Structural Characterization of the Cyclopentadienyliron Carbonyl Tetramer, $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$. A Cubane-Type Structure Containing a Completely Bonding Tetrametal Cluster Unit

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Abstract: A structural characterization by X-ray diffraction methods of the King complex, $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$, has ascertained its molecular geometry as a prototype structure of the particular class of molecules containing the cubane-like M_4X_4 architecture for which X is a symmetrically coordinated, triply bridging carbonyl group. The four iron atoms are positioned at the vertices of a bonded tetrahedron of average length 2.520 Å which is interlocked with a nonbonded tetrahedron of carbonyl carbon atoms of average length 3.046 Å such that the two interpenetrating tetrahedra form a distorted cube with 12 Fe–C edges of average length 1.986 Å. Each symmetrically bonded *pentahapto*cyclopentadienyl ring is oriented such that (on the basis of assumed cylindrical symmetry for each ring) the entire molecule approximately conforms to $T_d\text{-}\bar{4}3m$ geometry. Its principal structural features are compared to those of other related metal cluster carbonyl systems. The molecular parameters of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ are based on an anisotropic least-squares refinement of absorption-corrected data collected *via* a diffractometer with Mo Kα radiation. The final unweighted R_1 and weighted R_2 values of 3.5 and 3.8%, respectively, are for 2266 independent diffraction maxima (for which $I > 2\sigma(I)$). Cyclopentadienyliron carbonyl tetramer crystallizes in an orthorhombic unit cell of centrosymmetric symmetry *Pbca* with $a = 9.580$ (2), $b = 15.118$ (2), $c = 28.635$ (5) Å; $d_{\text{calcd}} = 1.91$ g cm^{-3} for $Z = 8$ *vs.* $d_{\text{obsd}} = 1.86$ g cm^{-3}.

The preparation by King[1] of the first tetranuclear cyclopentadienylmetal complex, $Fe_4(h\text{-}C_5H_5)_4(CO)_4$, aroused considerable interest with regard to its structure and nature of bonding. This air-stable compound was isolated from the refluxing of a solution of $[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$ in xylene under nitrogen. Its existence as a tetramer was demonstrated from molecular weight osmometric measurements in benzene solution and from a mass spectrum which showed the parent iron peak. Its diamagnetic character was established from proton nmr spectra which exhibited only one single sharp resonance, indicative (within the nmr time scale) of an equivalent environment for all four cyclopentadienyl rings. From the presence of one single strong absorption band in the infrared spectrum (KBr pellet) at a very low frequency of 1620 cm^{-1}, King[1] concluded that each carbonyl group was coordinated to three iron atoms. On the basis of these observations, he proposed a molecular model having the four iron atoms in a tetrahedral arrangement with bridging carbonyls situated above the four tetrahedral faces and with one $\pi\text{-}C_5H_5$ ligand bonded to each of the four equivalent iron atoms.

Both the uniqueness and high symmetry of this proposed model made this compound an obvious candidate for an X-ray diffraction study. A structural determination of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$, performed with three-dimensional film data by one of us[2] in 1965–1966, ascertained the overall molecular geometry suggested by King[1] and revealed the six chemically equivalent Fe–Fe distances to correspond to electron-pair bonds (in a localized valence-bond representation), but the relatively large esd's due mainly to the paucity of film data (as reflected in the small data-to-parameter ratio) precluded any detailed analysis involving the molecular parameters of the carbonyl and cyclopentadienyl ligands. The stereochemical importance of this closed metal carbonyl cluster as a prototype structure of cubic $T_d\text{-}\bar{4}3m$ symmetry (based on the assumed cylindrical nature of the cyclopentadienyl rings) was magnified in a recent focusing on the bonding consequences caused by the addition or removal of valence electrons from this kind of metal cluster system.[3,4] Of particular interest to us was the stereochemical relationship between this neutral molecule and the oxidized monocation whose structure was just determined.[5] The availability of a diffractometer has now made it possible for substantially more X-ray data of much higher quality to be re-collected. Hence, the detailed molecular parameters of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ presented here are based on least-squares anisotropic refinement of the initially determined[2] (but unreported) structure utilizing diffractometer data. Because these results represent a high degree of precision, they offer the opportunity to compare the structural features of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ with those of other related complexes.

Experimental Section

Single-Crystal X-Ray Data. Dark green crystals of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ utilized for the structural determination were generously supplied by Dr. R. B. King of Mellon Institute (now at the Chemistry Department, University of Georgia). Crystals used in the subsequent collection of diffractometer data were synthesized by King's procedure[1] and were recrystallized from a dichloromethane–toluene solution.

Preliminary oscillation and Weissenberg photographs showed $D_{2h}\text{-}2/m2/m2/m$ Laue symmetry characteristic of the orthorhombic system. Intensity data totaling 782 independent reflections were

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(1) R. B. King, *Inorg. Chem.*, **5**, 2227 (1966).

(2) M. A. Neuman, Ph.D. Thesis, University of Wisconsin (Madison), 1966.

(3) A. S. Foust and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7337 (1970).

(4) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, Abstracts of Papers, 161st National Meeting of the American Chemical Society, Los Angeles, Calif., March 28–April 2, 1971, INOR 130; submitted for publication.

(5) Trinh-Toan, W. P. Fehlhammer, and L. F. Dahl, *J. Amer. Chem. Soc.*, **94**, 3389 (1972).

