Triiron Dodecacarbonyl: An Analysis of Its Stereochemistry[1]

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Abstract: The statistically disordered crystal structure and molecular architecture of Fe$_3$(CO)$_{12}$ have been unambiguously determined from a three-dimensional, single-crystal X-ray photographic analysis. Anisotropic least-squares refinement of 15 independent atoms has yielded discrepancy factors of $R_1 = 7.1\%$ and $R_2 = 7.6\%$ based on 539 independent reflections. The molecular structure of Fe$_3$(CO)$_{12}$ is comprised of an isosceles triangular arrangement of iron atoms in which an Fe(CO)$_4$ group is symmetrically coordinated by only iron–iron bonds to an Fe$_2$(CO)$_8$ residue containing two identical Fe(CO)$_3$ groups connected to each other by two bridging carbonyl groups and by an iron–iron bond. This configuration can be simply considered as that of Fe$_2$(CO)$_9$ with one of the three bridging carbonyl groups replaced by an Fe(CO)$_4$ unit. The crystal-disordered model successfully utilized in the least-squares refinement assumes a random distribution of each Fe$_3$(CO)$_{12}$ molecule in one of two orientations related to each other by a crystallographic center of symmetry such that on the average one-half of an atom occupies each atomic site. The icosahedral-like molecular arrangement of 12 carbonyl groups enclosing the triiron cluster results in a near-superposition of the corresponding half-weighted carbon and oxygen atoms for the two orientations and thereby produces a "Star of David" arrangement for the two isosceles triangles of six iron half-atoms. Either orientation of the triangle of iron half-atoms together with the twelve "whole" carbonyl groups (of which only six are crystallographically independent) yields the same molecular configuration. Although the resulting disorder-averaged configuration of Fe$_3$(CO)$_{12}$ precludes the accurate determination of molecular parameters for the carbonyl groups, there is definite evidence that the two bridging carbonyl groups are somewhat unsymmetrical such that the idealized geometry of C$_{2v}$-2mm symmetry based on two symmetrical bridging carbonyl groups is reduced by their asymmetry to C$_2$-2 symmetry. The structural features of Fe$_3$(CO)$_{12}$ are correlated with those of the HFe$_3$(CO)$_{11}^-$ anion and Fe$_3$(CO)$_{11}$P(C$_6$H$_5$)$_3$. A structural interrelationship between Fe$_3$(CO)$_{12}$ and Co$_4$(CO)$_{12}$ is shown to exist in that the removal of any of the three equivalent basal metal atoms from the tetrahedron of cobalt atoms in Co$_4$(CO)$_{12}$ along with a concomitant deformation of the quasi-regular carbonyl icosahedron surrounding the cobalt tetrahedron leads to the geometry of Fe$_3$(CO)$_{12}$. To explain the infrared solution spectra of Fe$_3$(CO)$_{12}$, it is proposed that an intramolecular rearrangement of Fe$_3$(CO)$_{12}$ occurs on dissolution to give an instantaneous geometry of C$_{3v}$-3m symmetry consisting of three identical Fe(CO)$_3$ groups positioned at the vertices of an equilateral triangle and linked in pairs to one another by a bridging carbonyl group and an iron–iron bond. Both the established solid-state and postulated solution geometries are shown to be stereochemically analogous to the established molecular configurations of the two solid-state isomeric forms of the electronically equivalent Rh$_3$(C$_5$H$_5$)$_3$(CO)$_3$ complex.

No organo–transition metal complex has aroused more interest or provoked more speculation concerning its structure than triiron dodecacarbonyl. The controversial structural reports that preceded the elucidation of its correct architecture in the solid state (briefly outlined in a previous communication[3] and reported here in detail) are sketched not only to assess (after-the-fact) the various experimental data and resulting stereochemical explanations but also to propose a molecular rearrangement of the Fe$_3$(CO)$_{12}$ *in solution* to account for the observed infrared solution spectra, which do not appear to conform with the determined solid-state molecular configuration.

First synthesized in 1906 by the thermal decomposition of Fe$_2$(CO)$_9$,[4] this dark green hydrophobic compound was shown from magnetic susceptibility measurements to be diamagnetic.[5-7] In 1930 Hieber and Becker[8] formulated iron tetracarbonyl to be trimeric from freezing point depression studies in iron pentacarbonyl solvent. Consequently, they postulated three possible atomic arrangements including both the 3–3–3–3 model[9] of D$_{3d}$-$\bar{3}$2/m symmetry and the 4–2–2–4 model[9] of D$_{2d}$-$\bar{4}$2m symmetry. Further proposals of other possible molecular configurations were made,[10-12] but (mainly after a revival of interest in this structural problem in 1951 due to the first infrared and electronic spectral characterization of Fe$_3$-

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[3] C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966).

[4] J. Dewar and H. O. Jones, *Proc. Roy. Soc.* (London), **A79**, 66 (1906).

[5] H. Freudlich and E. J. Cuy, *Chem. Ber.*, **56B**, 2264 (1923).

[6] S. Berkman and H. Zocher, *Z. Physik. Chem.*, **124**, 318 (1926).

[7] H. G. Cutforth and P. W. Selwood, *J. Am. Chem. Soc.*, **65**, 2414 (1943).

[8] W. Hieber and E. Becker, *Chem. Ber.*, **63B**, 1405 (1930).

[9] The 3–3–3–3 model contains a linear array of iron atoms with three bridging carbonyl groups linking the central iron atom to each of two Fe(CO)$_3$ groups such that each iron atom has six carbonyl groups octahedrally disposed about it; the resulting configuration, which is structurally similar to Fe$_2$(CO)$_9$, can be viewed as having been formed by the junction of two octahedra at the opposite faces of an octahedron. The 4–2–2–4 model also possesses a linear array of iron atoms with two Fe(CO)$_4$ groups each connected to the central iron atom by two carbonyl groups; to conform to D$_{2d}$ symmetry the four bridging carbonyls are tetrahedrally arranged about the unique iron atom.

[10] W. Klemm, H. Jacobi, and W. Tilk, *Z. Anorg. Allgem. Chem.*, **20**, 1 (1931).

[11] N. V. Sidgwick and R. W. Bailey, *Proc. Roy. Soc.* (London), **A144**, 521 (1934).

[12] R. K. Sheline, *J. Am. Chem. Soc.*, **73**, 1615 (1951).

$(CO)_{12}$ by Sheline[12]) support for either one or the other of the two above-cited Hieber–Becker linear-iron models was generated from interpretations of infrared spectra,[12,13] preliminary X-ray crystal data,[14−18] and rates of exchange with isotopically labeled carbon monoxide.[19] The suggested incompatibility[12] of the D_{3d} model with the magnetic criterion was removed by a molecular orbital treatment[20] which rationalized a diamagnetic ground state for this model. During this period other investigators[21−23] concluded from solution infrared measurements in the carbonyl region[24] that $Fe_3(CO)_{12}$ probably does not contain bridging carbonyls in solution and that the two observed 1800-cm^{-1} bands of very weak intensity are not fundamentals but are instead overtones and/or combinations.

Strong experimental evidence for a triangular arrangement of iron atoms was first presented by Dahl and Rundle[18] from a three-dimensional X-ray investigation which showed that no linear iron array would account for the experimentally obtained three-dimensional Patterson maps. Their efforts to obtain the complete structure were unsuccessful primarily because of a crystal order–disorder phenomenon which renders invalid the normally assumed space group symmetry requirements, which in this crystal structure demand that each of the two trimeric molecules in the unit cell lie on a crystallographic center of symmetry and thereby possess a linear array of iron atoms. Furthermore, from polarized single-crystal infrared spectra of $Fe_3(CO)_{12}$, which showed a strong band at 1875 cm^{-1} (in the frequency range for bridging carbonyls), they suggested[25] that the most probable structure in the crystalline state consists of a symmetrical triangular array of iron atoms with association of some carbonyls with more than one iron atom. They also mentioned[25] the possibility that the iron atoms are not all equivalent with respect to carbonyl bonding. The long Fe–Fe distances of 2.75 Å for the presumed equilateral triangle of iron atoms[26−28] and their relative similarity (with allowance for the expected difference in Fe and Os radii) to the Os–Os distances of 2.88 Å in the equilateral triangular array of osmium atoms in $Os_3(CO)_{12}$ led Corey and Dahl[29] to postulate in 1962 that the molecular configuration of $Fe_3(CO)_{12}$ may be analogous to that determined for $Os_3(CO)_{12}$, even though the two crystalline compounds are not isomorphous and possess different infrared spectral solution patterns.[30]

At this time the validity of any triangular iron model was challenged by several groups[31−33] who concluded that the Mössbauer experiments[34] on *solid* $Fe_3(CO)_{12}$ were compatible only with a linear iron molecule—either the D_{2d} 4–2–2–4 model[31,32] or the D_{3d} 3–3–3–3 model.[33] Additional support for the latter linear iron model in solution was given in 1963 by Dobson and Sheline,[35] who, from infrared solvent shift studies, provided evidence that the two weak bands in the bridging carbonyl region are indeed fundamental vibrations.

This contradiction between the interpretations of the Mössbauer and the X-ray data, concerning the iron models allowable in the solid state, generated considerable impetus which culminated in three independent postulations

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(13) J. W. Cable and R. K. Sheline, *Chem. Rev.*, **56**, 1 (1956).

(14) In 1931 Brill[15] reported from X-ray oscillation photographs that $Fe_3(CO)_{12}$ is monoclinic with 12 $Fe(CO)_4$ species in a unit cell of symmetry $C2/c(C_{2h}^6)$ and dimensions a = 13.00 A, b = c = 11.41 A, β = 94° 24.9′. His morphological examination by optical goniometry indicated C_{2h} symmetry for the prismatic crystals. Although no structural analysis was carried out, from the pseudo-tetragonal symmetry of the crystals Brill[15] suggested the 4–2–2–4 structure with D_{2d} symmetry as the most likely structure. Our diffraction data showed Brill's unit cell to be *B*-centered instead of *C*-centered; hence an axial transformation was made from the *B*-centered cell to a primitive monoclinic one (with half the *B*-centered cell volume) of symmetry $P2_1/n$. Our crystal data agree (except for an arbitrary choice of axes) with those given by Florio and Rundle[16] and by Mills[17] who deduced from the normally correct space group requirements (with the inherent assumption of no order–disorder phenomenon) that the trimeric molecules in the solid state must necessarily be centrosymmetric. Hence, Mills[17] eliminated the D_{2d} version of the 4–2–2–4 model but pointed out that it was not possible from these crystallographic observations to distinguish unequivocally between the D_{3d} 3–3–3–3 model and a square-planar centrosymmetrical modification of the 4–2–2–4 model. In the case of $Fe_3(CO)_{12}$, however, these symmetry arguments fail due to a crystal disorder.[18]

(15) R. Brill, *Z. Krist.*, **77**, 36 (1931).

