Organometallic Chalcogen Complexes. XXI. Stereochemical Analysis of the Mixed-Metal $FeCo_2(CO)_9S$ Cluster System and Resulting Bond-Length Evidence for Antibonding Trimetal Character of the Unpaired Electron in the Isostructural $Co_3(CO)_9S$ Cluster System[1]

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Abstract: A direct operational test that the unpaired electron in $Co_3(CO)_9S$ occupies a molecular orbital that is strongly antibonding with respect to the cobalt AO's (and which thereby results in the lengthening and weakening of the metal–metal bonds) has been established from an X-ray crystallographic analysis of the diamagnetic iron dicobalt nonacarbonyl sulfur complex, $FeCo_2(CO)_9S$, together with a detailed comparison of its molecular dimensions with those of the isomorphous, paramagnetic $Co_3(CO)_9S$. This investigation provides the first definitive bond-length evidence that electrons in excess of a closed-shell electronic configuration of each metal atom in an organometallic cluster system occupy *strongly antibonding* metal symmetry orbital combinations. A removal of the unpaired electron from the $Co_3(CO)_9S$ molecule (which contains one electron in excess of the "magic number" of each cobalt atom) by the formal substitution of an iron atom in place of one cobalt atom is shown to give rise to a remarkably large decrease in the metal–metal distances of average value 0.083 Å. The crystal-disordered model successfully utilized in the least-squares refinement of $FeCo_2(CO)_9S$ assumes a statistical distribution of the iron and two cobalt atoms over the three metal positions in each molecule. As also found in $Co_3(CO)_9S$, the molecular parameters for each of the two crystallographically independent molecules ideally conform to C_{3v}-$3m$ symmetry; the idealized geometry of the $FeCo_2(CO)_9S$ molecule *per se* then is C_s-m. The average metal–metal bond length of 2.554 Å (with average esd 0.003 Å) in $FeCo_2(CO)_9S$ is much shorter than the corresponding average distance of 2.637 Å (with average esd 0.003 Å) in $Co_3(CO)_9S$, whereas the average metal–sulfur distance in $FeCo_2(CO)_9S$ (2.158 Å, with average esd 0.004 Å) is only slightly longer than the average cobalt–sulfur distance in $Co_3(CO)_9S$ (2.139 Å, with average esd 0.004 Å). The lattice parameters of the reduced triclinic cell of $FeCo_2(CO)_9S$ are a = 9.56, b = 13.12, c = 13.38 Å, α = 109° 50′, β = 107° 37′, and γ = 97° 31′. The space group is $P\bar{1}$ with four molecules per unit cell. Isotropic least-squares refinement yielded an unweighted R_1 value of 9.5% for 2459 independent diffraction maxima collected photographically about two rotation axes by the equiinclination Weissenberg method.

The synthesis of $FeCo_2(CO)_9S$ by Markó, Bor, and coworkers[2] provided an unprecedented opportunity to determine the effect of an unpaired electron on the detailed structural parameters of an organometallic cluster system. The research reported here was the outgrowth of an accidental synthesis (in our attempt to prepare another desired complex) and resulting structural characterization of the $Co_3(CO)_9S$ cluster system which among the many varied organometallic complexes represents one of the relatively few known species possessing one electron *in excess* of the "closed"-shell electronic configuration of each metal atom.[3] Synthesis of the $Co_3(CO)_9S$ complex was first carried out by Markó, Bor, and their coworkers,[4] who correctly predicted its overall molecular geometry from their infrared carbonyl spectral data. At the time the structural analysis of $Co_3(CO)_9S$ was completed, we did not appreciate the fact that its unpaired electron could have a notable effect on the molecular geometry. This realization of the possible importance of the unpaired electron was a consequence of a subsequent structural analysis[5] of the diamagnetic Markó–Bor complex $[Co_3(CO)_7S]_2S_2$[4a] which is closely related to its chemical precursor, $Co_3(CO)_9S$, by substitution of a three-electron-donating disulfide group for two two-electron-donating carbonyl ligands to give two essentially identical $Co_3(CO)_7S$ moieties linked to each other by a disulfide bridge. The salient structural difference observed between $Co_3(CO)_9S$ and $[Co_3(CO)_7S]_2S_2$ was that the average value of 2.637 (7) Å for the three equivalent Co–Co distances in the former molecule is more than 0.1 Å longer than either of the average values of 2.474 (3) Å and 2.531 (5) Å for the two sets of Co–Co distances in the latter molecule, whereas the average Co–S_{ap} bond lengths are the same (2.14 Å) in both molecules. It was then apparent that this difference in Co–Co distances must be ascribed to an unusual effect of the disulfide bridge in $[Co_3(CO)_7S]_2S_2$ (for which each metal atom conforms to a noble-gas electronic configuration) and/or the influence of the unpaired electron in $Co_3(CO)_9S$.

