_2PdCl_4 of the palladium compound $(ClCH_2CH_2SCH_3)_2PdCl_2$, completely analogous to other $(R_2S)_2PdCl_2$ compounds.[23]

The existence of cyclic acyl derivatives such as V with a five-membered ring containing a metal atom, a sulfur atom, two methylene groups, and an acyl carbonyl group suggested the existence of similar cyclic alkyl derivatives (VII) with a five-membered ring containing a metal atom, a sulfur atom, and three methylene groups. However, irradiation of the crude $CH_3SCH_2CH_2CH_2Fe(CO)_2C_5H_5$ obtained from $NaFe(CO)_2C_5H_5$ and 3-chloropropyl methyl sulfide in benzene solution as described in the Experimental section gave only $CH_3SFe(CO)_2C_5H_5$. This and the similar failure to obtain appreciable quantities of a manganese compound with the ring system VII from $NaMn(CO)_5$ and 3-chloropropyl methyl sulfide suggest the need for different synthetic techniques for such cyclic alkyl derivatives.

Acknowledgment.—We are indebted to the U. S. Air Force Office of Scientific Research for partial support of this work under Grant AFOSR-580-64.

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[22] The work of T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **3**, 104 (1956), suggests $NaMo(CO)_3C_5H_5$ to be less reactive than $NaFe(CO)_2C_5H_5$.

[23] F. G. Mann and D. Purdie, *J. Chem. Soc.*, 1549 (1935).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN 53706

Crystal Structure of a 1:1 Mixture of Two Iron Carbonyl Sulfur Complexes, $S_2Fe_3(CO)_9$ and $S_2Fe_2(CO)_6$[1]

BY CHIN HSUAN WEI AND LAWRENCE F. DAHL[2]

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The structure of $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$ (previously formulated incorrectly as $S_2Fe_3(CO)_9$) has been determined by X-ray diffraction. Three-dimensional isotropic least-squares refinement of all atoms yielded a final unweighted reliability index of $R_1 = 8.9\%$. The crystals contain four formula species in an orthorhombic unit cell of dimensions $a = 13.23 \pm 0.01$ Å., $b = 11.08 \pm 0.01$ Å., $c = 17.95 \pm 0.01$ Å. and of symmetry Pnma. The structure consists of an ordered array of two different molecular species of formulas $S_2Fe_3(CO)_9$ and $S_2Fe_2(CO)_6$, both of which possess crystallographic C_s-m symmetry. The molecular configuration of the $S_2Fe_2(CO)_6$ molecule is in close agreement with that of triclinic $S_2Fe_2(CO)_6$, prepared by the Hieber–Gruber reaction. The $S_2Fe_3(CO)_9$ molecule is found to be a conformer of the isomorphous Hieber–Gruber compounds $X_2Fe_3(CO)_9$ (X = S, Se).

Introduction

The preparation of $S_2Fe_3(CO)_9$ was first performed by Hieber and Gruber,[3] who allowed $HFe(CO)_4^-$ to react with sulfite ion to obtain a diamagnetic red-black crystalline compound, whose infrared spectrum possessed bands characteristic of only terminal carbonyl groups. Single crystal X-ray diffraction studies in this laboratory[4] showed the compound to be isomorphous with the Hieber–Gruber analog, $Se_2Fe_3(CO)_9$,[3] which contains a new type of seven-coordinated metal.[5] Recently King[6] isolated red-purple crystals with the presumably identical formula, $S_2Fe_3(CO)_9$, from the reaction between $Fe_3(CO)_{12}$ and cyclohexene sulfide or 3-chloropropylene sulfide. King[6] concluded from the

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[1] Presented in part at the National Meeting of the American Crystallographic Association, Montana State College, Bozeman, Mont., July 26–31, 1964.

[2] Fellow of the Alfred P. Sloan Foundation.

[3] W. Hieber and J. Gruber, *Z. anorg. allgem. Chem.*, **296**, 91 (1958).

[4] C. H. Wei, unpublished work (1963).

[5] L. F. Dahl and P. W. Sutton, *Inorg. Chem.*, **2**, 1067 (1963).

[6] R. B. King, *ibid.*, **2**, 326 (1963).

comparison of degradation products, melting points, and infrared and n.m.r. spectra that the new presumed $S_2Fe_3(CO)_9$ was a structural isomer of the Hieber–Gruber complex. This investigation of the King compound was undertaken to determine the structural relationship between the two complexes.

Experimental

A sample of the presumed $S_2Fe_3(CO)_9$ was kindly furnished to us by Dr. R. B. King of Mellon Institute and was used for our X-ray investigation without further recrystallization. An optical examination under a microscope together with preliminary X-ray photographs revealed two different crystalline forms in the sample, red-purple needle-shaped crystals of orthorhombic symmetry and red-orange nonneedle-shaped crystals of triclinic symmetry. The triclinic crystals, which were a small contaminant of the sample, were identified from Weissenberg diffraction patterns as the known $[SFe(CO)_3]_2$ whose structure we already had determined.[7]

A suitable orthorhombic needle crystal of dimensions 0.05 × 0.08 × 0.49 mm. was mounted in a thin-walled glass capillary (with the needle direction along the cylinder axis) and used to determine the unit cell parameters from both Weissenberg and precession photographs. Multiple-film equi-inclination Weissenberg photographs of this crystal were obtained with Zr-filtered Mo Kα radiation (λ 0.7107 Å.) for eleven reciprocal levels, $h0l$ through $h10l$. Timed-exposure precession photographs of $k0l$, $h1l$, $h2l$, and $hk0$ layers were taken in order to obtain additional data as well as to place a total of 635 independent observed diffraction maxima on an initially common scale. The intensity of each reflection was visually estimated by comparison with sets of standard intensity strips. The intensity data thus measured first were corrected for Lorentz-polarization effects and then scaled. The maximum absorption parameter, μR, was estimated to be less than 0.2, and hence no absorption correction was applied to the intensity data.

Results

Unit Cell and Space Group.—The lattice parameters of King's orthorhombic crystals are $a = 13.23 \pm 0.01$ Å., $b = 11.08 \pm 0.01$ Å., $c = 17.95 \pm 0.01$ Å.; volume of unit cell = 2631 Å.^{3}; $\rho_{\text{obsd}} = 2.08$ g. cm.$^{-3}$ (obtained by the flotation method). The observed absences of $\{0kl\}$ with $k + l$ odd and $\{hk0\}$ with h odd indicated the probable space groups D_{2h}^{16}-Pnma and C_{2v}^{9}-Pn2$_1$a; the former centrosymmetric one was verified by the successful refinement of the derived structure.

Determination of the Structure.—Initial efforts to interpret both regular and sharpened three-dimensional Patterson functions,[8] computed from the corrected intensity data on the basis of the presumed formula $S_2Fe_3(CO)_9$, were unsuccessful. This difficulty plus the poor agreement between the experimental density (2.08 g. cm.$^{-3}$) and the calculated one (2.44 g. cm.$^{-3}$) based on eight $S_2Fe_3(CO)_9$ species in a unit cell indicated that the assumed formula of $S_2Fe_3(CO)_9$ was incorrect. Since crystals of the triclinic $[SFe(CO)_3]_2$ were found in the sample, a double complex of formula $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$, which for four formula species per unit cell gives a calculated density value (2.09 g. cm.$^{-3}$) in excellent agreement with the observed value, was assumed. Re-examination of the sharpened Patterson function on the basis of the formula $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$ and the space group Pnma resulted in an interpretation of most of the high peaks and led to a set of approximate coordinates for one sulfur and five iron atoms. For Pnma the five independent iron atoms were found to occupy five fourfold sets of special positions (4c); the two independent sulfur atoms occupy two eightfold sets of general positions (8d); the ten independent carbonyl carbon and oxygen atoms each occupy five sets of 4c and five sets of 8d positions. These positions are as follows: 8d: $\pm(x, y, z;\ ^1/_2 + x, ^1/_2 - y, ^1/_2 - z;\ -x, ^1/_2 + y, -z;\ ^1/_2 - x, -y, ^1/_2 + z)$. 4c: $\pm(x, ^1/_4, z;\ ^1/_2 - x, ^3/_4, ^1/_2 + z)$.[9]

A block-diagonal least-squares isotropic refinement[10] of these atomic coordinates was then carried out in which initial isotropic temperature factors of 2.0 and 3.0 Å.^{2} were arbitrarily assumed for each iron and sulfur atom, respectively. Variable weights were assigned to the observed structure factors according to the following functions

$$\sqrt{w} = 20/F_o \quad \text{if } I_0 \geq 4I_0(\text{min.})$$

$$\sqrt{w} = 1.25I_0^2/F_oI_0(\text{min.})^2 \quad \text{if } I_0 < 4I_0(\text{min.})$$

Scattering factors given by Thomas and Umeda[11] were used for iron, while those of Dawson[12] were used for sulfur. For carbon and oxygen the scattering factors of Berghuis, *et al.*,[13] were chosen. After two cycles the unweighted discrepancy factor, $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$, of 30.5% was obtained.