(16) J. Florio and R. E. Rundle, private communication to L. F. Dahl, 1951.

(17) O. S. Mills, *Chem. Ind.* (London), 73 (1957).

(18) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **26**, 1751 (1957).

(19) D. F. Keeley and R. F. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).

(20) D. A. Brown, *ibid.*, **5**, 289 (1958).

(21) F. A. Cotton and G. Wilkinson, *J. Am. Chem. Soc.*, **79**, 752 (1957).

(22) S. L. Shufler and R. A. Friedel, private communication to L. F. Dahl, 1956.

(23) K. Noack, *Helv. Chim. Acta*, **45**, 1847 (1962).

(24) Under fairly high resolution the infrared solution spectrum of $Fe_3(CO)_{12}$ contains only two strong, well-defined bands in the terminal carbonyl stretching region and two very weak bands in the bridging carbonyl stretching region.[12,20−23]

(25) L. F. Dahl and R. E. Rundle, *J. Chem. Phys.*, **27**, 323 (1957).

(26) No X-ray evidence existed for other than an approximately equilateral triangle of iron atoms (or essentially regular hexagon of half-iron atoms) in $Fe_3(CO)_{12}$ until the structural determination[27] of the $HFe_3(CO)_{11}^-$ anion revealed an isosceles iron triangle. The observed variations of 0.1 A in the Fe–Fe distances obtained in the Dahl–Rundle X-ray study[18] of $Fe_3(CO)_{12}$ from both the three-dimensional Patterson and Fourier maps (the latter phased only on the iron atoms) were then not deemed unusual or particularly significant (due mainly to lack of present-day knowledge of metal carbonyl structures). Subsequently, a three-dimensional Patterson function based on the original Dahl–Rundle X-ray data of $Fe_3(CO)_{12}$ was computed (with a grid size of only 0.12 A), and a careful analysis (involving a 27-point interpolation with Gaussian approximation) of the peaks attributable primarily to the Fe–Fe vectors gave vector distances of 2.64, 2.73, and 2.75 Å for the triangle of iron atoms.[27] These values are in reasonable agreement with the Fe–Fe bond lengths obtained by least-squares refinement of the structure of $Fe_3(CO)_{12}$ (presented here) and the closely related structures of the $HFe_3(CO)_{11}^-$ anion[27] and $Fe_3(CO)_{11}P(C_6H_5)_3$[28] (*vide infra*).

(27) L. F. Dahl and J. F. Blount, *Inorg. Chem.*, **4**, 1373 (1965).

(28) D. J. Dahm and R. A. Jacobson, *Chem. Commun.*, 496 (1966); *J. Am. Chem. Soc.*, **90**, 5106 (1968).

(29) E. R. Corey and L. F. Dahl, *Inorg. Chem.*, **1**, 521 (1962).

(30) In light of the presumably much greater Fe–Fe distances than those known then for other metal carbonyl complexes containing normal symmetrical bridging carbonyls, Corey and Dahl[29] rationalized (incorrectly) that the strong 1875-cm^{-1} band[25] in the single-crystal infrared spectrum of $Fe_3(CO)_{12}$ may possibly be a consequence of Fermi resonance or unusual crystalline interactions.

(31) M. Kalvius, U. Zahn, P. Kienle, and H. Eicher, *Z. Naturforsch.*, **17a**, 494 (1962).

(32) E. Fluck, W. Kerler, and W. Neuwirth, *Angew. Chem. Intern. Ed. Engl.*, **2**, 277 (1963).

(33) R. H. Herber, W. R. Kingston, and G. K. Wertheim, *Inorg. Chem.*, **2**, 153 (1963).

(34) The Mossbauer spectrum of $Fe_3(CO)_{12}$[31−33] consists of three lines of similar intensity. For a trinuclear iron molecule the outer two lines were interpreted as being due to a marked quadrupole splitting of a resonance line caused by *two* equivalent iron atoms possessing a large electric field gradient at their nuclei; the central line, which exhibits little (if any) quadrupole splitting, then is interpreted to arise from the third (unique) iron atom possessing a relatively small electric field gradient at its nucleus. These results eliminated the proposed symmetrical triangular models in which the three iron atoms are all equivalent. The earlier Mossbauer workers[31−33] also presumed (erroneously as it turned out) that any unsymmetrical triangular iron model could also be rejected on the basis that the localized site symmetry of the unique iron atom should be sufficiently lower than cubic (tetrahedral or octahedral) symmetry such as to give rise to an easily detectable quadrupole splitting of its resonance peak.

(35) G. R. Dobson and R. K. Sheline, *Inorg. Chem.*, **2**, 1313 (1963).

of an unsymmetrical triangular iron model: (1) by Dahl and Blount[27] from their reinterpretation of the Mössbauer and the solid-state infrared data of $Fe_3(CO)_{12}$, based on its structure being analogous to the determined structure of the $HFe_3(CO)_{11}^-$ anion by the replacement of the bridging hydrogen with a bridging carbonyl; (2) by Erickson and Fairhall[36] from a structural model intuitively deduced from the Mössbauer equivalence of $Fe_3(CO)_{12}$ and the $HFe_3(CO)_{11}^-$ anion; (3) by Dahm and Jacobson[28] from analogy with the determined $Fe_3(CO)_{11}P(C_6H_5)_3$ structure.

Although this new model appeared to account convincingly for most of the experimental evidence (at least that in the solid state), it still was of great importance to ascertain directly the molecular configuration of the $Fe_3(CO)_{12}$ and thereby to alleviate completely all further speculation and frustration concerning its solid-state structure. This paper presents the results of an intensive effort to obtain the ultimate structure of $Fe_3(CO)_{12}$.

Experimental Section

Charcoal-black crystals of triiron dodecacarbonyl were obtained from oxidation of a solution of $HFe(CO)_4^-$ with freshly prepared MnO_2 followed by acidification as described elsewhere.[37] A single crystal with dimensions 0.23 × 0.34 × 0.35 mm was mounted inside a thin-walled glass capillary about the 0.35-mm direction (corresponding to the *c* rotation axis). Multiple-film equiinclination Weissenberg data (*hk*0 through *hk*9) and multiple-exposure precession data (0*kl*, 1*kl*, and *h*0*l*) were obtained with Zr-filtered Mo Kα radiation (λ 0.7107 Å). Unit cell parameters were determined from precession photographs. Intensities were estimated visually by comparison with a standard set of intensities prepared with the same crystal. Correction for spot extension[38] was applied to the Weissenberg data. No corrections were made for extinction or absorption. The linear absorption coefficient, μ, of 28 cm^{-1} for Mo Kα radiation results in a μR_{max} of 0.5 for which the variation of absorption correction factors with θ is not appreciable.[39] Reflections which appeared in both Weissenberg and precession films were utilized to assign an individual relative scale factor for each of these 13 reciprocal levels. A total of 539 independent observed diffraction maxima, of which 495 reflections were recorded from Weissenberg data and an additional 44 reflections from precession data, were used throughout this investigation. Minimum observed intensities, $I_o(\min)$, were estimated for each reciprocal lattice level, and variable weights were assigned to individual observed reflections according to the following scheme: if $I_o < 4I_o(\min)$, $\sqrt{w}(F_o) = 1.25I_o^2/F_oI_o^2(\min)$; if $I_o \geqslant 4I_o(\min)$, $\sqrt{w}(F_o) = 20/F_o$.

Unit Cell and Space Group. Crystals of $Fe_3(CO)_{12}$ (mol wt, 503.7) are monoclinic with $a = 8.36 \pm 0.01$ Å, $b = 11.30 \pm 0.02$ Å, $c = 8.87 \pm 0.01$ Å, $\beta = 97° 5' \pm 10'$. These cell dimensions do not differ significantly from the values of $a = 8.35$ Å, $b = 11.33$ Å, $c = 8.88$ Å, $\beta = 97° 9.5'$ reported by Dahl and Rundle.[18,40] The volume of the monoclinic unit cell is 831.5 Å^3. The observed density of 2.05 g cm^{-3} (obtained by flotation) compares satisfactorily with the calculated value of 2.01 g cm^{-3} based on two formula units of $Fe_3(CO)_{12}$ in a unit cell. The total number of electrons per unit cell, $F(000)$, is 246. Systematic absences are $\{h0l\}$ for $h + l$ odd and $\{0k0\}$ for k odd. The uniquely defined centrosymmetric space group, $P2_1/n$ [nonstandard setting of $P2_1/c$ (C_{2h}^5, no. 14)[41]], was confirmed by the structural analysis. This symmetry for the *average* unit cell arises from a crystal disorder in which each molecule assumes a random distribution in one of two orientations related to each other by a center of symmetry. Since the electron-density maps showed a nearly complete overlap of peaks for the corresponding pairs of carbon and oxygen half-atoms for the two orientations of each molecule, the least-squares refinement was based on a half-atom weighting for the disordered iron atoms and a whole-atom weighting for each of the carbon and oxygen atoms. Hence, the solution of the structure involved the determination of the coordinates of three half-weighted iron atoms and six whole-weighted carbonyl groups; all of these crystallographically independent atoms occupy the following general fourfold set of positions (4e) in $P2_1/n$: $\pm(x, y, z;\ ^1/_2 + x,\ ^1/_2 - y,\ ^1/_2 + z)$. That there is no evidence of diffuse streaking on the X-ray photographs indicates that the nature of the disorder is that of a true statistical distribution.