The availability of the mixed-metal iron–dicobalt analog, $FeCo_2(CO)_9S$, for a structural investigation provided the opportunity to ascertain the nature and degree of the influence of an unpaired electron (in excess of the magic number for each metal atom) on the molecular dimensions of an organometallic cluster system. The $FeCo_2(CO)_9S$ molecule can be considered as equivalent to the oxidized cation of $Co_3(CO)_9S$ due to the removal of the unpaired electron by the formal replacement of one cobalt atom with an iron atom; the estimated

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[1] Previous paper in this series: N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7472 (1970).

[2] S. A. Khattab, L. Markó, G. Bor, and B. Markó, *J. Organometal. Chem.*, **1**, 373 (1964).

[3] C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **6**, 1229 (1967).

[4] L. Markó, G. Bor, E. Klumpp, B. Markó, and G. Almásy, *Chem. Ber.*, **96**, 955 (1963); (b) L. Markó, G. Bor, and E. Klumpp, *Chem. Ind.* (*London*), 1491 (1961).

[5] D. L. Stevenson, V. R. Magnuson, and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 3727 (1967).

single-bond covalent radii[6] of 1.165 and 1.162 Å for iron and cobalt, respectively, are virtually identical.

$FeCo_2(CO)_9S$ was prepared in good yield from the reaction of thiophene with a gas mixture comprised of two parts carbon monoxide to one part molecular hydrogen in the presence of dicobalt octacarbonyl and iron pentacarbonyl under hydroformylation conditions, as well as in poorer yields by a variety of other reaction routes.[2,7] From an infrared carbonyl analysis a structure similar to that for $Co_3(CO)_9S$ was suggested by Markó, *et al.*[4a] It is noteworthy that this complex together with two triphenylphosphine-substituted derivatives $FeCo_2\{(CO)_8P(C_6H_5)_3\}S$ and $FeCo_2\{(CO)_7[P(C_6H_5)_3]_2\}S$ have been recently characterized by Mössbauer spectroscopy.[8]

Experimental Section

Data Collection. Dark violet, air-stable crystals of $FeCo_2(CO)_9S$ were generously supplied to us by Drs. L. Markó and G. Bor of the Hungarian Oil and Gas Research Institute (Veszprém). Preliminary X-ray examination of a number of crystals mounted in thin-walled Lindemann glass capillaries was made; two orthorhombic-shaped crystals, each of approximate dimensions 0.30 × 0.25 × 0.12 mm, were utilized for the collection of intensity data, with each crystal oriented such that the direction of its smaller length was parallel to the spindle axis. Lattice lengths and angles were measured at room temperature (~22°) from *hk*0 and *h*0*l* precession photographs which were calibrated by the superimposing of a zero-layer NaCl exposure on the same films.

In order to obtain the maximum number of high-angle reflections for an accurate merging of the data, two zones of multiple-film equiinclination Weissenberg intensity data were taken. Ten reciprocal levels (0*kl*–9*kl*) of data about the [100] axis and five reciprocal levels of data (0*'k'l'*–4*'k'l'*) about the [011] axis of the primitive reduced cell were collected with Zr-filtered Mo Kα radiation (λ 0.7107 Å). Two separate sets of film data corresponding to a 360° rotation range were obtained for all nonzero reciprocal levels of each zone in order to record all accessible independent reflections on the upper half of the film and thereby eliminate the problem of spot compaction.[9] All intensities were estimated visually by comparison with a calibrated set of spots obtained from the same crystal. The intensities of the reflections in each zone were averaged,[10] and corrections for the usual Lorentz–polarization effects and spot extension[11] were applied. The averaging procedure[10] excluded reflections which were so weak that they were observed on only one film of a given packet of multiple films. The indices of the reflections in the second zone were transformed to the reduced-cell indices by the following transformation: $h_r = h' + k'$, $k_r = h' - l'$, and $l_r = l'$. The two zones of data were then merged *via* least squares[12] on the basis of common reflections to give a total of 2459 independent diffraction maxima. The low merging *R* value of 4.7% indicates that this process introduced little systematic error into the data. No corrections for either absorption or extinction were made. For Mo Kα radiation the linear absorption coefficient (μ) is 35 cm^{-1}, for which the maximum variation in intensity on a given reciprocal layer due to absorption was estimated to be less than 10%.