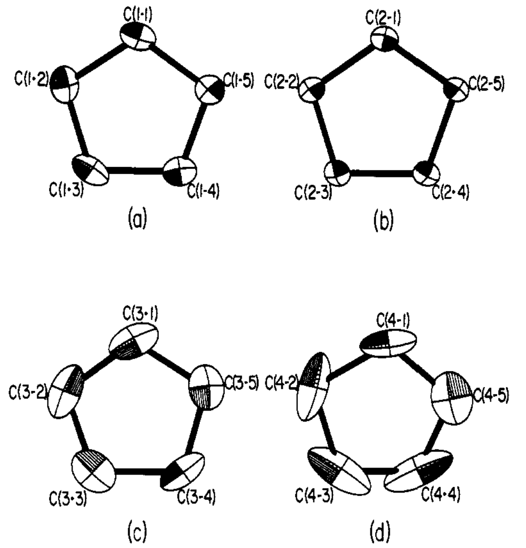

Figure 1. View perpendicular to the mean plane of each of the four crystallographically independent C_5H_5 rings depicting the 20% probability thermal ellipsoids for the carbon atoms. (a), (b), (c), and (d) correspond to rings 1, 2, 3, and 4, respectively. The elongated thermal ellipsoids of rings 3 and 4 relative to those of the other two C_5H_5 rings have been attributed to high librational ring motion coupled with possible crystal disordering involving the superposition of two or more orientations in the crystalline state.

initially collected with Mo Kα radiation on a small cylindrically shaped crystal of 0.1-mm diameter and 0.3-mm length from multiple-film packets of equiinclination Weissenberg photographs for reciprocal levels $0kl$–$7kl$ and from time-exposed sets of precession photographs for the $h0l$ and $h1l$ levels. No absorption corrections were made, since the estimated variation in maximum intensities on a given reciprocal layer due to absorption was estimated to be less than 10%.

Diffractometer intensity data were collected with Mo Kα radiation on a crystal of dimensions 0.22 × 0.26 × 0.32 mm aligned such that the a axis was collinear with the ϕ axis of the diffractometer. The procedures of crystal line-up, collection, and treatment of data are described elsewhere.[5,6] Intensity data for three symmetry equivalent octants (*viz.*, hkl, $hk\bar{l}$, and $h\bar{k}\bar{l}$) were measured *via* the θ–2θ scan technique for $2\theta \leq 48°$, with scan ranges of 1.4° for $2\theta \leq 8°$ and of 1.3° for $2\theta > 8°$. Since transmission coefficients (calculated from the size and shape of the crystal on the basis of a value of 28.4 cm^{-1} for the linear absorption coefficient) ranged from 0.49 to 0.56, absorption corrections of the diffractometer data were made.[7] The data from the three octants of reciprocal lattice were then merged[8] into a single set of 3239 independent reflections (corresponding to one octant); 2266 diffraction maxima with $I > 2\sigma(I)$ were utilized in the structural refinement. No extinction corrections were made.

Unit Cell and Space Group. Least-squares refinement[9] of the diffractometer settings for selected reflections produced lattice lengths (with uncertainties of precision given in parentheses)[10] of a = 9.580 (2), b = 15.118 (2), c = 28.635 (5) Å for the orthorhombic crystal of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$. The calculated density for eight molecules of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ (mol wt 595.8) per cell is 1.91 g cm^{-3} which agrees well with the experimental density of 1.86 g cm^{-3} measured by the flotation method. The total number of electrons per unit cell, $F(000)$, is 2400. Observed systematic absences of $\{0kl\}$ for k odd, $\{h0l\}$ for l odd, and $\{hk0\}$ for h odd uniquely indicate the centrosymmetric space group *Pbca*, which was subsequently verified by the structural refinement. All atoms were shown to be in general eightfold positions of set 8c: $\pm(x, y, z;\ {}^1/_2 + x, {}^1/_2 - y, \bar{z};\ \bar{x}, {}^1/_2 + y, {}^1/_2 - z;\ {}^1/_2 - x, \bar{y}, {}^1/_2 + z)$.[11]

Solution of the Structure

The solution of the structure required the location of one molecular unit of 32 nonhydrogen atoms consisting of 4 irons, 4 oxygens, and 24 carbons. In the initial determination of the structure, the correct location of the four independent iron atoms required a detailed analysis of the computed three-dimensional Patterson map[12] (which provided no clearcut assignment of the four iron positions) coupled with packing considerations of King's proposed spherical-like molecules in a unit cell of *Pbca* symmetry. After failure of several trial models, a correct set of initial coordinates for the four iron atoms was finally obtained as indicated from structure factor calculations by the low R_1 value of 26%. Successive Fourier syntheses were utilized to locate the 28 independent oxygen and carbon atoms. Several cycles of least-squares refinement[13,14] of all nonhydrogen atoms were then performed to obtain input parameters for a rigid-body least-squares refinement. In this latter refinement,[15] each cyclopentadienyl ring was constrained to be a regular pentagon of length 1.42 Å, and individual isotropic thermal parameters were utilized for all atoms. After four cycles, reliability factors of R_1 = 10.2 and R_2 = 9.6% were obtained.[16] Subsequently, the rigid-body constraints were removed and a normal isotropic least-squares refinement was allowed. The R_1 value remained constant at 10.2%, while R_2 dropped to 9.1%. When the diffractometer data became available, further refinement of the structure was undertaken. Before each full-matrix least-squares cycle, the idealized positions of the ring hydrogen atoms were calculated[17] and then included in the structure factor calculations as fixed-atom contributions. All nonhydrogen atoms were refined with anisotropic thermal coefficients. The final reliability values were R_1 = 3.5 and R_2 = 3.8%. During the last cycle, no positional parameters changed by more than 0.2σ and no temperature parameters shifted by more than 0.3σ except for cyclopentadienyl ring 4, where some thermal parameters still oscillated with shifts as

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(6) *Cf.* V. A. Uchtman and L. F. Dahl, *ibid.*, 91, 3756 (1969).