Determination of the Structure. A sharpened three-dimensional Patterson function,[42] computed with the Blount program[43] from the Lp-corrected intensities, showed a distribution of vector peaks closely similar to that obtained by Dahl and Rundle[18] from their intensity data. This vector map is distinctly characterized by an observed hexagonal concentration of 18 large peaks about *both* the origin and center of the unit cell in planes nearly perpendicular to the *b* symmetry axis (the angle between the vector perpendicular to the iron plane and the *b* axis is approximately 19.4°). Six of the nine crystallographically independent vectors about the Patterson origin are approximately of double weight; furthermore, the three closest independent peaks about 0, 0, 0 correspond to interatomic vectors of only 1.4–1.6 Å. This peak distribution does not allow a successful deconvolution in terms of any linear iron model but instead conforms only to the Dahl–Rundle disordered triangular iron model. In this disordered crystalline model the two trimeric molecules which are centered about 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ in the unit cell are each comprised of a triangular arrangement of iron atoms randomly oriented in one of two positions such as to produce a center of symmetry for the average structure and therefore for the observed space group symmetry.[44,45] The innermost hexagonal array of peaks about the Patterson origin, corresponding to interatomic distances of 1.4–1.6 Å, primarily must represent the Fe–Fe vectors from an iron triangle in one orientation to an iron triangle in the other disordered orientation in the unit cell.[46–49]

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(36) N. E. Erickson and A. W. Fairhall, *Inorg. Chem.*, **4**, 1320 (1965).

(37) R. B. King, "Organometallic Syntheses," Vol. 1, Academic Press, New York, N. Y., 1965, pp 95–98.

(38) D. C. Phillips, *Acta Cryst.*, 7, 746 (1954).

(39) "International Tables for X-Ray Crystallography," Vol. II, The Kynoch Press, Birmingham, England, 1959, p 295.

(40) This particular labeling of the unit cell axes arbitrarily differs from the original coordinate scheme of Dahl and Rundle[18] by an interchange of the *a* and *c* axes. The space group $P2_1/n$ is invariant to this axial transformation.

(41) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 99.

(42) See, *e.g.*, H. Lipson and W. Cochran, "The Determination of Crystal Structure," G. Bell and Sons, Ltd., London, England, 1957, p 170.

(43) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, Madison, Wis., 1965.

(44) To a first approximation, the hexagonal array of peaks about the origin shown in the sharpened Patterson section, $P(u,0,w)$,[18,45] can be explained in terms of intramolecular Fe–Fe vectors arising from six iron half-atoms located at the vertices of an approximately regular hexagon nearly normal to the *b* axis, while the hexagonal-like allotment of peaks about $^1/_2$, $^1/_2$, $^1/_2$ in the $P(u,^1/_2,w)$ section[18,45] is the result of intermolecular Fe–Fe vectors between the two hexagons of half-iron atoms in the unit cell. (For these qualitative considerations the reasonable assumption is made that any enhancement of these peaks by coincidences of other interatomic vectors can be ignored.) The favorable comparison of the $P(u,0,w)$ section[18,45] with the vector peaks produced by a regular hexagon of identical atoms [*cf.* Figure 184(c) of Lipson and Cochran,[42] p 184; Figure 12.4(a) of G. H. Stout and L. H. Jensen, "X-Ray Structure Determination," The Macmillan Co., New York, N. Y., 1968, p 305] was cited by Dahl and Rundle[18] as strong evidence for their disordered triangular iron model.

(45) L. F. Dahl, Ph.D. Thesis, Iowa State College, Ames, Iowa, 1956.

(46) These results demonstrate that a disordered (or submicroscopically twinned) crystalline structure, for which coherently diffracted interference must occur, can sometimes be distinguished from an incoherently twinned crystal by the presence of peaks on a Patterson map attributable to interatomic vectors between alternate positions of atoms disordered in the unit cell. This observation was shown to be applicable to the crystalline structures of $Co_4(CO)_{12}$[3,47,48] and $Rh_4(CO)_{12}$[48,49] which possess similar lattice parameters. The Patterson function of $Co_4(CO)_{12}$ (found[3,47,48] to have a crystalline disorder involving the cobalt atoms) shows peaks characteristic of Co–Co vectors between the two different orientations of each cobalt tetrahedron, whereas for $Rh_4(CO)_{12}$ (found[47–49] to conform to an incoherent twinning model) these Patterson peaks are absent.

(47) P. Corradini, *J. Chem. Phys.*, **31**, 1676 (1959); P. Corradini and A. Sirigu, *Ric. Sci.*, 36, 188 (1966).

(48) C. H. Wei, submitted for publication.

(49) C. H. Wei, G. R. Wilkes, and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 4792 (1967).

Table I. Positional and Anisotropic Thermal Parameters (× 10^4) for the Averaged Disordered Structure of $Fe_3(CO)_{12}$[a, b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe_1	−0.0544 (4)	−0.0191 (4)	−0.1683 (3)	140 (7)	60 (5)	110 (4)	15 (5)	−7 (4)	1 (4)
Fe_2	0.1727 (5)	−0.0170 (5)	0.0719 (4)	127 (8)	172 (8)	147 (5)	44 (6)	11 (5)	−5 (5)
Fe_3	−0.1131 (4)	0.0483 (4)	0.1087 (4)	110 (7)	141 (6)	138 (5)	25 (5)	20 (5)	−29 (4)
C_1	−0.0791 (17)	−0.1648 (19)	−0.1118 (16)	119 (26)	153 (24)	165 (20)	21 (24)	4 (18)	1 (24)
C_2	−0.0192 (18)	0.1259 (18)	−0.1977 (17)	144 (27)	162 (29)	157 (22)	−4 (23)	−31 (19)	−23 (19)
C_3	−0.2875 (23)	−0.0101 (14)	−0.2586 (17)	369 (51)	88 (21)	225 (25)	−19 (24)	−101 (26)	27 (17)
C_4	0.0990 (23)	−0.0733 (14)	−0.3075 (19)	505 (55)	68 (19)	220 (32)	−76 (26)	7 (31)	−37 (19)
C_5	0.2815 (20)	0.0595 (17)	−0.0709 (19)	201 (35)	124 (25)	267 (29)	26 (24)	−46 (29)	−23 (23)
C_6	0.2379 (23)	−0.1654 (22)	−0.0028 (20)	202 (42)	205 (32)	262 (34)	−64 (31)	56 (29)	64 (33)
O_1	−0.1114 (19)	−0.2593 (11)	−0.1114 (16)	353 (33)	119 (18)	321 (26)	−69 (19)	61 (20)	−59 (18)
O_2	−0.0051 (17)	0.2133 (12)	−0.2438 (14)	366 (34)	156 (19)	242 (21)	50 (20)	87 (20)	83 (15)
O_3	−0.3936 (14)	−0.0229 (11)	−0.3406 (13)	236 (24)	149 (16)	275 (21)	−22 (16)	−66 (18)	−13 (15)
O_4	0.1435 (14)	−0.0908 (11)	−0.4197 (12)	295 (25)	185 (18)	201 (18)	45 (17)	43 (17)	−29 (13)
O_5	0.3784 (16)	0.1141 (13)	−0.0996 (18)	245 (31)	165 (22)	530 (39)	−11 (19)	112 (28)	−56 (21)
O_6	0.2973 (17)	−0.2549 (12)	0.0042 (15)	263 (30)	148 (19)	280 (23)	22 (17)	61 (19)	46 (17)

[a] The form of the anisotropic thermal factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. [b] Standard deviations of the last significant figure(s) are given in parentheses here and in succeeding tables.

Table II. Bond Distances (Å) with Standard Deviations for the Averaged Disordered Structure of $Fe_3(CO)_{12}$[a]

Fe_1-Fe_3	2.678 (5)	Fe_3-C_2'	2.35 (2)
Fe_1-Fe_2	2.668 (7)	Fe_2-C_2'	2.18 (2)
Fe_2-Fe_3	2.560 (6)	C_1-O_1	1.10 (2)
Fe_1-C_1	1.74 (2)	C_2-O_2	1.08 (2)
Fe_1-C_2	1.69 (2)	C_3-O_3	1.09 (2)
Fe_1-C_3	2.02 (2)	C_4-O_4	1.12 (2)
Fe_1-C_4	1.98 (2)	C_5-O_5	1.07 (2)
Fe_3-C_6'	1.87 (2)	C_6-O_6	1.13 (2)
Fe_2-C_5	1.86 (2)	$Fe_1 \cdots Fe_2'$	1.45 (1)
Fe_3-C_5'	1.86 (2)	$Fe_2' \cdots Fe_3$	1.66 (1)
Fe_2-C_6	1.91 (3)	$Fe_3 \cdots Fe_1'$	1.46 (1)
Fe_3-C_4'	1.78 (2)	$Fe_1 \cdots Fe_1'$	3.04 (1)
Fe_2-C_3'	1.83 (1)	$Fe_2 \cdots Fe_2'$	3.03 (1)
Fe_3-C_1'	2.08 (2)	$Fe_3 \cdots Fe_3'$	3.06 (1)
Fe_2-C_1'	2.24 (2)		

[a] The bond lengths are arranged into sets according to a pseudo-mirror plane passing through Fe_1 and the midpoint of Fe_2 and Fe_3.

Table III. Bond Angles (deg) with Standard Deviations for the Averaged Disordered Structure of $Fe_3(CO)_{12}$[a]