A three-dimensional Fourier synthesis[14] phased on one sulfur and five iron atoms was computed. This first approximation to the electron-density function showed no asymmetry of the heavy atom peaks and thereby supported the choice of Pnma indicated from the vector distribution on the Patterson maps. An assignment of twenty other peaks to represent one sulfur, nine carbon, and ten oxygen atoms was made. The resulting coordinates of these twenty atoms, together with those of the previously found six heavy atoms, were refined with the block-diagonal least-squares program[10]; initial isotropic thermal parameters for carbon and oxygen atoms were assumed to be 4.0 and 5.0 Å.^{2}, respectively. Two cycles of refinement carried out with the constraints of Pnma decreased the R_1 value to 13.5%. Another Fourier synthesis was calculated based on the phases of 24 atoms (*i.e.*, the phase contributions of two rather uncertain light atoms were excluded from the structure factor calculations); the results unambiguously showed the locations of all 27 independent atoms.

Further block-diagonal isotropic least-squares refinement of all atoms lowered the R_1 value to 11.3%, after which the Busing–Levy full-matrix least-squares pro-

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[7] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

[8] *Cf.* H. Lipson and W. Cochran, "The Determination of Crystal Structure," G. Bell and Sons Ltd., London, 1957, p. 170.

[9] "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p. 151.

[10] P. W. Sutton, "A Block-Diagonal Least-Squares Program for the CDC 1604," University of Wisconsin, 1962.

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

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

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

[14] J. F. Blount, "A Fourier Program for the CDC 1604," University of Wisconsin (1963).

gram[15] was used in order to obtain errors from the full inverse matrix. Of the 27 atoms, fifteen (*i.e.*, five iron atoms and five carbonyl groups) are fixed on the mirror plane. The final full-matrix isotropic least-squares refinement was continued until all parameter shifts were less than 30% with respect to the corresponding standard deviations. For the last full-matrix cycle during which 108 parameters, including individual isotropic thermal parameters and fifteen scale factors were varied, the values of the unweighted discrepancy factor, R_1, and the weighted discrepancy factor, $R_2 = [(\Sigma w||F_o| - |F_c||^2)^{1/2}/(\Sigma w|F_o|^2)^{1/2}] \times 100$, were 8.9 and 7.8%, respectively, for the 635 observed reflections; the final values of the error of fit function $[\Sigma w||F_o| - |F_c||^2/(m - n)]^{1/2}$ was 1.167. A three-dimensional difference synthesis, calculated on the basis of the refined parameters by means of the Sly–Shoemaker program,[16] gave no residual peak heights greater than 1.7 electrons/Å.^{3} or less than −1.5 electrons/Å.^{3}

Table I gives the final positional coordinates and thermal parameters with their standard deviations. The observed and calculated structure factors from the last cycle of the isotropic least-squares refinement are listed in Table II. The interatomic distances and bond angles calculated for the assigned parameters from the Busing–Levy function and error program[17] are listed in Tables III and IV, respectively, together with their standard deviations.

TABLE I

ATOMIC PARAMETERS AND STANDARD DEVIATIONS

Atom	x	y	z	B	σ_x	σ_y	σ_z	σ_B
Fe_1	0.2176	0.2500	0.0215	3.53	0.0005	0	0.0004	0.17
Fe_2	0.3248	0.2500	0.1919	3.67	0.0005	0	0.0004	0.18
Fe_3	0.4059	0.2500	0.0594	3.47	0.0005	0	0.0004	0.16
S_1	0.2891	0.1208	0.1007	3.67	0.0006	0.0007	0.0004	0.20
C_1	0.0904	0.2500	0.0594	5.91	0.0043	0	0.0026	1.28
O_1	0.0175	0.2500	0.0925	5.53	0.0025	0	0.0016	0.78
C_2	0.1996	0.1364	−0.0427	6.87	0.0024	0.0036	0.0018	1.02
O_2	0.1911	0.0567	−0.0845	6.92	0.0016	0.0020	0.0012	0.64
C_3	0.4075	0.2500	−0.0396	1.94	0.0028	0	0.0021	0.80
O_3	0.4136	0.2500	−0.1039	5.25	0.0022	0	0.0017	0.74
C_4	0.4959	0.1364	0.0679	5.25	0.0023	0.0028	0.0015	0.81
O_4	0.5545	0.0568	0.0803	8.10	0.0019	0.0021	0.0012	0.64
C_5	0.2114	0.2500	0.2384	4.93	0.0041	0	0.0024	1.15
O_5	0.1329	0.2500	0.2726	5.37	0.0024	0	0.0016	0.79
C_6	0.3910	0.1370	0.2460	5.51	0.0025	0.0032	0.0016	0.88
O_6	0.4272	0.0571	0.2752	7.61	0.0018	0.0025	0.0012	0.68
Fe_4	0.2988	0.2500	0.5640	3.78	0.0005	0	0.0004	0.18
Fe_5	0.2242	0.2500	0.6947	4.07	0.0006	0	0.0004	0.18
S_2	0.1574	0.1568	0.5975	3.85	0.0006	0.0007	0.0004	0.23
C_7	0.2942	0.2500	0.4842	4.80	0.0032	0	0.0031	1.11
O_7	0.2842	0.2500	0.4075	6.68	0.0026	0	0.0018	0.81
C_8	0.3898	0.1434	0.5696	7.66	0.0029	0.0034	0.0019	0.97
O_8	0.4456	0.0569	0.5790	5.96	0.0016	0.0019	0.0011	0.53
C_9	0.1265	0.2500	0.7601	11.75	0.0059	0	0.0037	2.26
O_9	0.0613	0.2500	0.8052	6.90	0.0027	0	0.0020	0.93
C_{10}	0.2986	0.1389	0.7346	6.08	0.0026	0.0033	0.0017	0.93
O_{10}	0.3470	0.0505	0.7567	6.85	0.0017	0.0022	0.0013	0.58

Discussion

The highly unusual feature of the crystals of King's presumed $S_2Fe_3(CO)_9$ compound is that the structure consists of an ordered array of two different molecular species, $S_2Fe_2(CO)_6$ and $S_2Fe_3(CO)_9$. The structures of both components have been determined previously.[4,5,7] The molecular configuration of the dinuclear species is in close agreement with that of triclinic $S_2Fe_2(CO)_6$,[7] while the trinuclear species is a conformer of the Hieber–Gruber compound, $Se_2Fe_3(CO)_9$[5] (and of the isomorphous Hieber–Gruber sulfur analog[4]).