Standard deviations were assigned to the structure amplitudes according to the following equations:[13] if $I_o(hkl) \geqslant \sqrt{10}I_{\min}$, $\sigma[F_o(hkl)] = F_o(hkl)/20$; if $I_o(hkl) < \sqrt{10}I_{\min}$, $\sigma[F_o(hkl)] = [F_o(hkl)/20][\sqrt{10}I_{\min}/I_o(hkl)]^2$.

The atomic form factors for all atoms were taken from the compilation of Hanson, *et al.*[14] No corrections to the atomic form factors for anomalous dispersion were made, as the relatively small corrections have been found in our laboratories not to affect significantly the atomic positional parameters for a centrosymmetric crystal.[15,16] Since the iron atom and two cobalt atoms are presumed to be statistically distributed over the three positions of the basal triangle,[17] the set of form factors used for the metal atoms is a weighted average of those for iron and cobalt.

Crystal Data. The lattice parameters (along with estimated uncertainties) measured at room temperature (~22°) of the reduced triclinic cell of $FeCo_2(CO)_9S$ are: $a = 9.56 \pm 0.02$, $b = 13.12 \pm 0.02$, $c = 13.38 \pm 0.02$ Å, $\alpha = 109° 50' \pm 10'$, $\beta = 107° 37' \pm 10'$, $\gamma = 97° 31' \pm 10'$. The calculated density of 2.09 g/cm^3 for four molecules in the unit cell agrees well with the experimental density of 2.05 g/cm^3 as measured by the flotation method. The centrosymmetric space group $P\bar{1}$ (C_i^1) was verified by the satisfactory least-squares refinement of the structure; all atoms occupy the general twofold set of positions: $\pm(x, y, z)$.[18] The solution of the structure required the determination of the atomic parameters for two distinct molecules comprising a total of 6 metal, 2 sulfur, 18 oxygen, and 18 carbon atoms.

Solution of the Structure. The final atomic parameters determined[3] for $Co_3(CO)_9S$ were taken as the initial atomic parameters for $FeCo_2(CO)_9S$. Four cycles of full-matrix least-squares isotropic refinement, based on the merged data, resulted in discrepancy factors of $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]100 = 9.5\%$ and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}100 = 10.2\%$. No parameter shifted by more than 0.7 of its standard deviation in the last refinement cycle.

A three-dimensional Fourier difference map calculated from the output parameters obtained from the last isotropic least-squares cycle indicated some anisotropic thermal motion for the metal atoms. A least-squares cycle in which anisotropic temperature factors were used for the metal atoms revealed that the weighted *R* value, R_2, would decrease from 10.2 to 9.1%; however, no positional parameter shifted from the corresponding final isotropic value by more than 1.1σ for the metal atoms or by more than 1.5σ for the remaining atoms during this cycle. Hence, because of these small parameter shifts and the large amount of computer time required for each least-squares cycle (41 min on the CDC 3600 computer), the anisotropic–isotropic refinement was terminated at this point. A difference Fourier map showed no residual electron-density peaks greater than 1.1 electrons/Å^3 or less than -1.2 electrons/Å^3 except for those peaks in the vicinity of the heavy atoms.

The positional and thermal parameters obtained from the final isotropic least-squares cycle are listed in Table I.[19] In order to verify the overall correctness of the structural determination, each unobserved but experimentally accessible reflection for which $\sin\theta \leq 0.49$ was assigned an intensity equal to the minimum observed intensity for the given reciprocal layer. After correction of these intensities for Lorentz–polarization and spot extension effects, the derived structure factors were compared with the corresponding calculated ones; no F_c exceeded $1.6F_o$ (minimum). Bond lengths

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(6) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 256.

(7) The molecular formula $FeCo_2(CO)_9S$ was assigned by the synthesizers[2] on the basis of the following analysis. *Anal.* Calcd: S, 7.01; Fe, 12.20; Co, 25.74; C, 23.53; CO, 55.05. Found: S, 7.0; Fe, 12.3; Co, 25.8; C, 23.7; CO, 54.2.

(8) K. Burger, L. Korecz, and G. Bor, *J. Inorg. Nucl. Chem.*, **31**, 1527 (1969).