M–M–M	
$Fe_3-Fe_1-Fe_2$	57.2 (2)
$Fe_1-Fe_3-Fe_2$	61.2 (2)
$Fe_1-Fe_2-Fe_3$	61.6 (2)
M–M–CO	
$Fe_3-Fe_1-C_1$	87.8 (5)
$Fe_2-Fe_1-C_1$	83.1 (5)
$Fe_3-Fe_1-C_2$	85.4 (5)
$Fe_2-Fe_1-C_2$	89.9 (5)
$Fe_3-Fe_1-C_3$	93.9 (5)
$Fe_2-Fe_1-C_4$	93.1 (5)
$Fe_3-Fe_1-C_4$	150.3 (5)
$Fe_2-Fe_1-C_3$	150.5 (5)
$Fe_1-Fe_3-C_1'$	87.8 (4)
$Fe_1-Fe_2-C_1'$	84.7 (4)
$Fe_1-Fe_3-C_2'$	86.3 (4)
$Fe_1-Fe_2-C_2'$	90.0 (4)
$Fe_1-Fe_3-C_4'$	163.6 (7)
$Fe_1-Fe_2-C_3'$	164.3 (6)
$Fe_1-Fe_3-C_6'$	84.0 (7)
$Fe_1-Fe_2-C_5$	79.5 (5)
$Fe_1-Fe_3-C_5'$	82.6 (6)
$Fe_1-Fe_2-C_6$	85.4 (6)
$Fe_2-Fe_3-C_1'$	56.7 (5)
$Fe_3-Fe_2-C_1'$	50.7 (4)
$Fe_2-Fe_3-C_2'$	52.6 (4)
$Fe_3-Fe_2-C_2'$	58.7 (5)
$Fe_2-Fe_3-C_4'$	102.9 (7)
$Fe_3-Fe_2-C_3'$	103.3 (7)
$Fe_2-Fe_3-C_6'$	127.8 (6)
$Fe_3-Fe_2-C_5$	119.7 (6)
$Fe_2-Fe_3-C_5'$	119.1 (6)
$Fe_3-Fe_2-C_6$	127.5 (6)
Star of David	
$Fe_1-Fe_2'-Fe_3$	118.9 (3)
$Fe_2'-Fe_3-Fe_1'$	117.4 (3)
$Fe_3-Fe_1'-Fe_2$	122.9 (3)
M–C–O	
$Fe_1-C_1-O_1$	163.0 (16)
$Fe_1-C_2-O_2$	166.7 (16)
$Fe_1-C_3-O_3$	158.3 (17)
$Fe_1-C_4-O_4$	156.6 (17)
$Fe_3-C_4'-O_4'$	157.0 (18)
$Fe_2-C_3'-O_3'$	157.0 (19)
$Fe_3-C_6'-O_6'$	151.7 (20)
$Fe_2-C_5-O_5$	151.0 (19)
$Fe_3-C_5'-O_5'$	155.5 (19)
$Fe_2-C_6-O_6$	156.1 (18)
$Fe_3-C_1'-O_1'$	143.6 (16)
$Fe_2-C_1'-O_1'$	142.9 (15)
$Fe_3-C_2'-O_2'$	145.6 (16)
$Fe_2-C_2'-O_2'$	143.9 (16)
C–M–C	
$C_1-Fe_1-C_2$	172.1 (7)
$C_1-Fe_1-C_3$	90.7 (7)
$C_1-Fe_1-C_4$	90.7 (7)
$C_2-Fe_1-C_3$	93.6 (7)
$C_2-Fe_1-C_4$	94.0 (7)
$C_3-Fe_1-C_4$	115.8 (7)
$C_6'-Fe_3-C_5'$	90.6 (8)
$C_5-Fe_2-C_6$	89.3 (8)
$C_5'-Fe_3-C_2'$	80.0 (7)
$C_6-Fe_2-C_2'$	83.8 (7)
$C_2'-Fe_3-C_1'$	101.3 (7)
$C_2'-Fe_2-C_1'$	101.4 (7)
$C_1'-Fe_3-C_6'$	86.6 (7)
$C_1'-Fe_2-C_5$	83.8 (7)
$C_4'-Fe_3-C_6'$	110.6 (9)
$C_3'-Fe_2-C_5$	107.0 (8)
$C_4'-Fe_3-C_5'$	103.8 (8)
$C_3'-Fe_2-C_6'$	108.7 (8)
$C_4'-Fe_3-C_1'$	86.0 (7)
$C_3'-Fe_2-C_1'$	81.9 (7)
$C_4'-Fe_3-C_2'$	80.1 (7)
$C_3'-Fe_2-C_2'$	-84.7 (7)
$C_6'-Fe_3-C_2'$	167.3 (8)
$C_5-Fe_2-C_2'$	167.9 (7)
$C_5'-Fe_3-C_1'$	170.6 (7)
$C_6-Fe_2-C_1'$	168.8 (6)
M–CO–M	
$Fe_2-C_1'-Fe_3$	72.6 (7)
$Fe_2-C_2'-Fe_3$	68.7 (6)

[a] The bond angles are arranged into sets according to a pseudo-mirror plane passing through Fe_1 and the midpoint of Fe_2 and Fe_3.

Initial positions for one set of three independent iron half-atoms corresponding to a nearly isosceles triangular array were estimated from a vector analysis of the sharpened Patterson function. These iron coordinates, together with individual atom isotropic temperature factors (for which initial values were arbitrarily assigned to be 2.0 Å^2) and the 13 reciprocal layer scale factors, were refined by full-matrix least squares.[50] After two cycles, the unweighted discrepancy factor, $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$, became 39.6%. A three-dimensional Fourier synthesis was next calculated[43] with phases based on the set of iron atoms. Only 12 peaks were unambiguously found in an asymmetric unit cell; these were assigned as six whole-carbon and six whole-oxygen atoms. After the construction of a ball-and-stick model for the structure, it was realized that *either* of the two sets of iron half-atoms related to each other by the center of symmetry taken together with the surrounding 12 carbonyls, of which six are crystallographically independent, comprises an appropriate configuration for the $Fe_3(CO)_{12}$ molecule. A full-matrix, least-squares refinement[50] of all 15 independent atoms (with 50% occupancy factor assigned to each iron atom and 100% occupancy factor to each carbon and oxygen atom) was performed with initial isotropic temperature factors of 4.0 and 5.0 Å^2 arbitrarily assigned for each carbon and oxygen atom, respectively. After five cycles, all parameter shifts became less than 2% of the corresponding standard deviations. At this stage the R_1 value remained at 12.5% and the weighted discrepancy factor, $R_2 = [\Sigma w||F_o| - |F_c||^2/$

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(50) 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, 1962.

Table IV. Equations of Best Molecular Planes and Distances (Å) of Atoms from These Planes for the Averaged Disordered Structure of $Fe_3(CO)_{12}$[a]

(a) Pseudo-Mirror Plane through Fe_1, Fe_2, and Fe_3

$0.258X + 0.943Y - 0.210Z - 0.039 = 0$

C_2	1.68	O_2	2.74	C_4	0.05
C_1	−1.73	O_1	−2.81	O_4	0.20
C_1'	1.65	O_1'	2.73	C_3	−0.22
C_2'	−1.76	O_2'	−2.82	O_3	−0.41
C_6'	1.20	O_6'	2.04	C_3'	0.14
C_5'	−1.43	O_5'	−2.28	O_3'	0.33
C_5	1.35	O_5	2.21	C_4'	−0.13
C_6	−1.28	O_6	−2.12	O_4'	−0.27
				i(000)	−0.04

(b) Pseudo-Mirror Plane through Fe_1, C_1, O_1, C_2, O_2, and the Midpoint of Fe_2–Fe_3

$0.967X - 0.215Y - 0.138Z + 0.002 = 0$

Fe_1	0.001	C_6'	−2.33	C_1'	−0.01
C_1	0.017	C_5	2.29	C_2'	0.01
O_1	−0.015	C_5'	−2.29	O_1'	0.02
C_2	−0.010	C_6	2.33	O_2'	0.01
O_2	−0.003			*i*(000)	0.00
		O_3	−2.35		
Fe_3	−1.28	O_4	2.34		
Fe_2	1.28	O_4'	−2.33		
C_3	−1.71	O_3'	2.35		
C_4	1.68	O_6'	−3.01		
C_4'	−1.67	O_5	3.01		
C_3'	1.71	O_5'	−3.01		
		O_6	3.01		

(c) Plane through C_1', C_2', C_5', and C_6'

$0.340X - 0.270Y - 0.901Z + 1.205 = 0$

C_1'	−0.001	O_1'	−0.19	Fe_3	−0.17
C_2'	0.002	O_2'	−0.16	C_4'	−1.85
C_5'	−0.002	O_5'	−0.35	O_4'	−2.96
C_6'	0.003	O_6'	−0.38		

(d) Plane through C_1', C_2', C_6, and C_5

$-0.663X - 0.055Y - 0.747Z + 1.190 = 0$

C_1'	−0.005	O_1'	−0.24	Fe_2	−0.18
C_2'	0.005	O_2'	−0.13	C_3'	−1.92
C_6	−0.010	O_6	−0.32	O_3'	−3.00
C_5	0.008	O_5	−0.40		

[a] The equations of the planes are given in an orthogonal Ångström coordinate system (X, Y, Z) which is related to the monoclinic fractional coordinate system (x, y, z) by the transformations: $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. Estimated standard deviations for positional parameters were taken into account in these calculations.[55]

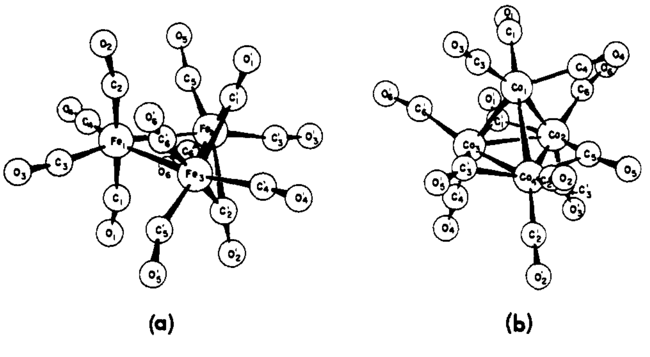

Figure 1. Molecular configurations of $Fe_3(CO)_{12}$ and the structurally related $Co_4(CO)_{12}$. The carbon and oxygen atoms with primed symbols are related to the corresponding atoms with nonprimed symbols in the ordered–disordered crystalline states of these compounds by a crystallographic center of symmetry in $Fe_3(CO)_{12}$ and by a twofold crystallographic axis in $Co_4(CO)_{12}$ passing through Co_4 and the center of the equilateral triangle of Co_1, Co_2, and Co_3.

$\Sigma w|F_o|^2]^{1/2} \times 100$, stood at 14.3%. The 13 reciprocal layer scale factors (whose values ranged from 0.313 to 0.408) obtained from the isotropic refinement were used to place all of the observed structure factors on a single relative scale. A full-matrix anisotropic refinement with one variable scale factor was then employed until changes of individual parameters again became negligible with respect to the corresponding standard deviations. After three cycles, R_1 and R_2 dropped considerably to 7.1 and 7.6%, respectively. A final difference Fourier synthesis revealed no peaks greater than 0.9 e/Å^3, which is approximately equivalent to 20% of the average peak height of a carbon atom in this structure. The atomic scattering factors used for iron were those of Thomas and Umeda,[51] and for carbon and oxygen were those of Berghuis, *et al.*[52] The output parameters with estimated standard deviations from the last cycle of the anisotropic least-squares refinement are given in Table I.[53] Bond lengths and angles and their estimated standard deviations, calculated with the Busing–Martin–Levy function and error program[54] from the full inverse matrix (containing estimated lattice parameter errors), are listed in Tables II and III, respectively. Least-squares calculations[55] of "best" molecular planes formed by certain atoms and the perpendicular distances of these and other atoms from these planes are given in Table IV.