(7) J. F. Blount, DEAR, based on a method of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, 10, 180 (1957).

(8) J. C. Calabrese, SORTMERGE, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1971.

(9) A. S. Foust, ANGSET, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1970.

(10) The uncertainties of the lattice lengths determined from least-squares refinement are unrealistically small estimates of precision resulting from the large number of data utilized in the refinement.

(11) "International Tables for X-Ray Crystallography," Vol. I, Kynoch Press, Birmingham, England, 1965, p 150.

(12) All Patterson and Fourier maps were computed with the Blount program (J. Blount, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1965).

(13) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1962.

(14) All least-squares refinements were based on the minimization of $\Sigma w_i \Delta F_i^2$, where $w_i = 1/\sigma_i^2(F_o)$. For the photographic data, weights were assigned by means of the functions defined as follows: if $I_o < \sqrt{10} I_{min}$, $\sigma_i(F_o) = F_o/20[\sqrt{10} I_{min}/I_o]^2$; if $I_o \geq \sqrt{10} I_{min}$, $\sigma_i(F_o) = F_o/20$. For the diffractometer data, the weighting scheme utilized is given elsewhere.[6] An empirical value of 0.0016 was employed for the so-called "ignorance" factor, E. Scattering factors for Fe, O, and C are those of H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964), while scattering factors of H are those of R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965). Real and imaginary anomalous dispersion corrections of $\Delta f' = 0.4$ and $\Delta f'' = 1.0$ (Mo Kα radiation) were made for the scattering factors of Fe (D. H. Templeton in ref 11, Vol. III, 1962, p 215).

(15) DBCGHW, a Fortran crystallographic least-squares rigid-body program, University of Wisconsin (Madison), 1965.

(16) The unweighted R_1 and weighted R_2 coefficients are defined as follows: $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]100$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2}100$.

(17) J. C. Calabrese, MIRAGE, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1971.

Table I. Positional and Thermal Parameters of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$[a,b]