The molecular configuration of the dinuclear species is shown in Figure 1 with bond distances and some selected bond angles. The essentially identical configuration of this molecule and the one in pure form is seen from a comparison of the corresponding molecular parameters of the triclinic $S_2Fe_2(CO)_6$ given in parentheses. The molecular structure, in which a disulfide group is symmetrically bonded to two iron tricarbonyl fragments (linked to each other by a presumed "bent" iron–iron bond which thereby explains the diamagnetism) possesses C_{2v} symmetry within experimental error and can be constructed from the intersection of the basal planes of two distorted tetragonal pyramids (each composed of two sulfurs and three carbonyl carbons) along the S–S line. The "bent" Fe–Fe bond involving the overlap of two iron orbitals at an angle of 129° is presumed together with the S–S bond to be responsible for the

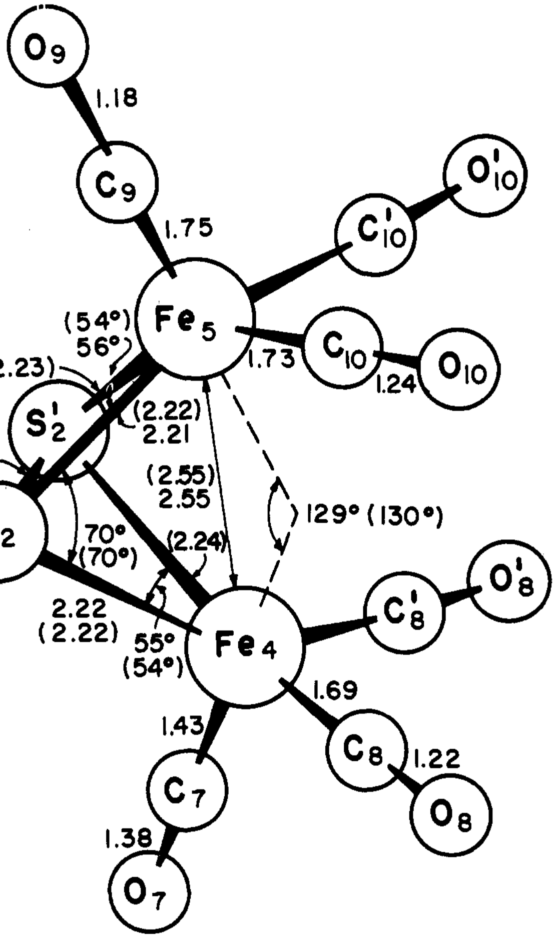

Figure 1.—The molecular configuration of the $S_2Fe_2(CO)_6$ species. The corresponding molecular parameters for the triclinic $S_2Fe_2(CO)_6$ are given in parentheses.

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(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, M.I.T. (1960).

(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).