The validity of the disordered model for $Fe_3(CO)_{12}$ is demonstrated by the final low discrepancy factors, previously mentioned, which clearly show the over-all correctness of the determined structure. The sensitivity of the discrepancy factors to the inclusion of the carbonyl groups in the least-squares refinements is given by the large unweighted R value of 39.6% obtained when only the three iron half-atoms were utilized in an isotropic least-squares refinement.

Discussion

Description of Structure and Consequence of Crystal Disorder. The molecular configuration of $Fe_3(CO)_{12}$ consists of an isosceles triangular arrangement of iron atoms in which an $Fe(CO)_4$ group is symmetrically coordinated by only Fe–Fe bonds to an $Fe_2(CO)_8$ fragment containing two identical $Fe(CO)_3$ groups linked to each other by both two bridging carbonyl groups and an Fe–Fe bond. The resulting idealized configuration shown in Figure 1a can be formally derived from that of $Fe_2(CO)_9$[56] by the replacement of one of the three bridging carbonyls with the *cis*-$Fe(CO)_4$ group. This configuration is in accord with the observed diamagnetism of the compound. Each one of the two bridged iron atoms is coordinated to three terminal carbonyl and two bridging carbonyl groups at the corners of a distorted rectangular pyramid; each of these iron atoms is similarly displaced from the mean basal plane of its carbonyl carbon pyramid by 0.18 Å (av) toward the terminal apical carbonyl ligand (Table IVc and d). The $Fe_2(CO)_8$ moiety then can be considered to arise from the intersection of the two basal planes along the common bridging carbonyl edge (*i.e.*, the $C_1' \cdots C_2'$ line) with a dihedral angle of 116.7°. This

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

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

(53) Calculated and observed structure factors together with the estimated standard errors utilized in the least-squares refinement are deposited as Document No. NAPS-00165 with the ASIS National Auxiliary Publication Service, c/o CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and remitting $1.00 for microfilm or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

(54) 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.

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

(56) H. M. Powell and R. V. Ewens, *J. Chem. Soc.*, 286 (1939).

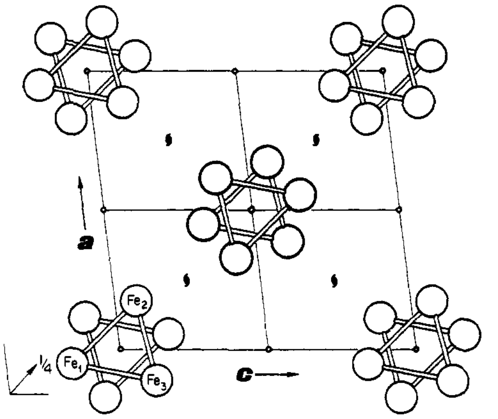

Figure 2. The "Star of David" disordered arrangement of half-weighted iron atoms about the centrosymmetric points 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ in the unit cell of $Fe_3(CO)_{12}$ corresponding to each of the two molecules per cell being randomly distributed in one of two orientations which are related by a crystallographic center of symmetry.

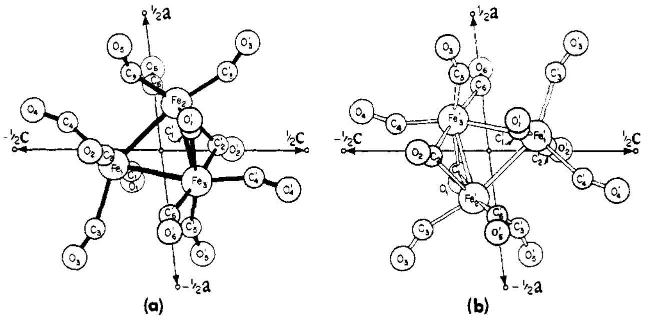

Figure 3. [010] projections of the $Fe_3(CO)_{12}$ molecule in its two statistical orientations about a "crystal-averaged" center of symmetry. The carbon and oxygen positions represent the *average* of the nearly identical positions of the corresponding half-weighted carbon and oxygen atoms for the two possible orientations. The different types of lines connecting the atoms in the two orientations are for comparison with Figure 4.

degree of deformation of the $Fe_2(CO)_8$ fragment from planarity results in each of the bridged iron atoms having its sixth octahedral-like direction, taken as the vector perpendicular to its mean carbonyl carbon basal plane, nearly collinear with the internuclear iron–iron line connecting the bridged iron atom with the $Fe(CO)_4$ group; the normals of the mean basal planes are directed only 3.6° (*i.e.*, the average value of 2.4 and 4.9°) off the iron–iron lines.

The crystal disorder necessarily requires the iron atoms in each molecule to appear as two sets of chemically equivalent isosceles triangular arrays of iron half-atoms around an average crystallographic symmetry center and thus to form a "Star of David"; this six-pronged star arrangement about the centrosymmetric points 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$ in the unit cell viewed down the *b* axis is shown in Figure 2.[57] These two centrosymmetrically related sets of iron half-atoms are not coplanar but are perpendicularly displaced in two parallel planes by 0.08 Å from each other; since the centroids of the two isosceles iron triangles nearly coincide with the crystallographic center of symmetry located midway between them, the 12 half-weighted carbonyl sites associated with one set of half-weighted iron sites overlap with the other 12 half-weighted carbonyl sites associated with the other set of half-weighted iron sites to such an extent that the two sets of carbonyl sites were not resolved. Hence, each of the six independent whole-weighted carbonyls in this structure represents the *average* of two nearly coincident, half-weighted carbonyl positions. It should be realized that the positions of the carbonyl atoms need to be nearly invariant to the disordered crystal structure as they are responsible for the mode of molecular packing in the crystal.

The [010] projections of the $Fe_3(CO)_{12}$ molecule in its two statistical orientations around a crystallographic center of symmetry are shown in Figure 3. To distinguish the molecular geometry in one orientation from that in the other, the lines connecting the atoms are solid in Figure 3a and open in Figure 3b. It is of particular interest that in the molecular orientation of Figure 3a, the two terminal carbonyl groups C_1–O_1 and C_2–O_2, coordinated to the nonbridged Fe_1 atom, are related by the center of inversion to the bridging carbonyls C_1'–O_1' and C_2'–O_2', which are coordinated to the two bridged iron atoms, Fe_2 and Fe_3. When the alternative set of iron atoms of Figure 3b is considered, the C_1–O_1 and C_2–O_2 (terminal in Figure 3a) are bridging groups coordinated to Fe_2' and Fe_3' while the centrosymmetrically related C_1'–O_1' and C_2'–O_2' (bridging in Figure 3a) are terminal groups attached to the nonbridged Fe_1' atom. Thus, each apparent carbon atom represents the average site of two actual carbon atoms, one of which is bonded to the nonprimed and the other to the primed iron atoms. The resulting consequence for this crystal structure is that either of the two possible orientations of the iron framework together with the 12 whole carbonyls (of which only *six* are crystallographically independent in our calculations) uniquely gives the identical molecular configuration.

The effect of the actual separation of the carbonyl sites no doubt was incorporated to a considerable extent into the anisotropic temperature factors as indicated by the substantial lowering of the discrepancy factors to the final satisfactory values when the isotropic thermal model was replaced by the anisotropic one. The precision implied by this good agreement applies, however, to the *averaged* statistical structure, not to the individual molecular components. Thus, the molecular parameters must be considered less certain than usual.

An idea of the displacements of the individual half-weighted carbonyl positions from the sites of the averaged structure may be gained by an examination of Figure 4 which illustrates the shapes of the atomic thermal ellipsoids obtained from the anisotropic refinement of the *averaged disordered* structure. For the sake of clarity only six terminal carbonyl groups, of which four are crystallographically independent, are shown. With the assumption of linear Fe–C–O angles, Figure 4 suggests that much greater deviations of each of the two sites for the nearly superimposable half-weighted atoms from that for the whole-weighted averaged atom occur in general for the carbon atoms than for the oxygen atoms; some of the individual deviations appear to be as great as 0.3 Å. Hence, it is not surprising that all terminal Fe–C–O angles

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(57) The drawings shown in Figures 2–5 were prepared by means of the Johnson program: C. K. Johnson, "A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," ORNL-3794, Oak Ridge National Laboratory, 1965.

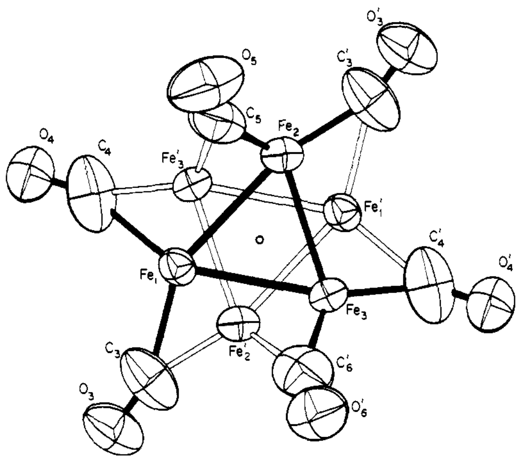

Figure 4. The 50% probability thermal ellipsoids obtained from the anisotropic least-squares refinement of $Fe_3(CO)_{12}$ based on a half-weighting for the disordered iron atoms and a whole weighting for each of the carbon and oxygen atoms whose coordinates represent the mean positions of the nearly superimposable half-atoms associated with the two alternative orientations of the $Fe_3(CO)_{12}$ molecule. The shapes of the ellipsoids for the carbonyl atoms appear to indicate qualitatively the approximate directions and rough magnitudes of the displacements of the individual half-atom sites. The cause of the severe distortions from linearity in the Fe-C-O angles as well as the considerable variations in the Fe-C and C-O distances, based on the mean atomic positions, is thus made apparent.