Atom	x	y	z	B_{11} ($\times 10^4$) or B, Å^2	B_{22} ($\times 10^4$)	B_{33} ($\times 10^4$)	B_{12} ($\times 10^4$)	B_{13} ($\times 10^4$)	B_{23} ($\times 10^4$)
Fe(1)	0.20665 (8)	0.13124 (5)	0.12096 (3)	53.0 (9)	21.4 (3)	6.8 (1)	1.6 (5)	2.1 (3)	0.2 (2)
Fe(2)	0.02753 (8)	0.20697 (5)	0.17210 (3)	49.0 (8)	20.2 (3)	5.3 (1)	0.3 (5)	−0.1 (2)	−0.2 (1)
Fe(3)	−0.01482 (9)	0.05137 (5)	0.14338 (3)	66.4 (10)	20.5 (4)	8.9 (1)	−6.7 (5)	1.4 (3)	−1.1 (2)
Fe(4)	−0.02434 (9)	0.17973 (6)	0.08753 (3)	81.3 (10)	29.8 (4)	5.9 (1)	10.1 (6)	−5.8 (3)	−0.8 (2)
O(1)	−0.2641 (4)	0.1620 (3)	0.1519 (2)	52 (5)	53 (3)	16 (1)	2 (3)	1 (2)	−7 (1)
O(2)	0.0917 (5)	0.0137 (3)	0.0492 (2)	127 (7)	41 (2)	10 (1)	12 (3)	−2 (2)	−8 (1)
O(3)	0.1782 (5)	0.3225 (3)	0.1723 (1)	114 (6)	20 (2)	12 (1)	−6 (3)	10 (2)	3 (1)
O(4)	0.1930 (5)	0.0684 (3)	0.2181 (1)	124 (6)	41 (2)	8 (1)	14 (3)	−8 (2)	6 (1)
C(1)	−0.1420 (7)	0.1544 (4)	0.1432 (2)	73 (7)	32 (3)	11 (1)	−12 (4)	−9 (2)	−4 (1)
C(2)	0.0746 (6)	0.0649 (4)	0.0809 (2)	71 (7)	37 (3)	8 (1)	4 (4)	−2 (2)	0 (1)
C(3)	0.1271 (6)	0.2516 (4)	0.1168 (2)	77 (7)	21 (2)	8 (1)	10 (4)	0 (2)	0 (1)
C(4)	0.1365 (6)	0.0972 (4)	0.1840 (2)	69 (7)	24 (3)	8 (1)	2 (4)	−2 (2)	1 (1)
C(1-1)	0.3844 (7)	0.1871 (5)	0.0883 (3)	62 (8)	42 (4)	17 (1)	−1 (4)	17 (3)	3 (2)
C(1-2)	0.3565 (8)	0.1051 (5)	0.0681 (3)	93 (9)	66 (5)	13 (1)	3 (5)	16 (3)	−8 (2)
C(1-3)	0.3667 (7)	0.0402 (5)	0.1043 (3)	75 (8)	33 (4)	24 (2)	9 (5)	17 (3)	−4 (2)
C(1-4)	0.4030 (7)	0.0849 (5)	0.1459 (3)	58 (7)	52 (4)	16 (1)	21 (4)	5 (3)	4 (2)
C(1-5)	0.4128 (6)	0.1749 (5)	0.1365 (3)	55 (7)	44 (4)	15 (1)	3 (4)	1 (2)	−1 (2)
C(2-1)	0.1184 (7)	0.3050 (4)	0.2154 (2)	88 (8)	33 (3)	9 (1)	−3 (4)	−1 (2)	−6 (1)
C(2-2)	0.0038 (7)	0.3418 (4)	0.1909 (2)	98 (8)	23 (2)	9 (1)	12 (4)	5 (2)	−5 (1)
C(2-3)	−0.1179 (6)	0.2957 (4)	0.2131 (2)	82 (8)	34 (3)	8 (1)	13 (4)	5 (2)	−3 (1)
C(2-4)	−0.0794 (6)	0.2289 (4)	0.2354 (2)	73 (7)	38 (3)	7 (1)	7 (4)	4 (2)	−4 (1)
C(2-5)	0.0674 (6)	0.2364 (4)	0.2440 (2)	81 (7)	34 (3)	5 (1)	3 (4)	−1 (2)	−4 (1)
C(3-1)	−0.0924 (15)	−0.0686 (7)	0.1170 (4)	275 (20)	49 (5)	23 (2)	−69 (9)	26 (5)	−14 (2)
C(3-2)	0.0174 (12)	−0.0862 (5)	0.1444 (5)	191 (16)	22 (3)	42 (3)	−5 (6)	41 (6)	4 (3)
C(3-3)	−0.0141 (13)	−0.0585 (6)	0.1883 (4)	236 (18)	40 (4)	26 (2)	−43 (8)	−12 (5)	21 (2)
C(3-4)	−0.1475 (12)	−0.0191 (5)	0.1883 (4)	241 (18)	30 (4)	22 (2)	−49 (7)	45 (5)	−6 (2)
C(3-5)	−0.1957 (9)	−0.0287 (6)	0.1423 (4)	125 (11)	43 (4)	32 (2)	−40 (6)	−3 (4)	3 (3)
C(4-1)	−0.1176 (21)	0.2897 (8)	0.0567 (4)	316 (26)	70 (7)	13 (14)	104 (12)	−33 (4)	−6 (2)
C(4-2)	−0.2125 (10)	0.2211 (19)	0.0574 (5)	74 (11)	238 (19)	23 (2)	28 (12)	−11 (4)	47 (6)
C(4-3)	−0.1472 (27)	0.1553 (8)	0.0295 (7)	478 (38)	71 (7)	32 (3)	−39 (15)	−113 (9)	9 (4)
C(4-4)	−0.0324 (24)	0.1862 (17)	0.0158 (3)	489 (40)	164 (19)	5 (1)	194 (23)	−10 (6)	1 (4)
C(4-5)	−0.0080 (18)	0.2647 (12)	0.0304 (6)	236 (29)	106 (9)	20 (2)	−4 (14)	−25 (7)	33 (4)
H(1-1)	0.3841	0.2499	0.0696	6.0[c]	H(3-1)	−0.0978	−0.0842	0.0799	8.0
H(1-2)	0.3310	0.0931	0.0315	6.0	H(3-2)	0.1143	−0.1180	0.1336	8.0
H(1-3)	0.3504	−0.0308	0.1004	6.0	H(3-3)	0.0542	−0.0645	0.2186	8.0
H(1-4)	0.4198	0.0542	0.1799	6.0	H(3-4)	−0.2027	0.0110	0.2176	8.0
H(1-5)	0.4382	0.2262	0.1619	6.0	H(3-5)	−0.2971	−0.0068	0.1296	8.0
H(2-1)	0.2269	0.3262	0.2133	6.0	H(4-1)	−0.1409	0.3501	0.0759	8.0
H(2-2)	0.0087	0.3969	0.1663	6.0	H(4-2)	−0.3147	0.2095	0.0736	8.0
H(2-3)	−0.2227	0.3084	0.1898	6.0	H(4-3)	−0.1758	0.0892	0.0179	8.0
H(2-4)	−0.1500	0.1812	0.2514	6.0	H(4-4)	0.0495	0.1572	−0.0063	8.0
H(2-5)	0.1296	0.1958	0.2677	6.0	H(4-5)	0.0797	0.3102	0.0257	8.0

[a] Estimated standard deviations of the last significant digits are given in parentheses. [b] Anisotropic temperature factors of the form exp$\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl]\}$ were used for all nonhydrogen atoms. [c] Positional and isotropic thermal parameters of ring hydrogen atoms were not varied in the course of refinement. New positions for the hydrogen atoms were calculated after each cycle.[17]

large as 2.5σ. The elongated shapes of the thermal ellipsoids for the carbon atoms of rings 3 and 4 compared to those for the other two rings (Figure 1) indicate a high librational motion together with possible crystal disordering involving the superposition of different orientations for each ring. This latter phenomenon has been observed for several C_5H_5 rings in the cubane-like monocations of the salts $[Fe_4(h^5\text{-}C_5H_5)_4S_4]Br$[4] and $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$.[5] In the case of the $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ salt, the two crystal-disordered C_5H_5 rings were refined both by a completely ordered model with anisotropic thermal parameters and by a D_{5h}-idealized rigid-body model with isotropic thermal parameters involving two orientations for each disordered ring. Although the R_1 index was expectedly lower by 1.8% for the anisotropic ordered model, it was found that both models yielded equivalent values within 2.0 esd's for the corresponding atomic coordinates and calculated bond lengths and angles for the central $Fe_4(CO)_4$ fragment. Hence, the anisotropic model was deemed to be adequate for the representation of the electron density of C_5H_5 rings 3 and 4 in $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$. A final difference Fourier synthesis verified the structural analysis in that it showed no peaks either greater or less than 0.5 e/Å^3.

The positional and thermal parameters obtained from the output of the last cycle of least-squares refinement are presented in Table I.[18] Interatomic distances and bond angles along with esd's, calculated from the full inverse matrix (containing the uncertainties in lattice dimensions), are listed in Tables II and III. Equations of the mean planes for the C_5H_5 rings, together with perpendicular distances of atoms from these planes and angles between the normals to these planes,[19] are given in Table IV.