(9) M. J. Buerger, "X-Ray Crystallography," Wiley, New York, N. Y., 1942, pp 227–229.

(10) J. F. Blount, Ph.D. Thesis, University of Wisconsin, Madison, 1965.

(11) D. C. Phillips, *Acta Crystallogr.*, 7, 746 (1954).

(12) P. W. Sutton and M. D. Glick, "A Crystallographic Data Correlation Program for the CDC Computer," University of Wisconsin, Madison, 1964.

(13) D. L. Smith, "DACOR—A Data Reduction Program for the CDC Computer," Ph.D. Thesis, Appendix I, University of Wisconsin, Madison, 1962.

(14) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964).

(15) For Mo Kα radiation the values of the dispersion corrections to the atomic scattering factors are $\Delta f' = 0.4$, $\Delta f'' = 1.1$ for cobalt and $\Delta f' = 1.1$, $\Delta f'' = 1.0$ for iron.[16]

(16) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

(17) On the basis that all three metal–metal distances in each of the two crystallographically independent molecules were found from the preliminary least-squares refinement to be equivalent within experimental error, a crystal ordered–disordered model was then utilized in the final least squares for which a statistical distribution of the iron and two cobalt atoms over the three metal positions was assumed in each molecule.

(18) Reference 16, Vol. I, 1952, p 75.

(19) Calculated and observed structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order $3.00 for photocopy or $2.00 for microfiche.

and angles, arranged according to the C_{3v}-$3m$ symmetry of the idealized crystal-disordered molecule,[17] are listed in Table II. "Best" least-squares planes determined by certain specific atoms (and midpoints between atoms in some cases) along with the perpendicular distances of these and other atoms from the planes were calculated with the Smith program;[20] these results are tabulated elsewhere.[21]

Table I. Final Atomic Parameters[a]

Atom	x	y	z	B
M(1)	0.3272 (3)	0.0991 (2)	0.2305 (2)	2.30 (5)
M(2)	0.4664 (3)	0.3069 (2)	0.3439 (2)	2.69 (5)
M(3)	0.6092 (3)	0.1673 (2)	0.2672 (2)	2.43 (5)
S	0.4213 (5)	0.2103 (4)	0.1663 (4)	3.05 (10)
C(1)	0.1374 (26)	0.1131 (19)	0.1993 (20)	5.17 (49)
O(1)	0.0151 (19)	0.1217 (13)	0.1801 (14)	6.04 (36)
C(2)	0.3626 (25)	0.0654 (18)	0.3471 (20)	4.90 (48)
O(2)	0.3781 (18)	0.0465 (13)	0.4324 (15)	5.95 (36)
C(3)	0.2870 (26)	−0.0371 (20)	0.1164 (21)	4.79 (46)
O(3)	0.2556 (19)	−0.1208 (15)	0.0420 (16)	6.45 (39)
C(4)	0.6052 (25)	0.4262 (18)	0.3823 (19)	4.75 (47)
O(4)	0.6983 (19)	0.5083 (14)	0.4057 (15)	6.27 (38)
C(5)	0.5075 (24)	0.3095 (18)	0.4837 (20)	4.42 (44)
O(5)	0.5430 (19)	0.3146 (14)	0.5761 (16)	6.55 (39)
C(6)	0.3091 (23)	0.3640 (16)	0.3320 (18)	3.89 (41)
O(6)	0.2088 (23)	0.4057 (16)	0.3137 (17)	7.88 (46)
C(7)	0.6252 (22)	0.0423 (16)	0.1683 (18)	3.69 (40)
O(7)	0.6454 (21)	−0.0353 (16)	0.1078 (17)	7.15 (41)
C(8)	0.6916 (20)	0.1505 (14)	0.3977 (16)	2.87 (34)
O(8)	0.7513 (17)	0.1369 (13)	0.4784 (14)	5.57 (34)
C(9)	0.7628 (21)	0.2603 (16)	0.2731 (17)	3.48 (38)
O(9)	0.8595 (20)	0.3245 (14)	0.2743 (15)	6.85 (40)
M(1′)	0.7283 (3)	0.6577 (2)	0.0805 (2)	2.32 (5)
M(2′)	0.9318 (3)	0.6123 (2)	0.2211 (2)	2.30 (5)
M(3′)	0.7938 (3)	0.7563 (2)	0.2958 (2)	2.58 (5)
S′	0.6937 (5)	0.5792 (4)	0.1932 (4)	2.60 (9)
C(1′)	0.7074 (23)	0.5454 (17)	−0.0479 (19)	3.92 (41)
O(1′)	0.6940 (18)	0.4699 (13)	−0.1321 (15)	6.06 (37)
C(2′)	0.8449 (22)	0.7696 (16)	0.0732 (18)	3.92 (41)
O(2′)	0.9204 (16)	0.8401 (12)	0.0638 (12)	4.69 (30)
C(3′)	0.5457 (20)	0.6827 (14)	0.0322 (16)	2.74 (33)
O(3′)	0.4282 (16)	0.6976 (11)	0.0007 (12)	4.72 (30)
C(4′)	1.0188 (24)	0.5938 (17)	0.3506 (20)	9.22 (52)
O(4′)	1.0715 (17)	0.5926 (13)	0.4419 (14)	5.51 (34)
C(5′)	1.0862 (23)	0.7063 (16)	0.2298 (18)	3.95 (42)
O(5′)	1.1880 (18)	0.7688 (13)	0.2289 (14)	5.70 (35)
C(6′)	0.9424 (23)	0.4833 (17)	0.1246 (18)	3.67 (39)
O(6′)	0.9476 (20)	0.3971 (15)	0.0614 (16)	6.93 (40)
C(7′)	0.6334 (22)	0.8113 (16)	0.2890 (17)	3.65 (40)
O(7′)	0.5325 (20)	0.8518 (14)	0.2859 (15)	6.39 (37)
C(8′)	0.9245 (22)	0.8797 (16)	0.3248 (17)	3.68 (40)
O(8′)	1.0135 (19)	0.9613 (14)	0.3462 (14)	6.05 (36)
C(9′)	0.8423 (23)	0.7636 (17)	0.4372 (19)	3.99 (41)
O(9′)	0.8733 (16)	0.7705 (12)	0.5311 (13)	5.22 (33)