Table II

Observed and Calculated Structure Factors

H	K	L	FO	FC
0	0	2	170.0	144.4
0	0	4	72.0	67.0
0	0	6	490.5	-476.5
0	0	8	212.8	-199.5
0	0	10	117.6	120.8
0	0	12	56.4	57.4
0	0	14	50.1	-39.3
0	0	16	43.3	24.9
0	0	20	47.0	37.8
1	0	3	41.1	40.4
1	0	4	70.9	-75.6
1	0	5	69.3	67.6
1	0	6	142.8	-131.3
1	0	7	40.7	34.7
1	0	8	67.3	71.2
1	0	10	64.8	60.7
1	0	12	94.0	-101.8
1	0	13	49.6	38.5
2	0	0	444.0	-362.3
2	0	4	55.5	-54.1
2	0	5	63.7	-63.3
2	0	6	39.5	-35.4
2	0	9	118.1	-122.9
2	0	10	107.9	-115.7
2	0	11	66.1	67.1
2	0	14	74.4	61.2
3	0	2	85.3	90.7
3	0	3	256.5	-266.9
3	0	4	182.4	-179.2
3	0	6	75.5	77.7
3	0	7	44.7	-49.1
3	0	8	58.3	-53.0
3	0	9	111.9	109.3
3	0	10	87.9	85.9
3	0	11	94.1	104.5
3	0	12	94.5	99.0
3	0	13	72.3	-78.2
4	0	1	108.1	-103.5
4	0	2	97.5	97.7
4	0	3	255.2	-258.5
4	0	5	132.8	127.7
4	0	6	91.6	89.9
4	0	7	76.7	74.8
4	0	9	201.1	205.9
4	0	10	73.2	72.6
4	0	11	107.2	-106.0
4	0	13	75.7	-85.4
4	0	19	82.1	68.0
5	0	1	148.0	142.0
5	0	2	41.1	36.2
5	0	3	222.7	224.2
5	0	5	49.2	-31.9
5	0	6	48.1	-45.5
5	0	8	52.9	-47.7
5	0	9	80.0	-77.2
5	0	11	104.9	-98.1
5	0	13	62.7	63.5
6	0	1	56.1	56.5
6	0	2	51.6	-49.2
6	0	3	64.0	-67.6
6	0	4	53.9	-56.8
6	0	5	107.6	-108.8
6	0	9	73.3	-74.1
6	0	10	40.1	57.5
6	0	11	76.5	75.3
7	0	1	96.4	-92.0
7	0	3	81.9	-80.2
7	0	4	47.1	40.2
7	0	5	40.4	-34.7
7	0	13	51.5	-50.9
8	0	0	130.4	-138.4
8	0	1	46.3	-42.6
8	0	8	58.1	51.5
9	0	1	48.9	34.1
9	0	6	68.0	54.8
10	0	0	111.1	109.8
10	0	2	86.5	78.7
10	0	8	53.9	-43.8
10	0	10	56.3	-39.8
11	0	6	51.5	-30.6
13	0	1	58.1	-40.3
13	0	7	60.9	38.1
14	0	0	51.3	42.4
16	0	0	64.0	-47.7
0	1	5	53.7	-53.6
0	1	7	47.1	-39.5
0	1	9	75.3	-76.3
0	1	11	42.1	-35.7
0	1	13	46.3	-37.5
1	1	2	93.8	85.3
1	1	3	84.4	-83.0
1	1	4	39.2	40.7
1	1	5	74.7	-71.7
1	1	6	106.3	126.5
1	1	7	88.2	-88.3
1	1	10	66.0	-76.1
1	1	12	70.1	-75.4
1	1	13	55.2	46.7
1	1	14	54.6	-56.3
2	1	0	146.0	146.7
2	1	3	40.4	-41.8
2	1	5	90.5	-93.4
2	1	6	68.1	-67.9
2	1	8	99.8	-102.6
2	1	9	82.3	84.1
2	1	10	56.9	-69.0
2	1	11	110.5	110.2
2	1	13	99.2	95.2
2	1	16	66.4	65.8
3	1	1	55.6	-50.7
3	1	2	48.3	-47.6
3	1	3	51.0	49.2
3	1	6	62.3	-61.9
3	1	7	115.7	116.3
3	1	9	107.4	108.5
3	1	10	59.0	52.2
3	1	11	43.9	31.2
3	1	12	54.2	55.8
3	1	14	55	55.9
3	1	15	64.5	-74.0
4	1	1	40.7	33.9
4	1	2	89.2	86.0
4	1	3	147.8	-157.7
4	1	4	53.9	50.0
4	1	7	110.3	108.1
4	1	8	54.9	46.1
4	1	9	52.7	-42.6
4	1	13	102.5	-99.3
4	1	15	52.5	-50.3
5	1	1	78.7	-78.4
5	1	2	36.8	34.4
5	1	3	80.9	-80.1
5	1	5	106.4	107.8
5	1	6	53.4	-44.2
5	1	7	35.1	-29.1
5	1	8	51.9	-47.8
5	1	9	48.0	-44.2
5	1	10	39.7	-41.7
6	1	3	119.6	115.3
6	1	4	94.9	-93.1
6	1	5	94.9	100.6
6	1	6	98.0	-103.2
6	1	7	66.7	-66.3
6	1	9	63.2	53.7
6	1	11	62.7	-53.9
7	1	1	73.8	67.9
7	1	2	74.5	-65.2
7	1	3	93.6	100.1
7	1	4	122.0	-125.1
7	1	5	96.5	-98.1
7	1	6	69.8	70.2
7	1	8	64.7	71.0
7	1	9	41.6	-28.4
7	1	10	68.1	66.4
7	1	11	55.7	-43.6
7	1	12	57.1	45.6
7	1	13	47.3	39.0
8	1	0	74.0	-71.2
8	1	2	95.1	-91.2
8	1	3	58.1	-50.3
8	1	4	99.0	103.2
8	1	5	53.5	-54.9
8	1	6	155.2	166.7
8	1	11	51.9	48.6
8	1	18	56.6	-45.1
9	1	1	62.7	58.0
9	1	4	108.6	109.1
9	1	6	74.7	-74.7
9	1	8	55.9	-46.6
9	1	12	71.1	-59.8
10	1	0	92.9	-82.9
10	1	4	69.9	-60.7
10	1	6	62.7	-59.9
11	1	2	56.6	50.8
11	1	6	67.1	74.5
12	1	0	109.5	97.6
12	1	7	56.8	-48.9
12	1	8	51.2	-40.7
13	1	7	59.0	47.4
0	2	0	683.3	-567.1
0	2	2	98.2	-106.8
0	2	4	82.0	-91.9
0	2	6	40.8	-45.2
0	2	8	170.5	186.2
0	2	10	47.2	-53.4
0	2	12	57.3	57.8
0	2	16	67.9	-60.0
1	2	1	61.4	60.2
1	2	2	283.0	249.8
1	2	3	47.6	-44.7
1	2	4	30.1	31.1
1	2	6	214.0	226.6
1	2	7	74.5	-70.3
1	2	10	54.4	-53.6
1	2	14	50.7	-46.8
1	2	16	55.2	39.3
2	2	0	291.1	292.2
2	2	4	91.9	97.2
2	2	6	44.3	48.2
2	2	7	34.0	-31.9
2	2	8	72.7	-71.0
2	2	9	80.4	88.6
2	2	10	57.9	66.0
3	2	2	58.1	-53.6
3	2	3	174.2	177.9
3	2	4	92.0	90.5
3	2	5	31.4	-27.2
3	2	6	69.1	-72.5
3	2	7	58.1	59.6
3	2	11	78.9	-73.8
3	2	12	79.1	-81.7
3	2	13	59.6	59.2
4	2	0	30.1	-31.5
4	2	1	69.7	63.5
4	2	3	201.3	-192.1
4	2	4	60.1	-61.1
4	2	5	134.3	-136.3
4	2	6	62.4	-64.0
4	2	9	45.3	-39.7
4	2	11	83.6	92.2
5	2	1	192.0	-170.1
5	2	3	173.8	-173.5
5	2	5	70.2	68.3
5	2	6	42.3	49.6
5	2	11	73.2	72.8
5	2	13	49.3	-50.8
6	2	0	37.2	35.9
6	2	2	64.9	60.0
6	2	3	83.6	81.7
6	2	4	44.5	39.2
6	2	5	96.7	102.2
6	2	9	72.4	72.2
6	2	10	45.9	-52.5
6	2	11	52.8	-39.6
7	2	1	71.9	64.4
7	2	2	49.1	40.6
7	2	3	82.8	76.7
7	2	4	35.9	-25.0
7	2	8	45.0	-38.1
8	2	5	43.5	-36.3
8	2	6	45.0	32.6
8	2	8	53.1	-34.5
9	2	1	58.9	-52.5
9	2	2	50.4	-44.8
9	2	3	40.2	-29.3
9	2	4	45.5	-38.5
9	2	6	79.3	-69.0
9	2	12	54.9	41.6
10	2	0	108.5	-104.0
10	2	2	71.3	-64.7
10	2	4	43.1	-30.2
10	2	6	52.5	36.7
10	2	8	54.5	44.2
10	2	10	54.4	42.9
11	2	1	44.7	51.7
11	2	4	45.6	41.0
0	3	3	49.8	46.0
0	3	5	103.5	109.3
0	3	7	57.5	60.9
0	3	9	63.5	69.1
1	3	2	49.9	61.1
1	3	3	55.7	61.2
1	3	4	130.0	135.9
1	3	5	117.3	119.1
1	3	6	80.9	-84.8
1	3	7	61.7	63.4
1	3	12	50.2	48.5
1	3	14	55.0	49.2
2	3	2	180.8	-180.7
2	3	3	97.9	97.5
2	3	4	117.3	114.6
2	3	5	36.1	-36.1
2	3	8	144.0	146.8
2	3	9	93.5	-103.4
2	3	11	50.7	-50.3
2	3	13	55.7	-59.0
2	3	15	41.9	-34.8
3	3	1	294.7	261.4
3	3	2	46.4	42.5
3	3	3	69.8	-60.7
3	3	5	124.6	-126.8
3	3	6	43.3	47.0
3	3	7	206.0	-209.8
3	3	8	34.4	-31.2
3	3	9	50.6	-59.1
3	3	10	75.0	-80.1
3	3	12	51.6	-59.0
3	3	14	51.1	-48.8
4	3	1	112.4	-99.4
4	3	2	35.9	-28.8
4	3	3	30.0	-24.4
4	3	4	31.4	-30.2
4	3	5	38.3	-22.7
4	3	8	89.1	-91.9
4	3	9	101.5	103.6
4	3	13	53.3	52.8
4	3	15	48.8	40.7
5	3	1	57.5	51.5
5	3	2	83.3	86.9
5	3	3	86.7	85.9
5	3	4	50.3	47.6
5	3	5	39.8	-35.9
5	3	6	36.8	36.5
5	3	10	50.2	48.8
5	3	12	44.5	40.5
5	3	13	54.7	52.8
6	3	0	68.5	62.3
6	3	1	123.8	119.5
6	3	3	109.7	-109.1
6	3	5	52.9	-52.4
6	3	6	55.6	46.3
6	3	9	57.7	-52.2
6	3	10	68.1	64.9