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(18) Observed and calculated structure factors for $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-3383. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(19) D. L. Smith, Ph.D. Thesis (Appendix IV), University of Wisconsin (Madison), 1962.

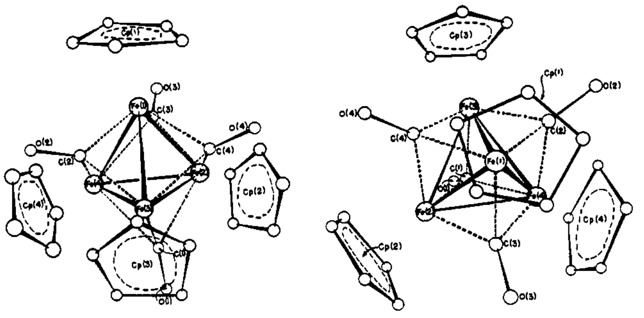

Figure 2. Two views of the $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule whose configuration closely conforms to cubic $T_d\text{-}\bar{4}3m$ symmetry. The left view emphasizes the tetrahedral architecture of the bonding iron atoms, while the right view, which is approximately along an idealized threefold molecular axis in the [100] crystal direction, emphasizes the cubane-like geometry of the $Fe_4(CO)_4$ fragment.

Results and Discussion

In the $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule (Figure 2) the four iron atoms are arranged at the corners of a bonded tetrahedron of average length 2.520 Å which is inter-

Table II. Interatomic Distances in $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$[a]

	Bonding Distances, Å		
Fe(1)–Fe(2)	2.530 (1)	Fe(1)–C(1-1)	2.119 (6)
Fe(1)–Fe(3)	2.524 (1)	Fe(1)–C(1-2)	2.122 (7)
Fe(1)–Fe(4)	2.519 (1)	Fe(1)–C(1-3)	2.115 (7)
Fe(2)–Fe(3)	2.525 (1)	Fe(1)–C(1-4)	2.130 (7)
Fe(2)–Fe(4)	2.506 (1)	Fe(1)–C(1-5)	2.130 (6)
Fe(3)–Fe(4)	2.516 (1)		
			2.123 (av)
	2.520 (av)	Fe(2)–C(2-1)	2.119 (6)
Fe(1)–C(2)	1.980 (6)	Fe(2)–C(2-2)	2.120 (6)
Fe(1)–C(3)	1.976 (6)	Fe(2)–C(2-3)	2.127 (6)
Fe(1)–C(4)	1.995 (6)	Fe(2)–C(2-4)	2.107 (6)
Fe(2)–C(1)	1.988 (6)	Fe(2)–C(2-5)	2.142 (5)
Fe(2)–C(3)	1.969 (6)		2.123 (av)
Fe(2)–C(4)	1.991 (6)	Fe(3)–C(3-1)	2.101 (8)
Fe(3)–C(1)	1.977 (7)	Fe(3)–C(3-2)	2.103 (8)
Fe(3)–C(2)	1.994 (6)	Fe(3)–C(3-3)	2.102 (7)
Fe(3)–C(4)	1.984 (6)	Fe(3)–C(3-4)	2.099 (7)
Fe(4)–C(1)	1.990 (7)	Fe(3)–C(3-5)	2.114 (8)
Fe(4)–C(2)	1.987 (6)		
Fe(4)–C(3)	1.996 (6)		2.104 (av)
		Fe(4)–C(4-1)	2.084 (8)
	1.986 (av)	Fe(4)–C(4-2)	2.094 (9)
C(1)–O(1)	1.201 (7)	Fe(4)–C(4-3)	2.070 (10)
C(2)–O(2)	1.204 (7)	Fe(4)–C(4-4)	2.059 (10)
C(3)–O(3)	1.209 (7)	Fe(4)–C(4-5)	2.087 (10)
C(4)–O(4)	1.197 (7)		
			2.079 (av)
	1.203 (av)	Fe(1)· · ·centroid(1)	1.753
C(1-1)–C(1-2)	1.39 (1)	Fe(2)· · ·centroid(2)	1.749
C(1-2)–C(1-3)	1.43 (1)	Fe(3)· · ·centroid(3)	1.748
C(1-3)–C(1-4)	1.41 (1)	Fe(4)· · ·centroid(4)	1.740
C(1-4)–C(1-5)	1.39 (1)	C(3-1)–C(3-2)	1.34 (2)
C(1-5)–C(1-1)	1.42 (1)	C(3-2)–C(3-3)	1.36 (1)
		C(3-3)–C(3-4)	1.41 (1)
	1.41 (av)	C(3-4)–C(3-5)	1.40 (1)
C(2-1)–(C2-2)	1.42 (1)	C(3-5)–C(3-1)	1.37 (1)
C(2-2)–C(2-3)	1.40 (1)		
C(2-3)–C(2-4)	1.42 (1)		1.38 (av)
C(2-4)–C(2-5)	1.43 (1)	C(4-1)–C(4-2)	1.38 (2)
C(2-5)–C(2-1)	1.41 (1)	C(4-2)–C(4-3)	1.42 (2)
		C(4-3)–C(4-4)	1.26 (2)
	1.42 (av)	C(4-4)–C(4-5)	1.28 (2)
		C(4-5)–C(4-1)	1.35 (2)
			1.34 (av)

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

Table III. Bond Angles (deg) in $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$[a]