[a] Standard deviations of the last significant figures are given in parentheses.

The three-dimensional Fourier electron-density difference maps were calculated with the Blount program.[22] A local version of the Busing-Martin-Levy ORFLS program[23] was used to carry out the full-matrix least-squares refinement cycles. Bond lengths and angles together with their estimated standard deviations were calculated from the full inverse matrix (which included the estimate errors in lattice parameters) with the Busing-Martin-Levy ORFFE program.[24]

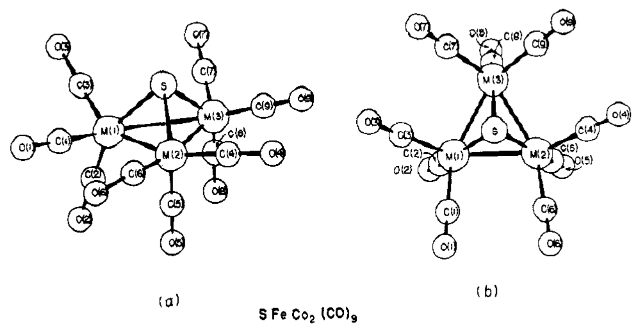

Figure 1. Molecular configuration of $FeCo_2(CO)_9S$.

Results and Discussion

The solid-state structure of $FeCo_2(CO)_9S$ is comprised of individual molecules which have the configuration shown in Figure 1. On the basis of the disordered crystal model which assumes each iron dicobalt molecule to be randomly distributed at a given crystal site over its three statistical orientations (in harmony with the experimentally equivalent metal–metal distances), the *averaged* structure may be considered to possess a C_{3v}-$3m$ geometry involving the symmetrical linkage of a basal $M_3(CO)_9$ fragment with an apical sulfur atom. This basal $M_3(CO)_9$ fragment is composed of three $M(CO)_3$ groups identically positioned at the corners of an equilateral triangle with the metal atoms joined to one another by direct metal–metal interactions as well as by the triply bridging sulfur atom. In accord with this C_{3v} description of the *averaged* disordered structure in the crystalline state, each molecule of $FeCo_2(CO)_9S$ *per se* thereby has C_s-m symmetry. The extent of the deviations of each of the two crystallographically independent molecules from a C_{3v} averaged structure can be readily seen by a comparison of the perpendicular distances of related carbonyl atoms from the three vertical mirror planes, each of which is defined by the sulfur atom, one metal atom, and the midpoint of the line joining the other two metal atoms. Although the observed variations in the above distances (tabulated elsewhere[21]) of the corresponding carbonyl atoms are in general small (*viz.*, <0.1 Å), there are a few differences as large as 0.25 Å which may be attributed to angular distortions of the carbonyl ligands due primarily to combined *intra-* and *intermolecular* atomic repulsions.[25] Since the two crystallographically independent molecules are identical within the limits of experimental error, all distances and angles reported in this discussion are arithmetic means for the two independent molecules of $FeCo_2(CO)_9S$, each based on the assumed C_{3v} *averaged* disordered structure.