6	3	11	64.5	65.2
7	3	1	61.4	-56.9
7	3	2	75.8	-76.0
7	3	3	102.6	-103.1
7	3	5	71.1	73.0
7	3	9	51.1	43.5
7	3	10	52.7	-51.6
7	3	11	46.0	52.3
7	3	12	92.3	-103.5
8	3	0	55.5	-46.3
8	3	2	68.0	63.3
8	3	3	46.8	38.0
8	3	6	67.9	-72.8
8	3	10	92.0	-94.5
8	3	11	42.3	-21.8
9	3	2	71.1	63.1
9	3	4	67.3	-65.4
9	3	5	62.1	-64.8
9	3	6	49.8	44.1
9	3	12	73.0	86.9
10	3	0	145.7	127.1
10	3	10	57.0	45.7
11	3	1	49.1	-39.9
11	3	2	61.0	-58.7
11	3	6	51.4	-56.5
12	3	0	80.2	-85.7
12	3	1	51.9	36.6
12	3	8	53.1	39.9
12	3	9	54.1	-49.8
13	3	7	69.1	-45.6
14	3	9	65.1	40.6
0	4	0	288.7	297.2
0	4	4	147.1	157.9
0	4	6	91.4	98.3
0	4	8	172.1	-183.1
0	4	12	58.4	-55.6
0	4	14	42.7	42.5
0	4	16	75.7	83.2
1	4	4	51.6	51.5
1	4	5	63.0	-65.9
1	4	6	225.7	-238.5
1	4	8	116.3	-133.4
1	4	9	48.6	48.1
1	4	10	45.3	42.3
1	4	14	89.6	93.6
1	4	16	67.7	-58.5
1	4	18	66.3	-55.5
2	4	0	84.7	-90.3
2	4	3	98.7	-101.5
2	4	4	119.9	-128.4
2	4	5	37.9	-47.6
2	4	6	106.1	-112.1
2	4	7	109.7	120.4
2	4	8	77.7	80.0
2	4	9	53.6	-55.3
2	4	13	53.0	-66.1
2	4	16	50.4	-50.8
3	4	1	88.4	-77.2
3	4	3	105.6	-99.0
3	4	4	91.0	-85.9
3	4	5	148.0	150.3
3	4	6	100.6	108.3
3	4	7	42.4	-43.2
3	4	9	37.6	-47.8
3	4	15	58.4	50.4
4	4	3	213.1	186.1
4	4	5	118.7	110.7
4	4	6	38.3	44.9
4	4	7	40.3	-36.1
4	4	9	46.3	33.1
4	4	10	53.7	45.4
5	4	1	259.1	222.6
5	4	3	147.9	135.2
5	4	4	42.9	-43.0
5	4	5	175.3	-163.9
5	4	7	49.3	-48.1
5	4	13	53.9	39.4
6	4	0	102.4	-87.8
6	4	2	98.3	-88.8
6	4	3	194.0	-174.5
6	4	5	90.1	-80.8
7	4	1	55.1	-48.8
7	4	3	52.6	-49.1
8	4	0	60.0	-49.4
8	4	8	53.6	50.9
9	4	2	50.9	32.1
9	4	4	52.0	38.9
9	4	6	61.6	61.9
10	4	0	58.1	54.3
10	4	2	60.0	63.9
11	4	1	61.7	-52.4
0	5	3	34.5	-41.7
0	5	5	47.0	-50.4
0	5	7	45.9	-48.1
1	5	1	39.4	-50.2
1	5	2	62.8	68.2
1	5	3	40.0	-32.7
1	5	4	44.3	44.0
1	5	10	55.4	-67.8
2	5	0	113.4	120.1
2	5	3	35.5	-35.5
2	5	4	34.1	-37.5
2	5	6	49.0	-55.3
2	5	8	72.5	-76.4
2	5	9	70.3	78.6
2	5	11	45.1	51.3
2	5	13	51.5	55.2
3	5	1	103.0	-98.8
3	5	2	74.2	-78.1
3	5	3	33.9	29.1
3	5	5	54.4	58.5
3	5	7	81.5	85.6
3	5	8	50.4	58.6
3	5	9	60.0	64.6
3	5	10	72.0	73.9
4	5	1	85.8	74.0
4	5	3	89.7	84.1
4	5	4	28.9	37.8
4	5	8	50.1	46.8
4	5	9	110.1	-121.9
5	5	1	82.6	70.7
5	5	3	97.2	-90.3
5	5	5	43.4	-36.8
5	5	7	74.2	-81.8
5	5	11	52.1	65.2
6	5	0	83.8	-76.2
6	5	1	63.5	-53.7
6	5	5	77.3	81.1
6	5	9	53.3	61.5
6	5	10	61.0	-58.9
6	5	11	63.1	-72.4
7	5	1	47.4	44.4
7	5	2	47.9	43.3
7	5	3	97.5	95.7
7	5	4	58.2	-51.9
7	5	5	53.0	-52.5
7	5	9	59.4	-57.3
7	5	10	67.2	68.3
7	5	11	44.5	-50.7
7	5	12	80.7	97.6
8	5	0	93.2	83.6
8	5	2	58.8	-53.5
8	5	3	67.8	-67.5
8	5	10	79.6	88.8
9	5	2	102.3	-95.2
9	5	12	77.8	-81.3
10	5	0	140.6	-122.8
12	5	0	53.5	41.3
13	5	1	50.2	-44.6
0	6	0	345.7	-336.3
0	6	4	78.8	-87.3
0	6	8	122.1	136.7
0	6	16	58.9	-55.8
1	6	2	58.9	65.8
1	6	6	133.7	151.0
1	6	8	49.4	60.5
1	6	14	58.1	-61.5
1	6	16	56.3	34.1
2	6	0	103.6	113.1
2	6	3	64.1	68.9
2	6	4	58.1	61.5
2	6	6	60.3	61.9
2	6	7	70.9	-74.5
2	6	8	43.0	-42.0
2	6	9	41.2	39.3
3	6	1	58.8	56.4
3	6	2	57.0	-54.6
3	6	3	92.2	89.6
3	6	4	54.4	51.0
3	6	5	92.6	-94.0
3	6	6	48.0	-55.8
3	6	12	54.0	-57.8
4	6	0	67.1	-64.2
4	6	3	82.2	-77.6
4	6	5	87.5	-83.7
4	6	9	49.0	-49.7
4	6	10	58.3	-61.3
4	6	11	47.9	39.1
5	6	1	141.3	-129.9
5	6	2	51.0	48.9
5	6	3	132.6	-119.8
5	6	4	54.0	53.0
5	6	5	75.5	78.0
6	6	0	95.0	81.2
6	6	1	42.3	-38.8
6	6	2	71.6	64.5
6	6	3	82.1	79.1
6	6	5	64.8	66.3
6	6	6	48.0	-43.5
7	6	3	60.7	55.0
7	6	5	50.9	39.6
8	6	0	64.4	60.5
8	6	3	50.9	26.6
8	6	9	58.1	-52.3
9	6	2	53.8	-45.3
9	6	4	49.2	-40.4
9	6	5	44.7	-38.0
10	6	0	88.3	-80.4
10	6	2	65.0	-58.8
11	6	1	54.0	35.3
11	6	2	54.1	38.2
11	6	4	55.1	42.6
0	7	1	48.8	66.1
0	7	3	85.8	87.7
0	7	13	57.6	63.7
1	7	1	58.8	78.3
1	7	6	34.7	-36.4
1	7	9	42.7	40.2
2	7	0	101.2	-97.2
2	7	4	64.4	67.6
2	7	6	56.1	55.3
2	7	7	41.5	35.4
2	7	8	50.8	65.5
2	7	9	43.6	-34.1
2	7	11	59.0	-64.8
2	7	13	68.6	-72.6
3	7	1	55.2	62.4
3	7	2	88.5	84.4
3	7	4	28.1	31.4
3	7	7	85.1	-93.0
3	7	8	53.8	-62.5
3	7	9	49.3	-64.3
3	7	10	45.0	-42.6
4	7	0	56.3	52.6
4	7	1	55.6	-48.9
4	7	4	67.4	-68.4
4	7	6	51.9	-48.9
4	7	9	46.4	47.9
5	7	3	63.9	54.2
5	7	6	42.7	40.9
7	7	3	62.3	-63.9
7	7	4	50.5	40.2
8	7	2	40.1	40.0
8	7	6	68.9	-68.5
8	7	10	47.6	-42.6
9	7	4	72.2	-52.8
10	7	0	65.6	60.1
11	7	6	64.1	-46.4
12	7	0	50.5	-47.6
0	8	0	248.0	255.9
0	8	8	75.0	-79.9
1	8	2	113.2	-125.1
1	8	6	73.7	-83.7
1	8	7	31.2	37.2
1	8	8	35.7	29.4
2	8	0	150.7	-142.3
2	8	10	48.3	-52.8
3	8	2	49.2	50.3
3	8	3	77.2	-81.2
3	8	4	29.7	-18.8
3	8	11	49.3	41.0
3	8	12	59.5	58.5
4	8	0	51.7	44.5
4	8	1	35.6	-34.0
4	8	3	57.9	54.8
4	8	5	67.0	67.7
4	8	9	36.6	34.2
4	8	10	38.3	38.4
4	8	11	57.3	-56.9
5	8	1	47.4	50.6
5	8	3	92.9	91.5
5	8	9	49.5	-36.7
5	8	11	58.5	-56.1
6	8	5	53.7	-50.5
6	8	9	58.1	-50.0
7	8	3	61.6	-49.1
9	8	2	53.4	39.9
9	8	5	41.8	27.7
10	8	0	95.6	81.5
10	8	2	54.0	41.0
10	8	6	44.8	-37.3
1	9	6	33.0	35.0
2	9	0	47.9	52.1
2	9	5	24.2	-22.3
2	9	6	26.0	-26.1
2	9	8	38.9	-44.2
2	9	11	43.6	43.4
2	9	13	38.0	40.3
3	9	2	23.8	-21.2
3	9	7	46.9	54.1
3	9	9	37.9	42.6
4	9	1	26.4	21.3
4	9	2	32.8	29.0
4	9	3	35.8	-34.8
4	9	7	30.5	28.8
5	9	1	31.1	-27.0
5	9	3	31.6	-34.1
5	9	5	38.4	37.8
6	9	3	41.1	42.7
6	9	4	38.5	-35.6
6	9	5	39.6	33.9
6	9	6	32.8	-36.3
7	9	1	35.3	25.3
7	9	3	40.5	39.6
7	9	4	42.2	-39.7
7	9	5	39.6	-34.7
7	9	6	36.4	24.4
8	9	2	38.1	-33.7
8	9	4	39.1	33.8
8	9	6	61.9	61.5
9	9	4	52.5	45.0
10	9	0	43.1	-37.1
10	9	4	35.3	-22.0
12	9	0	48.1	43.4
0	10	0	190.2	-206.5
0	10	6	39.3	39.7
0	10	8	55.7	63.7
1	10	6	49.3	61.1
2	10	0	49.3	64.2
3	10	3	49.3	53.4
3	10	4	41.5	36.2
4	10	5	48.4	-41.1
4	10	6	39.5	-33.0
4	10	9	50.7	-39.7
5	10	1	58.8	-56.8
5	10	3	61.5	-57.1
5	10	5	42.3	27.0
5	10	6	41.3	19.5
6	10	3	59.0	47.2
6	10	5	43.1	34.3
7	10	1	54.0	37.9
0	11	7	45.5	48.2