Fe(2)–Fe(1)–Fe(3)	59.94 (2)	Fe(1)–C(2)–O(2)	132.5 (5)
Fe(2)–Fe(1)–Fe(4)	59.52 (3)	Fe(1)–C(3)–O(3)	132.3 (5)
Fe(3)–Fe(1)–Fe(4)	59.86 (2)	Fe(1)–C(4)–O(4)	132.8 (5)
Fe(1)–Fe(2)–Fe(3)	59.92 (3)	Fe(2)–C(1)–O(1)	132.1 (5)
Fe(1)–Fe(2)–Fe(4)	60.03 (3)	Fe(2)–C(3)–O(3)	132.9 (4)
Fe(3)–Fe(2)–Fe(4)	60.02 (3)	Fe(2)–C(4)–O(4)	132.8 (5)
Fe(1)–Fe(3)–Fe(2)	60.14 (3)	Fe(3)–C(1)–O(1)	132.4 (5)
Fe(1)–Fe(3)–Fe(4)	59.97 (3)	Fe(3)–C(2)–O(2)	132.0 (5)
Fe(2)–Fe(3)–Fe(4)	59.62 (3)	Fe(3)–C(4)–O(4)	133.0 (5)
Fe(1)–Fe(4)–Fe(2)	60.45 (3)	Fe(4)–C(1)–O(1)	134.4 (5)
Fe(1)–Fe(4)–Fe(3)	60.17 (3)	Fe(4)–C(2)–O(2)	134.3 (5)
Fe(2)–Fe(4)–Fe(3)	60.36 (3)	Fe(4)–C(3)–O(3)	133.0 (5)
	60.00 (av)		132.9 (av)
C(2)–Fe(1)–C(3)	100.7 (2)	Fe(2)–C(1)–Fe(3)	79.1 (2)
C(2)–Fe(1)–C(4)	100.3 (2)	Fe(2)–C(1)–Fe(4)	78.1 (2)
C(3)–Fe(1)–C(4)	99.4 (2)	Fe(3)–C(1)–Fe(4)	78.7 (3)
C(1)–Fe(2)–C(3)	101.4 (3)	Fe(1)–C(2)–Fe(3)	78.9 (2)
C(1)–Fe(2)–C(4)	99.6 (3)	Fe(1)–C(2)–Fe(4)	78.9 (2)
C(3)–Fe(2)–C(4)	99.8 (2)	Fe(3)–C(2)–Fe(4)	78.4 (2)
C(1)–Fe(3)–C(2)	100.5 (3)	Fe(1)–C(3)–Fe(2)	79.8 (2)
C(1)–Fe(3)–C(4)	100.2 (2)	Fe(1)–C(3)–Fe(4)	78.7 (2)
C(2)–Fe(3)–C(4)	100.2 (2)	Fe(2)–C(3)–Fe(4)	78.4 (2)
C(1)–Fe(4)–C(2)	100.3 (3)	Fe(1)–C(4)–Fe(2)	78.8 (2)
C(1)–Fe(4)–C(3)	100.4 (2)	Fe(1)–C(4)–Fe(3)	78.7 (2)
C(2)–Fe(4)–C(3)	99.7 (2)	Fe(2)–C(4)–Fe(3)	78.9 (2)
	100.2 (av)		78.8 (av)

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

Table IV. Equations of Planes Formed by Different Groups of Atoms, Distances of Atoms from These Planes, and Angles Between the Normals to These Planes[a]

(i) Equations of Best Planes and Distances (Å) of Ring Carbon Atoms from These Planes[b]

(A) Plane of Ring 1

$$0.971X - 0.115Y - 0.209Z - 2.723 = 0$$

C(1-1)	0.000	C(1-4)	0.006
C(1-2)	0.003	C(1-5)	−0.004
C(1-3)	−0.005		

(B) Plane of Ring 2

$$0.164X - 0.644Y - 0.747Z + 7.403 = 0$$

C(2-1)	0.011	C(3-1)	0.013
C(2-2)	−0.003	C(3-2)	−0.015
C(2-3)	−0.006		

(C) Plane of Ring 3

$$0.395X + 0.892Y - 0.219Z + 2.011 = 0$$

C(3-1)	0.002	C(3-4)	0.014
C(3-2)	0.008	C(3-5)	−0.010
C(3-3)	−0.014		

(D) Plane of Ring 4

$$-0.448X + 0.374Y - 0.812Z - 0.825 = 0$$

C(4-1)	−0.001	C(4-4)	0.000
C(4-2)	0.001	C(4-5)	0.001
C(4-3)	−0.001		

(E) Plane Containing Fe(2), Fe(3), and Fe(4)

$$0.978X - 0.105Y - 0.182Z + 0.969 = 0$$

(F) Plane Containing Fe(1), Fe(3), and Fe(4)

$$0.125X - 0.628Y - 0.769Z + 3.660 = 0$$

(G) Plane Containing Fe(1), Fe(2), and Fe(4)

$$0.395X + 0.889Y - 0.232Z - 1.742 = 0$$

(H) Plane Containing Fe(1), Fe(2), and Fe(3)

$$-0.453X + 0.363Y - 0.814Z + 2.997 = 0$$

(ii) Angles (deg) between Normals to Planes

A and B	67.1	B and D	73.0
A and C	70.9	B and F	2.7
A and D	107.9	C and D	70.5
A and E	1.7	C and G	0.8
B and C	110.2	D and H	0.7

[a] Unit weights were used for all atoms in the application of the Smith least-squares planes program.[19] [b] Equations of the planes are given in the form $AX + BY + CZ + D = 0$, with X, Y, Z in ångström units along a, b, and c.