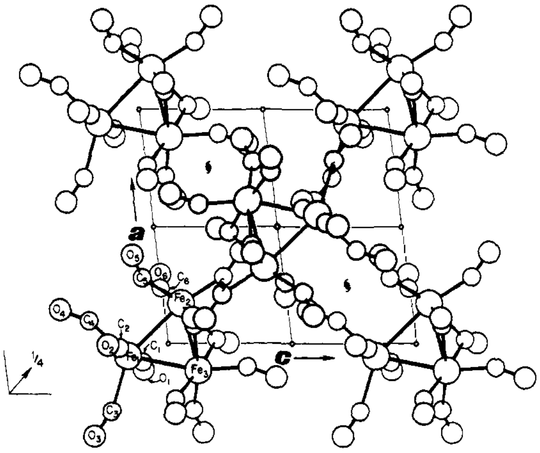

Figure 5. [010] projection of the unit cell of $Fe_3(CO)_{12}$. Only one orientation of the iron atoms per molecule is shown.

of range 151-167° sharply deviate from linearity. The exceptionally large range of 1.69-2.02 Å for the individual terminal Fe-C distances can also be nicely rationalized. Despite these large variations in individual distances and angles, a comparison of the bond distances given in Table II shows a remarkable internal self-consistency of the corresponding individual bond lengths related by C_{2v} symmetry to within 0.06 Å, except for those distances involving the bridging carbonyls. This approximate conformity of the *nonbridged* molecular parameters to C_{2v} symmetry indicates that the symmetrical displacements of the corresponding half-atoms from the mean positions can be correlated with the actual chemically equivalent symmetry of $Fe_3(CO)_{12}$ molecule (*vide infra*). This large variation in the individual molecular parameters is not an uncommon phenomenon for averaged disordered structures; other organometallic examples of its occurrence include $Co_4(CO)_{12}$ (disordered by a twofold axis)[3,47,48] and $Co_6(CO)_{16}C_2S_3$ (disordered by a mirror plane).[58]

Figure 5 shows the [010] projection of the $Fe_3(CO)_{12}$ unit cell and indicates the packing of the two molecules per cell. To make the drawing clearer, only one orientation of iron atoms per molecule is shown. The minimum intermolecular distances of 3.0 Å for O · · · O contacts and 3.1 Å for C · · · O contacts are reasonable ones and indicate that the molecules in $Fe_3(CO)_{12}$ are packed by the usual van der Waals cohesive forces.

Structural Comparison with $HFe_3(CO)_{11}^-$ and $Fe_3(CO)_{11}P(C_6H_5)_3$ Analogs. A. Iron-Iron Bond Lengths. The two iron-iron distances for the chemically equivalent bonds linking the *cis*-$Fe(CO)_4$ group with the $Fe_2(CO)_8$ fragment are 2.67 and 2.68 Å. The mean value of 2.67 Å is 0.11 Å longer than the value of 2.56 Å for the bond between the iron atoms connected by the two bridging carbonyl groups. These average values in bond lengths for nonbridged and bridged iron atoms are paralleled in the closely related triangular structures of the $HFe_3(CO)_{11}^-$ anion [2.69 (av) and 2.58 Å][27] and of the two geometrical isomers of $Fe_3(CO)_{11}P(C_6H_5)_3$ [2.70 (av) and 2.56 Å (av)].[28] The observed Fe-Fe distances of 2.56-2.58 Å between the carbonyl-bridged iron atoms in $Fe_3(CO)_{12}$ and its analogs are considerably longer than the bridged Fe-Fe distance of 2.46 Å in $Fe_2(CO)_9$;[56] they correspond to the upper end of the *normal* range of 2.4-2.6 Å for the bonding distances (found in a large number of organometallic complexes) between first-row transition metal atoms also linked by essentially symmetrical bridging carbonyl groups. The "constraining effect" of a bridging carbonyl group in shortening a metal-metal bond distance relative to that between two corresponding nonbridged metal atoms has been shown from structural work on other carbonyl complexes including $Co_4(CO)_{10}S_2$,[59] $Co_4(CO)_{10}Te_2$,[60] $Co_3[(SC_2H_5)_5(CO)](CO)_3$,[61] $Co_5(CO)_{10}(SC_2H_5)_5$,[62] $SCo_6(CO)_{11}(SC_2H_5)_4$,[63] and $Co_2(CO_6)[P(OC_6H_5)_3]_2$.[64]

B. Molecular Symmetry of $Fe_3(CO)_{12}$. The molecular structure of $Fe_3(CO)_{12}$, deduced from that of the $HFe_3(CO)_{11}^-$ anion by the substitution of a bridging carbonyl in place of the bridging hydrogen atom, was presumed to possess C_{2v}-2mm symmetry on the basis of the experimental conformity of the $HFe_3(CO)_{11}^-$ structure to C_s-m symmetry.[27] The symmetrical nature of the single bridging carbonyl group bisected by this mirror plane, which also passes through the unique iron atom and two of its attached carbonyl groups, is clearly evidenced by the equivalence of the two bridging Fe-CO bond lengths of 1.917 and 1.918 Å (individual esd, 0.012 Å). The subsequent structural determination and original isotropic

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(58) C. H. Wei and P. A. Agron, to be submitted for publication.

(59) C. H. Wei and L. F. Dahl, presented in part (Paper 15) at the National Meeting of the American Crystallographic Association, Atlanta, Ga., Jan 25-28, 1967.

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(62) C. H. Wei and L. F. Dahl, *ibid.*, **90**, 3969 (1968).

(63) C. H. Wei and L. F. Dahl, *ibid.*, **90**, 3977 (1968).

(64) J. A. Molin-Case and L. F. Dahl, to be submitted for publication.

least-squares refinement (to an R_1 of 12.5%) of $Fe_3(CO)_{12}$ (reported in a communication[3]) also supported the assignment of C_{2v} symmetry for the idealized molecular configuration in that it was felt that the relatively large uncertainties (beyond those indicated by the individual esd's) existing in the positional parameters of the carbonyl groups due to the crystal disorder did not make physically meaningful the observed differences in the Fe-CO bond lengths for the two bridging carbonyl groups.

The existence of unsymmetrical carbonyl bridges in $Fe_3(CO)_{12}$ was first proposed from an X-ray investigation by Dahm and Jacobson[28] of the crystal structure of $Fe_3(CO)_{11}P(C_6H_5)_3$. This monosubstituted triphenylphosphine derivative of $Fe_3(CO)_{12}$ exists in the solid state as a 1:1 mixture of two geometrical isomers: one with the $P(C_6H_5)_3$ ligand substituted in place of a terminal carbonyl group on one of the bridging carbonyl iron atoms and the other with the $P(C_6H_5)_3$ ligand coordinated to the nonbridged iron atom. Since the molecular configurations of both isomers showed each of the two bridging carbonyls to be unsymmetrically coordinated to the iron atoms with shorter Fe–C distances of average value 1.87 ± 0.02 Å *vs.* longer Fe–C distances of average value 2.04 ± 0.02 Å, Dahm and Jacobson[28] concluded that this bridging carbonyl asymmetry is more likely a property of the unsubstituted parent compound rather than an effect produced by the triphenyphosphine ligand. Hence, they suggested a similar asymmetric location of the two bridging carbonyls in $Fe_3(CO)_{12}$ such that the symmetry of the molecule would be C_2-2 instead of C_{2v}.

The results of the anisotropic least-squares refinement of $Fe_3(CO)_{12}$ (reported here) support their view that the two bridging carbonyl groups are indeed somewhat unsymmetrical such that the $Fe_3(CO)_{12}$ molecule can be considered within a good approximation to possess C_2 symmetry and to a lesser approximation to have C_{2v} symmetry. The extent of compatibility with C_{2v} molecular symmetry is shown by consideration of its two pseudo-mirror planes (Table IVa and b), which are almost perpendicular to each other (dihedral angle between plane *a* and plane *b*, 85.7°). The pairs of corresponding atoms related by these two pseudo-mirror planes are approximately equidistant from these planes. This C_{2v} geometry is further supported by the near equality of corresponding bond angles, as shown in Table III. Nevertheless, stereochemical evidence that the two bridging carbonyl groups, C_1'–O_1' and C_2'–O_2', are located somewhat asymmetrically with respect to the two bridged iron atoms (but are still approximately related by twofold symmetry) is given primarily by the fact that the twofold-related Fe_2–C_1' and Fe_3–C_2' bridging distances of average value 2.30 Å are 0.17 Å longer than the corresponding Fe_3–C_1' and Fe_2–C_2' bridging distances of average value 2.13 Å. This relative difference in the average Fe–C bridging bond length is comparable with the 0.17-Å difference in the average Fe–C bridging bond lengths for the two geometrical isomers of $Fe_3(CO)_{11}P(C_6H_5)_3$. Although there are large variations in the individual Fe–C distances and angles of $Fe_3(CO)_{12}$, it is noteworthy that the corresponding molecular parameters in this *averaged disordered* structure of $Fe_3(CO)_{12}$ closely conform to C_{2v} symmetry except for the bridging Fe–C bond distances. These observations lead us to conclude that the half-weighted carbonyl positions corresponding to the two statistically disordered orientations of the molecule are symmetrically displaced from the sites of the averaged structure. Hence the molecular configuration of $Fe_3(CO)_{12}$ also probably possesses two somewhat unsymmetrical bridging carbonyls such that its over-all symmetry is reduced from C_{2v} to C_2.

An asymmetrical bridging carbonyl arrangement involving symmetry-equivalent metal atoms is not without precedence in polynuclear metal carbonyl complexes;[65] structural results[65-67] have shown that carbonyl groups may take on a number of geometries which are intermediate between the terminal and symmetrically doubly bridging cases. The stereochemical principle that emerges from these structural studies is that the presence of two doubly bridging carbonyl groups between two metal atoms [*e.g.*, in $Fe_3(CO)_{12}$ and in both isomers of $Fe_3(CO)_{11}P(C_6H_5)_3$] allows the possibility of molecular distortion to produce unsymmetrical carbonyl bridges such that both bridging metal atoms can still remain chemically equivalent with the same localized identical environment; *i.e.*, in $Fe_3(CO)_{12}$ the two bridged iron atoms are related to each other by the twofold symmetry axis. However, an odd number of bridging carbonyl groups between two metal atoms as is found in $HFe_3(CO)_{11}^-$ (containing one)[27] and in $Fe_2(CO)_9$ (containing three)[56] necessitates (unless bridging carbonyl groups involving other metal atoms enter into the picture and cause equivalence of metal atoms)[68] that at least one bridging carbonyl be symmetrical in order for both bridging metal atoms to be equivalent and hence to possess the same charge density. The tendency to preserve as much as possible the symmetrical character between metal atoms in these metal atom cluster carbonyl systems appears to be a guiding tenet concerning their idealized polyhedral geometries.