molecular geometry with the sharply acute S–Fe–S and bridge Fe–S–Fe angles of 56° (av.) and 70° (av.), respectively. Since the standard deviations of the molecular bond distances and angles of the triclinic $S_2Fe_2(CO)_6$ are *very much lower* than those determined for the molecule in the double complex (which fact is also substantiated by a comparison of ranges of distances and angles for the two compounds), the reader is referred to the work on the pure triclinic form for a detailed description of the dinuclear molecule including a comparison of the configuration with that of $[C_2H_5SFe(CO)_3]_2$ and a discussion of the bonding with respect to those given for related μ-peroxo- and acetylene–dimetal complexes.

The molecular configuration of the diamagnetic trinuclear species, $S_2Fe_3(CO)_9$, is presented in Figure 2. This molecule ideally consists of a $S_2Fe_2(CO)_6$ moiety of C_{2v} symmetry bonded to an apical $Fe(CO)_3$ fragment by two Fe–Fe and two Fe–S bonds such that only the vertical mirror plane (demanded crystallographically

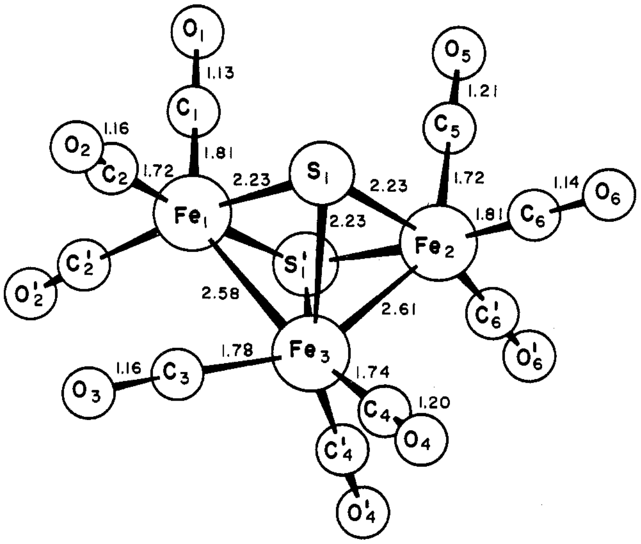

Figure 2.—The molecular configuration of the $S_2Fe_3(CO)_9$ species.

TABLE III

MOLECULAR BOND DISTANCES WITH STANDARD DEVIATIONS[a]

Bond	Distance, Å.	Std. dev., Å	Bond	Distance, Å	Std. dev., Å.
$Fe_1\cdots Fe_2$	3.371	0.010	Fe_4-Fe_5	2.545	0.011
Fe_1-Fe_3	2.582	0.009	Fe_4-S_2	2.220	0.007
Fe_2-Fe_3	2.609	0.010	Fe_5-S_2	2.212	0.009
Fe_1-S_1	2.228	0.009	Fe_4-C_7	1.43	0.05
Fe_2-S_1	2.225	0.009	Fe_4-C_8	1.69	0.04
Fe_3-S_1	2.233	0.009	Fe_5-C_9	1.75	0.08
Fe_1-C_1	1.81	0.06	Fe_5-C_{10}	1.73	0.04
Fe_1-C_2	1.72	0.04	C_7-O_7	1.38	0.05
Fe_2-C_5	1.72	0.05	C_8-O_8	1.22	0.04
Fe_2-C_6	1.81	0.04	C_9-O_9	1.18	0.07
Fe_3-C_3	1.78	0.04	$C_{10}-O_{10}$	1.24	0.03
Fe_3-C_4	1.74	0.03	S_2-S_2'	2.065	0.017
C_1-O_1	1.13	0.05	$C_8\cdots C_8'$	2.36	0.07
C_2-O_2	1.16	0.04	$C_{10}\cdots C_{10}'$	2.46	0.07
C_3-O_3	1.16	0.03			
C_4-O_4	1.20	0.03			
C_5-O_5	1.21	0.05			
C_6-O_6	1.14	0.03			
$S_1\cdots S_1'$	2.863	0.015			
$C_2\cdots C_2'$	2.52	0.08			
$C_4\cdots C_4'$	2.52	0.06			
$C_6\cdots C_6'$	2.50	0.07			

[a] Primed atoms are related to the basic atoms by the C_s-m symmetry operation at $b/4$.

by the space group symmetry) passing through the three iron atoms is retained in the entire molecule. This trinuclear species is found to be a conformer of the Hieber–Gruber molecular compound $Se_2Fe_3(CO)_9$, in

TABLE IV

BOND ANGLES WITH STANDARD DEVIATION

Angle	Degrees	Angle	Degrees
$Fe_1-Fe_2-Fe_3$	49.2 ± 0.2	$S_1-Fe_1-C_1$	98.9 ± 1.1
$Fe_2-Fe_1-Fe_3$	49.9 ± 0.2	$S_1-Fe_2-C_5$	99.9 ± 1.1
$Fe_1-Fe_3-Fe_2$	81.0 ± 0.3	$S_1-Fe_1-C_2$	90.0 ± 1.1
$S_1-Fe_1-S_1'$	80.0 ± 0.4	$S_1-Fe_2-C_6$	93.0 ± 1.0
$S_1-Fe_2-S_1'$	80.1 ± 0.4	$S_1-Fe_1-C_2'$	162.7 ± 1.2
$S_1-Fe_3-S_1'$	79.7 ± 0.5	$S_1-Fe_2-C_6'$	160.5 ± 1.0
$S_1-Fe_1-Fe_2$	40.8 ± 0.2	$S_1-Fe_3-C_3$	109.9 ± 1.0
$S_1-Fe_2-Fe_1$	40.8 ± 0.2	$S_1-Fe_3-C_4$	88.9 ± 1.0
$S_1-Fe_1-Fe_3$	54.7 ± 0.3	$S_1-C_1-S_1'$	55.3 ± 1.0
$S_1-Fe_3-Fe_1$	54.6 ± 0.3	$S_1-C_5-S_1'$	56.3 ± 0.9
$S_1-Fe_2-Fe_3$	54.3 ± 0.3	$S_1-O_1-S_1'$	43.4 ± 0.4
$S_1-Fe_3-Fe_2$	54.0 ± 0.2	$S_1-O_5-S_1'$	42.2 ± 0.4
$Fe_1-S_1-Fe_2$	98.4 ± 0.4	$C_1-Fe_1-C_2$	97.0 ± 1.4
$Fe_2-S_1-Fe_3$	71.6 ± 0.3	$C_2-Fe_1-C_2'$	93.8 ± 2.3
$Fe_3-S_1-Fe_1$	70.7 ± 0.3	$C_2'-Fe_1-C_1$	97.0 ± 1.4
$Fe_1-S_1-S_1'$	50.0 ± 0.2	$C_5-Fe_2-C_6$	99.3 ± 1.4
$Fe_2-S_1-S_1'$	50.0 ± 0.2	$C_6-Fe_2-C_6'$	87.5 ± 1.9
$Fe_3-S_1-S_1'$	50.1 ± 0.2	$C_6'-Fe_2-C_5$	99.3 ± 1.4
$Fe_1-C_1-O_1$	170.4 ± 4.3	$C_3-Fe_3-C_4$	94.6 ± 1.2
$Fe_1-C_2-O_2$	176.8 ± 3.0	$C_4-Fe_3-C_4'$	92.7 ± 2.0
$Fe_2-C_5-O_5$	178.5 ± 3.8	$C_4'-Fe_3-C_3$	94.6 ± 1.2
$Fe_2-C_6-O_6$	172.4 ± 2.8	$C_1-C_2-C_2'$	61.6 ± 0.9
$Fe_3-C_3-O_3$	176.6 ± 3.7	$C_2-C_2'-C_1$	61.6 ± 0.9
$Fe_3-C_4-O_4$	173.9 ± 2.8	$C_2'-C_1-C_2$	56.7 ± 1.8
$C_5-C_6-C_6'$	62.3 ± 0.8	$S_2-Fe_4-C_7$	103.6 ± 1.6
$C_6-C_6'-C_5$	62.3 ± 0.8	$S_2-Fe_5-C_9$	103.6 ± 1.9
$C_6'-C_5-C_6$	55.5 ± 1.7	$S_2-Fe_4-C_8$	105.0 ± 1.2
$C_3-C_4-C_4'$	60.8 ± 0.7	$S_2-Fe_5-C_{10}$	102.8 ± 1.1
$C_4-C_4'-C_3$	60.8 ± 0.7	$S_2-Fe_4-C_8'$	155.4 ± 1.2
$C_4'-C_3-C_4$	58.3 ± 1.5	$S_2-Fe_5-C_{10}'$	152.3 ± 1.1
$Fe_3-Fe_1-C_1$	142.7 ± 1.5	$C_7-Fe_4-C_8$	95.2 ± 1.8
$Fe_3-Fe_2-C_5$	143.4 ± 1.5	$C_8-Fe_4-C_8'$	88.7 ± 2.5
$Fe_3-Fe_1-C_2$	108.0 ± 1.1	$C_8'-Fe_4-C_7$	95.2 ± 1.8
$Fe_3-Fe_2-C_6$	106.9 ± 1.0	$C_9-Fe_5-C_{10}$	98.2 ± 1.8
$S_2-Fe_4-S_2'$	55.4 ± 0.4	$C_{10}-Fe_5-C_{10}'$	90.7 ± 2.2
$S_2-Fe_5-S_2'$	55.6 ± 0.4	$C_{10}'-Fe_5-C_9$	98.2 ± 1.8
$Fe_4-S_2-Fe_5$	70.1 ± 0.3	$C_7-C_8-C_8'$	59.3 ± 1.1
$Fe_4-S_2-S_2'$	62.3 ± 0.2	$C_8-C_8'-C_7$	59.3 ± 1.1
$Fe_5-S_2-S_2'$	62.2 ± 0.2	$C_8'-C_7-C_8$	61.4 ± 2.1
$Fe_4-C_7-O_7$	176.9 ± 4.1	$C_9-C_{10}-C_{10}'$	62.1 ± 1.1
$Fe_4-C_8-O_8$	170.9 ± 3.2	$C_{10}-C_{10}'-C_9$	62.1 ± 1.1
$Fe_5-C_9-O_9$	179.1 ± 6.1	$C_{10}'-C_9-C_{10}$	55.9 ± 2.1
$Fe_5-C_{10}-O_{10}$	172.4 ± 2.7		