The [100] projection given in Figure 2 shows the orientations of the four molecules in the centrosymmetric triclinic unit cell. The closest intermolecular approaches of 3.1 Å for O···O contacts, 3.2 Å for O···C contacts, 3.3 Å for S···O contacts, and 3.5 Å for S···C contacts indicate that there are no unusual interactions among molecules. The packing of crystal-

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

(21) D. L. Stevenson, Ph.D. Thesis, University of Wisconsin, Madison, Jan 1967.

(22) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC Computer," Ph.D. Thesis, Appendix, University of Wisconsin, Madison, 1965.

(23) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FLS - A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, 1963.

(24) W. R. Busing, K. O. Martin, and H. A. Levy, "OR FFE - A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, 1964.

(25) Deformations of each $M(CO)_3$ group may also arise from π-bonding effects (*cf.* S. F. A. Kettle, *Inorg. Chem.*, 4, 1661 (1965); *J. Chem. Soc. A*, 421 (1966)).

Table II

	Molecule A	Molecule B
A. Bond Lengths, Å[a]		
M(1)–M(2)	2.555 (8)	2.554 (6)
M(2)–M(3)	2.550 (6)	2.544 (6)
M(3)–M(1)	2.566 (7)	2.555 (7)
	2.557 (av)	2.551 (av)
M(1)–S	2.156 (6)	2.169 (6)
M(2)–S	2.152 (8)	2.150 (7)
M(3)–S	2.164 (7)	2.158 (8)
	2.158 (av)	2.159 (av)
M(1)–C(1)	1.78 (2)	1.78 (2)
M(1)–C(3)	1.81 (3)	1.78 (2)
M(2)–C(4)	1.73 (2)	1.79 (2)
M(2)–C(6)	1.76 (2)	1.79 (2)
M(3)–C(7)	1.78 (2)	1.77 (2)
M(3)–C(9)	1.74 (2)	1.77 (2)
	1.77 (av)	1.78 (av)
M(1)–C(2)	1.71 (2)	1.77 (2)
M(2)–C(5)	1.78 (2)	1.74 (2)
M(3)–C(8)	1.79 (2)	1.76 (2)
	1.76 (av)	1.76 (av)
C(1)–O(1)	1.15 (2)	1.18 (2)
C(3)–O(3)	1.13 (3)	1.14 (2)
C(4)–O(4)	1.18 (2)	1.18 (2)
C(6)–O(6)	1.17 (2)	1.18 (2)
C(7)–O(7)	1.15 (3)	1.16 (2)
C(9)–O(9)	1.16 (2)	1.17 (2)
	1.16 (av)	1.17 (av)
C(2)–O(2)	1.22 (2)	1.16 (2)
C(5)–O(5)	1.15 (2)	1.19 (2)
C(8)–O(8)	1.14 (2)	1.17 (2)
	1.17 (av)	1.17 (av)
B. Bond Angles, Deg[a]		
M–M–M		
M(1)–M(2)–M(3)	60.3 (2)	60.1 (2)
M(2)–M(3)–M(1)	59.9 (2)	60.1 (2)
M(3)–M(1)–M(2)	59.7 (2)	59.7 (2)
	60.0 (av)	60.0 (av)
M–S–M		
M(1)–S–M(2)	72.8 (3)	72.5 (2)
M(2)–S–M(3)	72.4 (3)	72.4 (3)
M(3)–S–M(1)	72.9 (2)	72.4 (2)
	72.7 (av)	72.4 (av)
S–M–M		
S–M(1)–M(2)	53.6 (2)	53.4 (2)