Stereochemical Relationship of $Fe_3(CO)_{12}$ with $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$. The 12 carbonyl groups which encompass the iron atom framework in $Fe_3(CO)_{12}$ form a relatively close-packed distorted icosahedron.[3,69-71] This particular nonbinding polyhedral conformation of carbonyl ligands also encloses the tetrahedral metal atom cluster in the isostructural tetranuclear metal dodecacarbonyl molecules, $Co_4(CO)_{12}$[3,47,48] and $Rh_4(CO)_{12}$,[48,49] in contrast with the cuboctahedral polyhedron of 12 carbonyl ligands disposed about the tetrahedral iridium atom cluster in $Ir_4(CO)_{12}$.[72]

A formal structural interrelationship between Fe_3-

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(65) R. J. Doedens and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 4847 (1966).

(66) A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

(67) R. P. Dodge and V. Schomaker, *J. Organometal. Chem.*, **3**, 274 (1965).

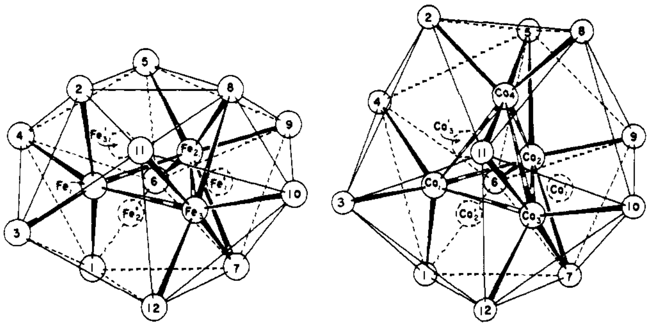
(68) An example of this possibility is found in the $[Fe_4(CO)_{13}]^{2-}$ anion for which each pair of the three basal iron atoms located at the vertices of an equilateral triangle is connected by one highly unsymmetrical bridging carbonyl in such a way that the basal iron atoms are still experimentally equivalent to one another by the threefold axis possessed by the anion.[65]

(69) The icosahedral shape of the $Fe_3(CO)_{12}$ molecule was independently deduced by Corradini and Paiaro[70] from the proposed structure[27] of $Fe_3(CO)_{12}$ based on the structure of the $HFe_3(CO)_{11}^-$ anion. To show that the quasi-regular icosahedral carbonyl geometries of $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$ should result in similar inclusion compounds, the Italian workers[70] obtained from the crystallization of $Fe_3(CO)_{12}$ with CCl_4 a pseudo-cubic form of $Fe_3(CO)_{12} \cdot CCl_4$ with lattice constants similar to that for the cubic form of $Co_4(CO)_{12} \cdot CCl_4$ previously synthesized by Corradini and Ercoli.[71]

(70) P. Corradini and G. Paiaro, *Ric. Sci.*, **36**, 365 (1966).

(71) P. Corradini and R. Ercoli, *Angew. Chem.*, **72**, 37 (1960).

(72) G. R. Wilkes, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1965; G. R. Wilkes and L. F. Dahl, to be submitted for publication.



(a) (b)

Figure 6. Comparison of the icosahedral carbonyl environments around the triangular iron atom cluster in $Fe_3(CO)_{12}$ and the tetrahedral cobalt atom cluster in $Co_4(CO)_{12}$. Primed carbonyl groups, 1′ through 6′, for both configurations in Figure 1 correspond to numbers 8, 7, 9, 10, 12, and 11 for $Fe_3(CO)_{12}$ in (a) and to numbers 7, 8, 9, 10, 11, and 12 for $Co_4(CO)_{12}$ in (b). In $Co_4(CO)_{12}$ the crystallographic twofold axis relating the two statistical orientations of half-molecules to each other is coincident with the particular localized threefold axis of the tetrahedron of cobalt atoms which passes through a basal cobalt atom, Co_4. The near invariance of the icosahedral carbonyl positions results from the crystallographic twofold axis approximately conforming to one of the 15 C_2 axes of an idealized icosahedron of I_h symmetry. In $Fe_3(CO)_{12}$ the near invariance of the flattened icosahedron of carbonyl atoms to the crystallographic center of symmetry arises from the persistence of the center of symmetry in an idealized icosahedron when symmetrically deformed in the direction normal to the triiron plane. The alternative positions of the metal atom cluster fragments due to the nature of the statistical disorder are indicated.

$(CO)_{12}$ and $Co_4(CO)_{12}$ (Figure 1) is provided from a consideration of the relative orientations of the triiron isosceles triangle and tetracobalt tetrahedron with respect to the icosahedral-like arrangement of carbonyl groups. The molecular configuration of $Co_4(CO)_{12}$ (Figure 1b) (and $Rh_4(CO)_{12}$) is comprised of four tetrahedrally arranged metal atoms in which an apical $M(CO)_3$ fragment is symmetrically coordinated by only M–M bonds to a basal $M_3(CO)_9$ segment containing three identical basal $M(CO)_2$ fragments arrayed at the corners of an equilateral triangle and connected in pairs to one another by both a bridging carbonyl group and a metal–metal bond; this idealized geometry has C_{3v}-3m symmetry. The structure of $Fe_3(CO)_{12}$ can be formally obtained from that of $Co_4(CO)_{12}$ by the removal of any one of the three basal metal atoms from the tetrahedral metal framework of cobalt atoms. This structural transformation and its consequence concerning the stereochemical disposition of carbonyl ligands is made apparent from an examination of Figure 6. In both complexes the icosahedral-like arrays of 12 carbonyl groups are similarly numbered for the purpose of comparison. With the extraction of the basal metal atom Co_4 from $Co_4(CO)_{12}$, the relative orientation of the other three metal atoms is seen to remain approximately the same but the almost regular icosahedral polyhedron in $Co_4(CO)_{12}$ is observed to become somewhat flattened in $Fe_3(CO)_{12}$ in the direction normal to the triiron plane in order that the 12 carbonyl groups conform in $Fe_3(CO)_{12}$ as well as in $Co_4(CO)_{12}$ to normal metal–carbonyl bonding distances. Figure 6 shows this deformation of the icosahedron in $Fe_3(CO)_{12}$ to primarily involve the two terminal carbonyl groups 2 and 8 and the two bridging carbonyl groups 5 and 11 attached to the Co_4 atom in $Co_4(CO)_{12}$. In the formal conversion to the triiron dodecacarbonyl structure by the removal of the Co_4 atom, carbonyl 2 becomes terminally bonded to Fe_1, and carbonyl 8 becomes a bridging group linking Fe_2 and Fe_3, while carbonyls 5 and 11 become terminally coordinated to Fe_2 and Fe_3, respectively; by this operation the apical $Co(CO)_3$ group in $Co_4(CO)_{12}$ is transmuted into the unique *cis*-$Fe(CO)_4$ group in $Fe_3(CO)_{12}$. The considerable distortion of the carbonyl icosahedron from regularity for $Fe_3(CO)_{12}$ is shown by the variation of its 15 independent carbon–carbon edge distances, which range from 2.63 to 3.04 Å, and by the large range of 1.09–1.91 Å for the six independent altitudes of the pentagonal pyramids, each consisting of one apical and five basal carbon atoms.

Structural Dissimilarity of $Fe_3(CO)_{12}$ to $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ and Resulting Consequences. The molecular configuration of $Fe_3(CO)_{12}$ differs from that of the trimetal dodecacarbonyls of the congener elements ruthenium and osmium for which the molecular unit of D_{3h} symmetry consists of an equilateral triangular array of three $M(CO)_4$ fragments linked to one another by only metal–metal bonds.[29,73,74] This basic structural contradistinction (with and without bridging carbonyl groups) is manifested in the different mass spectrometric fragmentation patterns of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, and $Os_3(CO)_{12}$.

Mass spectrometric analyses of $Fe_3(CO)_{12}$[75–77] show not only all of the possible triiron carbonyl ions formed by stepwise loss of carbonyl groups but also a considerable relative abundance of $Fe_2(CO)_4^+$ and $Fe(CO)_n^+$ (n = 1–5) fragments. The presence in relatively large portion of the $Fe(CO)_5^+$ ion (with the reasonable assumption based on general observations of no migration of carbonyl groups from one iron atom to another during fragmentation) indicates that fission of the parent $Fe_3(CO)_{12}$ molecule by electron impact may occur through an unsymmetrical cleavage of the two bridging carbonyl groups such as to leave both bridging carbonyls coordinated to one iron atom.[75,77] In contrast, the mass spectrum of $Ru_3(CO)_{12}$ consists primarily of $Ru_3(CO)_n^+$ (n = 0–12) fragments including the occurrence of the bare Ru_3^+ cluster ion as the most abundant species; in accord with the absence of bridging carbonyl groups in the $Ru_3(CO)_{12}$ structure no $Ru(CO)_5^+$ ion is found, and the relative amounts of the $Ru(CO)_n^+$ ions (n = 1–4) are small.[75–77] With $Os_3(CO)_{12}$ only trinuclear osmium ions were observed in the mass spectrum.[77] These results support the view that the metal–metal bonds in $Fe_3(CO)_{12}$ are much weaker relative to the metal–carbonyl bonds than those in $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$. The appearance of the doubly charged ions $[Os_3(CO)_n]^{2+}$ (n = 0–12) and Ru_3^{2+} was interpreted[77] in terms of the greater stability of heavy metal cluster systems toward increased oxidation.

The considerable dissimilarity in metal–metal bond strength between $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$ is also

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[73] E. R. Corey and L. F. Dahl, *J. Am. Chem. Soc.*, **83**, 2203 (1961); E. R. Corey, E. Rodulfo de Gil, and L. F. Dahl, submitted for publication.

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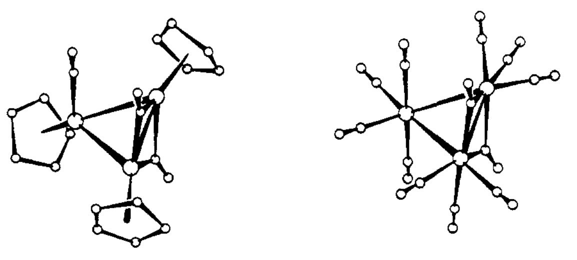
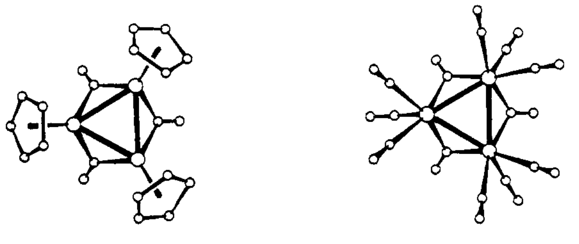
[77] J. Lewis and B. F. G. Johnson, *Accounts Chem. Res.*, **1**, 245 (1968).