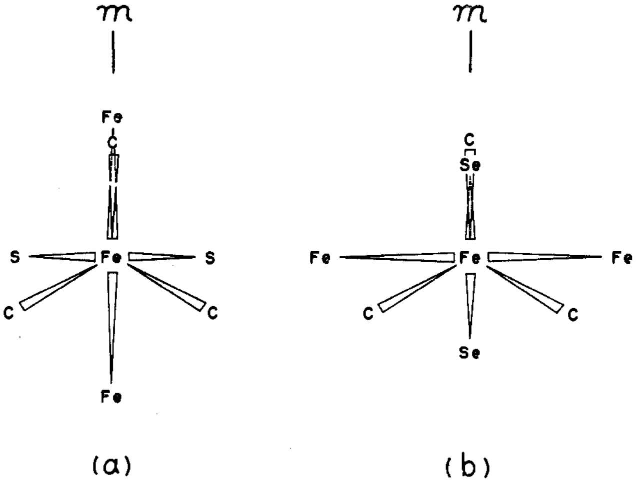

Figure 3.—Schematic representation of the orientation of the seven ligands (two irons, two chalcogens, and three carbonyl groups) about the apical iron atom for the King $S_2Fe_3(CO)_9$ mixed compound and the Hieber–Gruber $Se_2Fe_3(CO)_9$ compound.[5] Note that the two conformations are related to each other by a 90° rotation of the iron–chalcogen ligands about the localized principal axis normal to the paper.

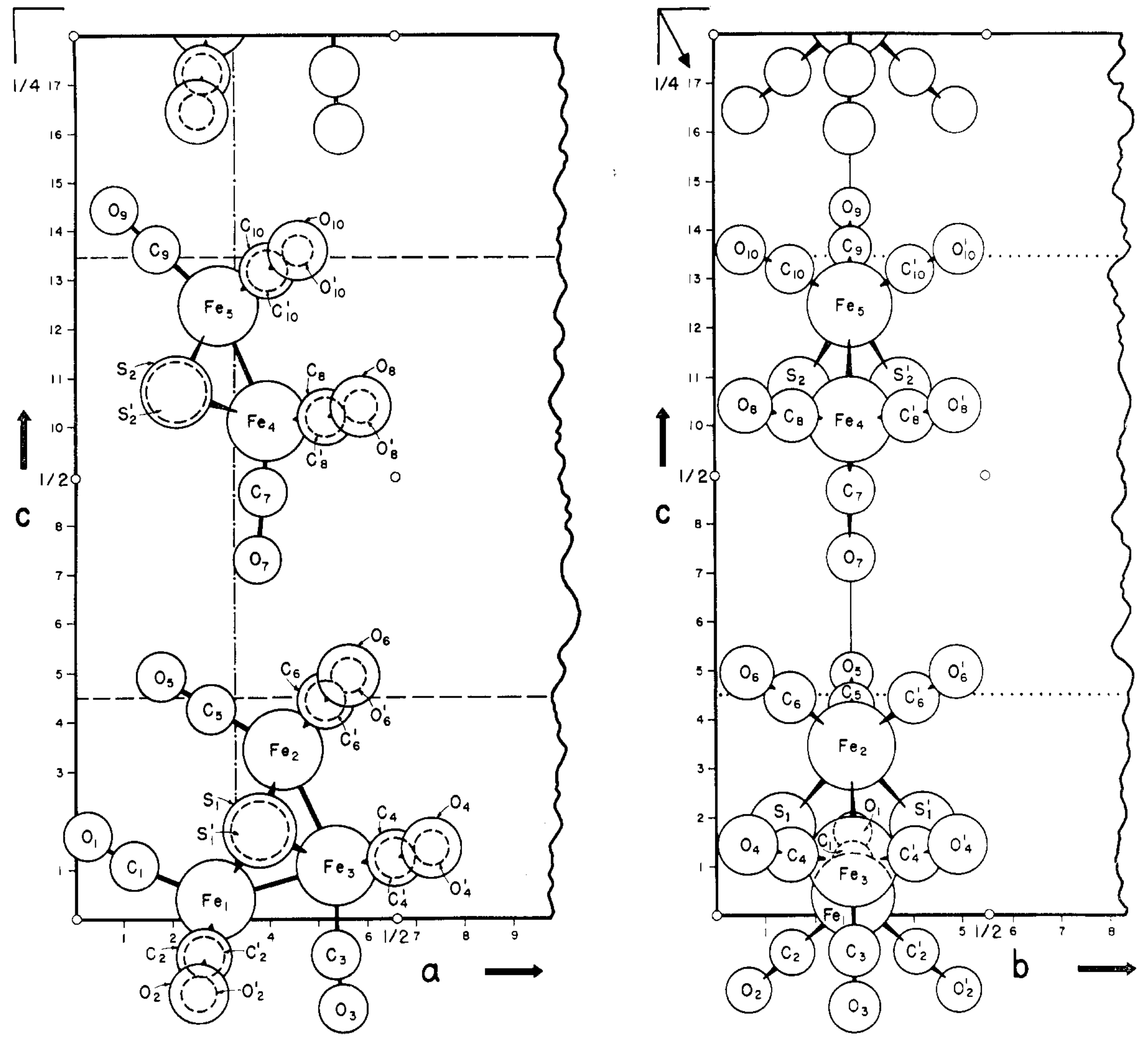

Figure 4.—[010] and [100] projections of the basic molecules.