S–M(1)–M(3)	53.7 (2)	53.6 (2)
S–M(2)–M(1)	53.7 (2)	54.1 (2)
S–M(2)–M(3)	54.0 (2)	53.9 (2)
S–M(3)–M(1)	53.4 (2)	54.0 (2)
S–M(3)–M(2)	53.6 (2)	53.7 (2)
	53.7 (av)	53.8 (av)
M–M–CO(eq)		
M(1)–M(2)–C(4)	154.3 (8)	155.2 (7)
M(1)–M(3)–C(9)	152.6 (6)	154.7 (7)
M(2)–M(1)–C(3)	153.1 (8)	151.2 (6)
M(2)–M(3)–C(7)	154.5 (6)	153.8 (7)
M(3)–M(1)–C(1)	153.1 (7)	155.4 (6)
M(3)–M(2)–C(6)	153.3 (7)	154.1 (7)
	153.5 (av)	154.1 (av)
M–M–CO(eq)		
M(1)–M(2)–C(6)	99.3 (7)	99.3 (7)
M(1)–M(3)–C(7)	97.4 (7)	97.6 (7)
M(2)–M(1)–C(1)	98.1 (8)	98.4 (7)
M(2)–M(3)–C(9)	99.3 (7)	99.4 (7)
M(3)–M(1)–C(3)	98.0 (8)	98.3 (6)
M(3)–M(2)–C(4)	96.3 (8)	98.4 (7)
	98.0 (av)	98.6 (av)
M–M–CO(ax)		
M(1)–M(2)–C(5)	97.9 (7)	96.3 (7)
M(1)–M(3)–C(8)	99.2 (6)	99.4 (7)
M(2)–M(1)–C(2)	95.7 (8)	99.0 (7)
M(2)–M(3)–C(8)	95.6 (6)	99.6 (7)
M(3)–M(1)–C(2)	94.2 (8)	94.3 (7)
M(3)–M(2)–C(5)	100.6 (7)	97.1 (7)
	97.2 (av)	97.6 (av)
S–M–CO(eq)		
S–M(1)–C(1)	101.7 (7)	105.4 (6)
S–M(1)–C(3)	101.9 (8)	99.2 (6)
S–M(2)–C(4)	105.1 (8)	104.2 (7)
S–M(2)–C(6)	100.6 (7)	101.9 (7)
S–M(3)–C(7)	104.5 (7)	103.0 (7)
S–M(3)–C(9)	100.6 (6)	102.6 (7)
	102.4 (av)	102.7 (av)
S–M–CO(ax)		
S–M(1)–C(2)	142.6 (7)	144.1 (7)
S–M(2)–C(5)	147.6 (7)	145.0 (7)
S–M(3)–C(8)	145.1 (6)	148.1 (7)
	145.1 (av)	145.7 (av)
(eq)OC–M–CO(eq)		
C(1)–M(1)–C(3)	98.1 (11)	97.8 (9)
C(4)–M(2)–C(6)	99.0 (10)	97.0 (10)
C(7)–M(3)–C(9)	97.7 (10)	97.5 (10)
	98.3 (av)	97.4 (av)
(eq)OC–M–CO(ax)		
C(1)–M(1)–C(2)	103.6 (11)	100.7 (10)
C(3)–M(1)–C(2)	101.3 (10)	101.2 (8)
C(4)–M(2)–C(5)	96.8 (10)	98.7 (10)
C(6)–M(2)–C(5)	99.2 (10)	101.1 (10)
C(7)–M(3)–C(8)	99.9 (9)	97.5 (9)
C(9)–M(3)–C(8)	100.5 (8)	98.6 (10)
	100.2 (av)	99.6 (av)
M–C–O		
M(1)–C(1)–O(1)	179.3 (21)	179.0 (18)
M(1)–C(3)–O(3)	176.4 (21)	179.3 (16)
M(2)–C(4)–O(4)	178.0 (19)	172.2 (20)
M(2)–C(6)–O(6)	171.4 (20)	178.8 (19)
M(3)–C(7)–O(7)	175.6 (20)	177.1 (17)
M(3)–C(9)–O(9)	176.5 (17)	178.6 (19)
	176.2 (av)	177.5 (av)
M(1)–C(2)–O(2)	174.0 (21)	177.2 (19)
M(2)–C(5)–O(5)	175.9 (20)	176.1 (19)
M(3)–C(8)–O(8)	175.4 (18)	178.4 (17)
	175.1 (av)	177.2 (av)

[a] The standard deviations of the last significant figures are enclosed in parentheses.

line $FeCo_2(CO)_9S$ is virtually identical with that of the isomorphous $Co_3(CO)_9S$.[3]