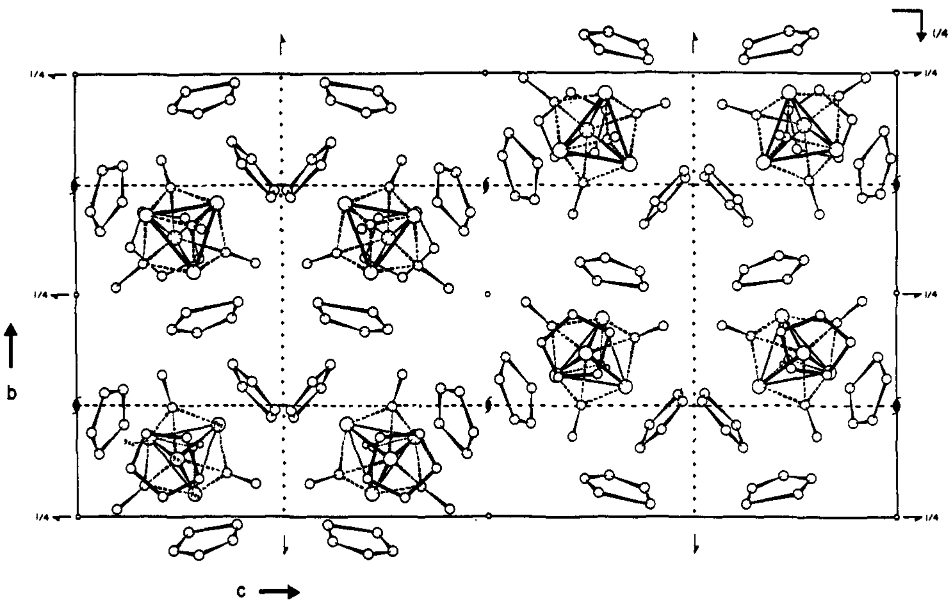

Figure 3. [100] projection of the orthorhombic unit cell of symmetry *Pbca* showing the orientations of the eight $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecules.

locked with a nonbonded tetrahedron of average length 3.046 Å formed by the carbonyl carbon atoms such that taken together the two interpenetrating tetrahedra constitute a distorted cube with 12 Fe–C edges. Each *pentahapto*cyclopentadienyl ring is symmetrically bonded to an iron atom such that within experimental error the normal which passes through the centroid of each cyclopentadienyl ring coincides with a pseudo-threefold axis of the $Fe_4(CO)_4$ fragment. With the assumption of cylindrical symmetry for each of the cyclopentadienyl rings, the tetrameric molecule possesses an idealized $T_d\text{-}\bar{4}3m$ geometry; the resulting site symmetry at each iron atom is $C_{3v}\text{-}3m$. The shortest nonbonding *intramolecular* distances among the ligands are expectedly found between the C_5H_5 rings and the carbonyl groups, but the closest CH···OC contacts of 2.4 Å do not provide any evidence of unusual *intramolecular* interactions between these ligands.

The packing of the unit cell viewed along the [100] direction is shown in Figure 3. Except for one close contact of 2.19 Å, the shortest *intermolecular* CH···HC distance between cyclopentadienyl rings of 2.4–2.5 Å is consistent with van der Waals H···H separation of 2.4 Å.

Four *intermolecular* CH···OC distances of 2.24, 2.27, 2.31, and 2.44 Å, which are considerably shorter than the normal van der Waals H···O separation of 2.6 Å, may possibly reflect weak hydrogen bonding between the cyclopentadienyl hydrogen atoms and the electronegative triply bridging carbonyl oxygen atoms. In this connection, it is worthy to point out that Shriver and coworkers[20] were able to synthesize the oxygen–aluminum adduct $Fe_4(h^5\text{-}C_5H_5)_4(COAl(C_2H_5)_3)_4$ by reaction of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ with aluminum triethyl as Lewis acid.

The geometry of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ can be primarily attributed to the stereochemical constraints imposed by the formation of the $Fe_4(CO)_4$ central core. In fact, $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ represents a prototype structure with respect to being the first member (and parent) of the particular class of cubane-like molecules containing the M_4X_4 architecture for which X is a triply bridging carbonyl ligand. Offspring of the neutral $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$ molecule (n = 0) are the well-known, structurally characterized monocation (n = 1+)[1,5] together with the dication (n = 2+) and monoanion (n = 1−) recently observed electrochemically by Ferguson and Meyer.[21]

These $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$ complexes (n = −1, 0, +1, +2) may also be classified as members of the small but rapidly expanding group of metal carbonyl cluster systems containing "face" bridging carbonyl ligands. Complexes of this kind which have been characterized by single-crystal X-ray diffraction investigations include the hexapyridineiron(II) salt of the $[Fe_4(CO)_{13}]^{2-}$ anion,[22] the isostructural $Co_6(CO)_{16}$[23] and $Rh_6(CO)_{16}$,[24] $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$,[25,26] $CoNi_2(h^5\text{-}C_5H_5)_3(CO)_2$,[26] $Co_3(h^5\text{-}C_5H_5)_3(CO)(O)$,[27] $Co_3(h^5\text{-}C_5H_5)_3(CO)(S)$,[28] $Rh_3(h^5\text{-}C_5H_5)_3(CO)(S)$,[28] the isostructural potassium hexahydrate salts of the $[Co_6(CO)_{14}]^{4-}$ and $[Rh_6(CO)_{14}]^{4-}$ anions,[29,30] the cesium salt of the $[Co_6(CO)_{15}]^{2-}$ anion,[31] the $(CH_3)_4N^+$ salt of the $[Rh_7(CO)_{16}]^{3-}$ anion,[30,32] and the $(CH_3)_4N^+$ salt of the $[Rh_{12}(CO)_{30}]^{2-}$ anion.[33]

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Whereas the triply bridging carbonyl groups coordinated to nonequivalent metal atoms (*e.g.*, as occurs in the cobalt and rhodium carbonyl anions) show varying degrees of asymmetry for the three metal–carbonyl bond lengths, the triply bridging carbonyl ligands bonded to three equivalent metal atoms in the neutral $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule (and in the other above molecules possessing localized threefold axes) show symmetrical Fe–CO bond lengths.