TABLE V

COMPARISON OF TWO COMPLEXES[a]

$S_2Fe_3(CO)_9$		$Se_2Fe_3(CO)_9$[5]	
Fe–Fe	2.60 Å. (av.)	Fe–Fe	2.65 Å. (av.)
Fe···Fe	3.37 Å.	Fe···Fe	3.51 Å.
Fe–S	2.23 Å. (av.)	Fe–Se	2.35 Å. (av.)
S···S	2.86 Å.	Se···Se	3.10 Å.
Fe–C	1.76 Å. (av.)	Fe–C	1.79 Å. (av.)
C–O	1.17 Å. (av.)	C–O	1.14 Å. (av.)
Fe(B)–S–Fe(B)	98.4°	Fe(B)–Se–Fe(B)	96.6° (av.)
S–Fe(B)–S	80.1° (av.)	Se–Fe(B)–Se	82.4° (av.)
S–Fe(B)–Fe(A)	54.5° (av.)	Se–Fe(B)–Fe(A)	56° (av.)
S–Fe(A)–Fe(B)	54.3° (av.)	Se–Fe(A)–Fe(B)	
Fe(B)–S–Fe(A)	71.2° (av.)	Fe(B)–Se–Fe(A)	68° (av.)

[a] Fe(A) represents the apical iron atom; Fe(B) a basal iron atom.

which the only significant difference involves the relative orientation of the apical $Fe(CO)_3$ group. In Figure 3 a representation of the orientation of the seven ligands (comprised of the two basal iron and two chalcogen atoms as well as the three carbonyl groups) about the apical iron atom Fe_3 is given for the King $S_2Fe_3(CO)_9$ mixed compound (Figure 3a) and the Hieber–Gruber $Se_2Fe_3(CO)_9$ compound (Figure 3b). It is seen that the two conformers are related to each other by a 30° rotation of the three carbonyl groups about the localized threefold axis of the apical $Fe(CO)_3$ fragment (or alternatively by a 90° rotation of the four iron–chalcogen ligands about the same principal axis of the seven ligands). With the assumption (in terms of localized electron-pair bonds) of the *quasi*-equivalence of the seven regularly-coordinated iron, chalcogen, and carbonyl ligands about the apical iron, the two conformers are equivalent. Of significance is that this basic configuration was found[5] to represent a new type of seven-coordination. Examination of the molecular parameters for $S_2Fe_3(CO)_9$ and $Se_2Fe_3(CO)_9$ given in Table V shows the corresponding bond lengths and angles to be in reasonable agreement with each other.

The [010] and [100] projections (Figure 4) of $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$ show the orientations of the two different molecules as given by the positional parameters listed in Table II. The crystallographic mirror plane located at $b/4$, which bisects both molecules, can be clearly recognized in the [100] projection. A packing diagram of the individual $S_2Fe_3(Co)_9$ and $S_2Fe_2(CO)_6$ molecules in the unit cell is shown in Figure 5. The left-hand side shows only the four symmetry-related dinuclear species, and the right-hand side only

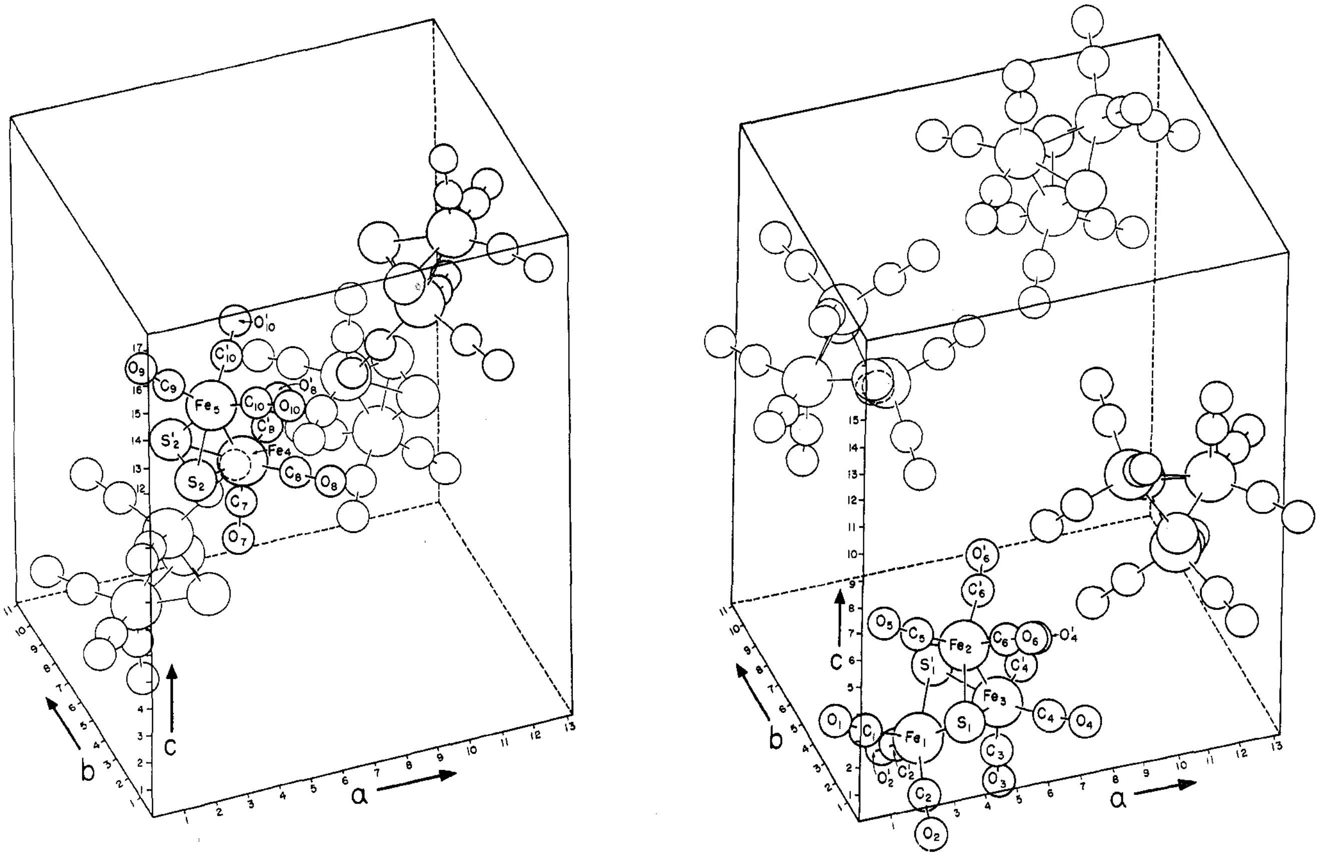

Figure 5.—Packing diagrams of the 1:1 mixture of four $S_2Fe_2(CO)_6$ species (left side) and four $(S_2Fe_3(CO)_9$ species (right side) in the unit cell.

the symmetry-related trinuclear species. All intermolecular contact distances are greater than 3.1 Å., which indicates that this molecular crystal is held together mainly by van der Waals forces.

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The Crystal Structure of Potassium Selenocyanate

BY DUANE D. SWANK AND ROGER D. WILLETT

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The crystal structure of KSeCN has been determined. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 4.59$ Å., $b = 7.64$ Å., $c = 11.89$ Å., and $\beta = 101.13°$. The structure contains the linear $SeCN^-$ ion with a C–N distance of 1.12 Å. and a Se–C distance of 1.83 Å.

Introduction

Recently Morgan[1] has investigated the infrared spectrum of solid KSeCN. His study indicated the existence of the linear $SeCN^-$ ion which was slightly perturbed by the influence of the crystal lattice. Although the $SeCN^-$ ion is isoelectronic (in the valence electrons) with the better-known OCN^- and SCN^- ions, a crystallographic study of the $SeCN^-$ ion had not been made. Because of a theoretical interest in the electronic structure of linear triatomic molecules and ions, it was decided to study the crystal structure of

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[1] H. W. Morgan, *J. Inorg. Nucl. Chem.*, **16**, 367 (1961).