The average metal–metal–CO(equatorial) angles of 154 and 98° in $FeCo_2(CO)_9S$ compare favorably to the corresponding average angles of 152 and 97° in $Co_3(CO)_9S$; the average metal–metal–CO(axial) angles are 97° in each complex. The average (equatorial)OC–M–CO(equatorial) and (equatorial)OC–M–CO(axial) angles of 98 and 100° in $FeCo_2(CO)_9S$ are similar to the corresponding average values of 101° in $Co_3(CO)_9S$. A molecular bonding rationale of the increase of the OC–M–CO angles over 90° is given[26] for the structurally analogous, diamagnetic $Co_3(CO)_9CCH_3$ molecule. In $FeCo_2(CO)_9S$ each CO(equatorial) ligand is tipped upward from the basal trimetal plane by an average

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(26) P. W. Sutton and L. F. Dahl, *J. Amer. Chem. Soc.*, **89**, 261 (1967).

angle of 16°; the corresponding value in $Co_3(CO)_9S$ is also 16°.

The only prominent stereochemical difference between the averaged disordered geometry of $FeCo_2(CO)_9S$ and that of $Co_3(CO)_9S$ is the startling but yet accountable variation in the metal-metal distances. In $FeCo_2(CO)_9S$ the six independent metal-metal distances distributed among the two independent molecules range from 2.544 (6) to 2.566 (7) Å. The average value of 2.554 Å (with average esd 0.003 Å) is 0.083 Å *shorter* than the corresponding average metal-metal distance of 2.637 Å (with average esd 0.003 Å) determined[3] in $Co_3(CO)_9S$ in contrast to the average metal-sulfur bond length in $FeCo_2(CO)_9S$ of 2.158 Å (with average esd 0.004 Å) being slightly *longer* by 0.019 Å (a difference of borderline significance) than the average metal-sulfur bond length in $Co_3(CO)_9S$ of 2.139 Å (with average esd 0.004 Å). Furthermore, the average metal-metal distance of 2.554 (3) Å in $FeCo_2(CO)_9S$ is in accord with the average value of 2.531 (5) Å found[5] for the Co-Co bonds not spanned by the disulfide bridge in the diamagnetic $[Co_3(CO)_7S]_2S_2$ molecule; in this latter molecule the average Co-S bond length is 2.145 (6) Å. Hence, the structural determination of $FeCo_2(CO)_9S$ has provided direct operational evidence that the unpaired electron in $Co_3(CO)_9S$ must be responsible for the remarkably large observed increase of nearly 0.10 Å in each of the Co-Co bond lengths. The only rational explanation of this striking bond-length difference is that the unpaired electron in $Co_3(CO)_9S$ must be accommodated in a MO which is strongly antibonding with respect to the cobalt AO's. It is noteworthy that Markó, Bor, and coworkers[2] suggested that the unpaired electron in $Co_3(CO)_9S$ causes this compound to be highly air sensitive, in contrast to $FeCo_2(CO)_9S$ which is air stable to oxidation. The results of this investigation have stimulated a number of studies[27,28] designed to gain more information about the specific nature of the molecular orbital containing the unpaired electron in $Co_3(CO)_9S$.

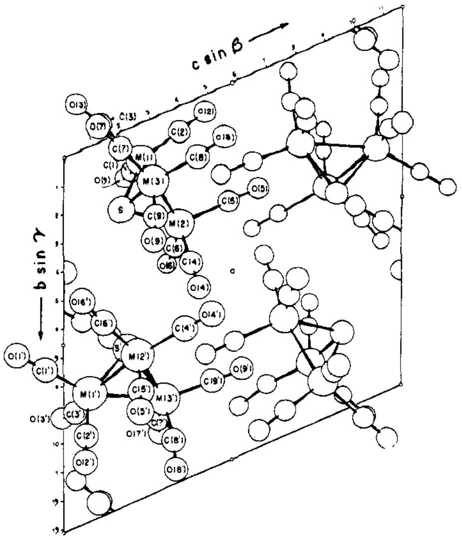

Figure 2. [100] projection of the centrosymmetric triclinic unit cell of $FeCo_2(CO)_9S$ showing the orientations of the two crystallographically independent molecules. A disordered-crystal model was invoked in the structural analysis which assumed that each $FeCo_2(CO)_9S$ molecule at its given crystal site is randomly distributed over three statistical orientations. The *averaged* molecular structure was experimentally found to possess equivalent metal-metal distances in accord with the disordered molecular model of idealized geometry C_{3v}.

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(27) C. E. Strouse and L. F. Dahl, *Discuss. Faraday Soc.*, **47**, 93 (1969).

(28) C. E. Strouse and L. F. Dahl, *J. Amer. Chem. Soc.*, **93**, 6032 (1971).