The six Fe–Fe bond lengths in the $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule range from 2.506 (1) to 2.530 (1) Å. The average Fe–Fe bond length of 2.520 Å is in good agreement with the average Fe–Fe bond length of 2.50 Å obtained[22] in the hexapyridineiron(II) salt of the $[Fe_4(CO)_{13}]^{2-}$ anion, the three basal iron atoms (of the completely bonding tetrahedron) of which are also linked by a symmetrical triply bridging carbonyl group. These iron–iron distances are well within the range of recorded electron-pair Fe–Fe bonds.[34]

The twelve triply bridging Fe–CO bond lengths vary from 1.969 (6) to 1.996 (6) Å. The average value of 1.986 Å compares favorably with the average value of 2.00 Å found[22] for the similar triply bridging carbonyl ligand in the $[Fe_4(CO)_{13}]^{2-}$ anion. In contrast, the Fe–CO distances for the nine terminal carbonyl ligands in the $[Fe_4(CO)_{13}]^{2-}$ anion range from 1.66 (3) to 1.81 (3) Å, with an average "normal" value of 1.72 Å.[22] This latter value (also representative of Fe–CO(terminal) distances in other iron carbonyl complexes) emphasizes that a significant Fe–CO bond lengthening of approximately 0.25–0.30 Å occurs when a terminal carbonyl ligand bonded to only one iron atom formally transmutes into a ligand symmetrically coordinated to three iron atoms. The 12 Fe–C–Fe bond angles in the $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule vary from 78.1 (2) to 79.8 (2)°. The average value of 78.8° is close to the average M–C–M angles found for the triply bridging carbonyl groups in other complexes—*viz.*, 77.9° in the $[Fe_4(CO)_{13}]^{2-}$ anion,[22] 79.5° in $Rh_6(CO)_{16}$,[24] 76.4° in $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$,[25,26] 75.1° in $CoNi_2(h^5\text{-}C_5H_5)_3(CO)_2$,[26] 75.4° in the $[Co_6(CO)_{14}]^{4-}$ anion,[29] 78° in the $[Co_6(CO)_{15}]^{2-}$ anion,[31] and 79.7° in the $[Rh_{12}(CO)_{30}]^{2-}$ anion.[33]

In $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$, the four "face" bridging carbonyl groups have C–O bond lengths of 1.197 (7), 1.201 (7), 1.204 (7), and 1.209 (7) Å; the mean of 1.203 Å is virtually identical with the value of 1.20 (3) Å for the lone triply bridging carbonyl ligand in the $[Fe_4(CO)_{13}]^{2-}$ anion[22] and is close to the average values for the triply bridging carbonyls in $Rh_6(CO)_{16}$ (1.20 Å),[24] $Ni_3(h^5\text{-}C_5H_5)_3(CO)_2$ (1.183 (13) Å),[25,26] $CoNi_2(h^5\text{-}C_5H_5)_3(CO)_2$ (1.183 (13) Å),[26] $[Co_6(CO)_{14}]^{4-}$ (1.21 Å),[29] $[Co_6(CO)_{15}]^{2-}$ (1.19 Å),[31] $[Rh_7(CO)_{16}]^{3-}$ (1.19 Å),[32] and $[Rh_{12}(CO)_{30}]^{2-}$ (1.19 Å).[33] A qualitative bonding description of a carbonyl ligand coordinated to three metal atoms is given elsewhere.[5,35]

In each of the "well-behaved" C_5H_5 rings 1 and 2 (Figure 1) of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$, the spread of the five C–C bond lengths is only 0.04 and 0.03 Å, respectively, while in the C_5H_5 rings 3 and 4 the spread over the five C–C bond lengths is considerably greater (*viz.*, 0.07 and 0.12 Å, respectively). Nevertheless, the average values of 2.123, 2.123, 2.104, and 2.079 Å for the Fe–C(cyclopentadienyl) distances in rings 1 through 4, respectively, are reasonably close to one another except for that of ring 4. Despite this latter variation, the range of the five Fe–C(cyclopentadienyl) distances for a given ring is ≤ 0.035 Å. The small differences both of the C–C bond lengths in rings 1 and 2 and of the Fe–C(cyclopentadienyl) distances within their esd's are consistent with an essentially uniform delocalized bonding of each C_5H_5 ring with its iron atom. The least-squares plane through each of the C_5H_5 rings (Table IV) shows that the ring atoms do not differ significantly from coplanarity in that the perpendicular deviations of any atoms from their respective mean planes are ≤ 0.015 Å. The distances from the centroids of the C_5H_5 ring to their respective attached iron atoms average to 1.75 Å for the four rings (Table II), in accord with the corresponding distances in other monocyclopentadienyliron complexes including monoclinic $Fe_4(h^5\text{-}C_5H_5)_4S_4$ (1.74 and 1.75 Å)[36] and orthorhombic $Fe_4(h^5\text{-}C_5H_5)_4S_4$ (1.757 (5) Å).[37]

A qualitative bonding description of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ is presented elsewhere,[5] together with the structural determination of the monocation which allowed the assessment of the stereochemical consequences of the removal of a valence electron from this metal cluster system containing a completely bonding tetrahedron of metal atoms. It should be mentioned that a portion of the basis of the MO bonding model utilized for $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ was set forth earlier by one of us.[2]

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