(a) $Rh_3(C_5H_5)_3(CO)_3$ (ISOMER II, SOLID STATE)

(b) $Fe_3(CO)_{12}$ (SOLID STATE)



(c) $Rh_3(C_5H_5)_3(CO)_3$ (ISOMER I, SOLID STATE)

(d) $Fe_3(CO)_{12}$ (PROPOSED STRUCTURE, SOLUTION)

Figure 7. Comparison of the configuration of isomer II of $Rh_3(C_5H_5)_3(CO)_3$ (a) with that of solid-state $Fe_3(CO)_{12}$ (b); the structure of isomer I of $Rh_3(C_5H_5)_3(CO)_3$ (c) is similarly related to our proposed structure of $Fe_3(CO)_{12}$ (d) in solution.

reflected in their markedly different chemical behavior. In many reactions of the ruthenium carbonyl the triruthenium cluster system is retained, whereas the triiron cluster system in analogous $Fe_3(CO)_{12}$ reactions is preserved only in a few cases under relatively mild conditions.[78]

Proposed Structure of $Fe_3(CO)_{12}$ in Solution and Stereochemical Relationship with Two Geometrical Isomers of $Rh_3(C_5H_5)_3(CO)_3$. To provide an explanation for the heretofore puzzling infrared solution spectra of $Fe_3(CO)_{12}$ with the resolution of only two observed terminal carbonyl stretching frequencies (far short of the nine predicted ir-active terminal carbonyl stretching modes based on the solid-state structure with C_{2v} symmetry), it has been widely presumed that the molecular structure in solution probably differs from that in the solid state. Precedence for the existence of tautomeric forms for polynuclear metal carbonyl complexes in solution already has been convincingly established for $Co_2(CO)_8$[79,80] and $[M(C_5H_5)(CO)_2]_2$ (M = Fe, Ru, Os)[81] and suggested for $Co_4(CO)_{12}$.[82] From the invariance of the relative intensities of the carbonyl bands in an infrared solution spectrum of $Fe_3(CO)_{12}$ over a temperature range of 15–60°, Angelici and Siefert[83] concluded that only one isomer is present in solution. The only proposed model to date for $Fe_3(CO)_{12}$ in solution is the linear D_{3d} 3-3-3-3 one favored by Dobson and Sheline[35] from their infrared evidence.

We wish to speculate that an intramolecular rearrangement of $Fe_3(CO)_{12}$ does indeed occur on dissolution and to present evidence that the instantaneous structure of the molecule in solution is of the configuration shown in Figure 7d. Its idealized configuration of C_{3v}-3m symmetry consists of three identical $Fe(CO)_3$ groups located at the vertices of an equilateral triangle and connected in pairs to one another by both a bridging carbonyl group and an Fe–Fe bond.

Both the established solid-state and proposed solution structures of $Fe_3(CO)_{12}$ have stereochemically existing cyclopentadienyl metal counterparts in being closely related to the X-ray analyzed molecular configurations of the two solid-state isomeric forms of the electronically equivalent complex $Rh_3(C_5H_5)_3(CO)_3$.[84,85] Figure 7 illustrates the essential invariance of the over-all molecular geometries on formal replacement of the three carbonyl groups by the cyclopentadienyl ring which occupies three coordination sites.[86] Isomer II[84] of $Rh_3(C_5H_5)_3(CO)_3$ (Figure 7a) is seen to structurally conform to $Fe_3(CO)_{12}$ in solid state (Figure 7b), while isomer I[85] of $Rh_3(C_5H_5)_3(CO)_3$ (Figure 7c) of approximate C_{3v} symmetry corresponds to the proposed structure of $Fe_3(CO)_{12}$ in solution. Of significance is the fact that a similar high C_{3v} symmetry for the proposed $Fe_3(CO)_{12}$ geometry in solution would greatly reduce the number of expected ir-active terminal carbonyl bands such that the observed solution infrared spectrum would not be inconsistent with the proposed solution model.

This model for $Fe_3(CO)_{12}$ can be further utilized to rationalize the observed infrared spectrum of $Fe_3(CO)_{11}P(C_6H_5)_3$ and the presence of two geometrical isomers in the crystal; both solid-state molecular isomers would be readily interconverted in solution *via* the presumably common phosphine-substituted bridging structure.

The recently prepared isoelectronic $MnFe_2(CO)_{12}^-$ anion, whose proposed structure is analogous to that of $Fe_3(CO)_{12}$ by formal substitution of an anionic *cis*-$Mn(CO)_4^-$ fragment in place of the neutral *cis*-$Fe(CO)_4$ one, was shown by Anders and Graham[88] to have an infrared solution spectrum (containing six distinguishable carbonyl terminal bands) which resembles that of the $HFe_3(CO)_{11}^-$ anion but not that of $Fe_3(CO)_{12}$ in the terminal carbonyl stretching region. These results together with the expected display of two bridging carbonyl bands for the $MnFe_2(CO)_{12}^-$ anion and a single bridging one for the $HFe_3(CO)_{11}^-$ anion indicate that their related solid-state molecular configurations remain unaltered in solution.

The equivalence of all three iron atoms in the proposed solution structure of $Fe_3(CO)_{12}$ immediately suggests the

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(78) For a recent comprehensive review of the physical and chemical properties of $Ru_3(CO)_{12}$ together with a comparison of its chemistry with that of $Fe_3(CO)_{12}$, see M. I. Bruce and F. G. A. Stone, *Angew. Chem. Intern. Ed. Engl.*, **7**, 427 (1968).

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(80) K. Noack, *ibid.*, **19**, 1925 (1963); *Helv. Chim. Acta*, **47**, 1064, 1555 (1964).

(81) See (a) F. A. Cotton and G. Yagupsky, *Inorg. Chem.*, **6**, 15 (1967); (b) R. D. Fischer, A. Vogler, and K. Noack, *J. Organometal. Chem.*, **7**, 135 (1967), and references contained therein.

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(85) O. S. Mills and E. F. Paulus, *ibid.*, **10**, 331 (1967).

(86) The electronically equivalent complexes $[Fe(CO)_3X]_2$ (X = C_2H_5S) and $[Co(C_5H_5)X]_2$ (X = $(C_6H_5)_2P$) represent another prime example that the basic molecular geometry can remain essentially unaltered by the substitution of $Fe(CO)_3$ groups with $M(C_5H_5)$ groups (where M represents the congener elements Co, Rh, and Ir).[87]

(87) J. M. Coleman and L. F. Dahl, *J. Am. Chem. Soc.*, **89**, 542 (1967).

(88) U. Anders and W. A. G. Graham, *Chem. Commun.*, 291 (1966).

possible characterization by Mössbauer measurements in frozen solutions (provided of course that it does not rearrange to the solid-state molecular structure). Unfortunately, reported attempts[89] to obtain the Mössbauer spectrum in frozen solutions have so far been unsuccessful because of the low solubility of the compound in inert solvents.

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One of us (L. F. D.) wishes to acknowledge the late Professor Robert E. Rundle for his invaluable lessons as a teacher and researcher and his stimulation and encouragement in the preliminary stage of this particular work.

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Electron Delocalization in Paramagnetic Metallocences. I. Nuclear Magnetic Resonance Contact Shifts[1,2]

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Abstract: The 1,1′-dimethylcyclopentadienyls of V, Cr, Co, and Ni were prepared, and the nmr contact shifts were determined at 60 MHz in toluene. Analysis of electron relaxation times and nmr line widths suggests that the dominant nuclear relaxation mechanism is dipolar. The temperature dependencies of the contact shifts were examined, and it was shown that the Curie law is obeyed in each case. It was shown that the pseudocontact (dipolar) shift should be negligible in all cases except perhaps at the methyl group in 1,1′-dimethylchromocene. Comparison of the methyl contact shifts and the ring contact shifts leads to the conclusion that the unpaired electron density in vanadium and chromium metallocenes is not in ring π orbitals (out of plane) as previously supposed. Instead the magnitudes and signs of the chromium and vanadium shifts strongly suggest that the unpaired spins are delocalized in σ (in-plane) cyclopentadienyl orbitals. Delocalization in π-type orbitals is found to predominate in cobalt and nickel metallocenes.

It is now widely recognized that the study of nuclear resonance in paramagnetic complexes can yield detailed information concerning metal–ligand bonding and electron delocalization. This appeared to be an excellent technique to apply to a study of the electronic structure of the metallocenes, an area that has been the subject of much controversy over the years. In this paper we discuss the proton nmr contact shifts for the unsubstituted and 1,1′-dimethyl-substituted metallocenes of the first transition series. We consider first the experimental results and then propose a unified electron delocalization scheme.

McConnell and Holm first observed proton resonance for paramagnetic, solid nickelocene.[3] Later, the same workers reported nuclear resonance shifts for solid manganocene, cobaltocene, vanadocene, and chromocene.[4] Fritz, Keller, and Schwarzhans[5,6] reported nmr data for all the paramagnetic unsubstituted metallocenes in solution. These workers have also observed nmr for substituted ferricenium cations.[7]

The extremely large nmr shift observed for solid nickelocene by McConnell and Holm[3] was the first example of what are now generally known as nmr contact shifts. Such shifts are observed only in paramagnetic molecules, and arise by virtue of the Fermi contact unpaired electron spin–nuclear spin hyperfine coupling, according to eq 1,[8] where A is the hyperfine

$$A = \frac{8\pi}{6S} g_e\beta_e g_N\beta_N |\psi(0)|^2 \qquad (1)$$

coupling constant, in ergs. g_e and g_N are electron and nuclear g values, respectively; β_e and β_N are Bohr and nuclear magnetons, respectively; and $\psi(0)$ is the molecular wave function evaluated at the nuclear position.

The contact shifts of the metallocenes pose an interesting problem, in that the vanadocene and chromocene proton shifts are negative, while those of manganocene, cobaltocene, and nickelocene are positive. And in fact, all of these shifts are quite large. In 1960, Levy

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(1) Abstracted from the Ph.D. Thesis of M. F. Rettig, University of Illinois, 1967; NSF Predoctoral Fellow, 1963–1967.

(2) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Paper M-42.

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