Structure and Bonding of the Tetrameric Cyclopentadienyliron Carbonyl Monocation, $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$. Stereochemical Effect Due to Oxidation of a Completely Bonding Tetrahedral Metal Cluster System

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Abstract: Crystalline $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ has been prepared and structurally characterized by three-dimensional X-ray diffraction techniques. The paramagnetic $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ monocation, which retains the same molecular framework of the neutral parent analog, is composed of a bonding tetrahedron of iron atoms with triply bridging carbonyl ligands situated above the four triangular faces and with a *pentahapto*cyclopentadienyl ring coordinated to each iron atom. A detailed comparison of geometries shows only a slight change of the central $Fe_4(CO)_4$ core from cubic T_d geometry in the neutral molecule toward a distorted tetragonal D_{2d} geometry in the monocation, together with a decrease of the iron–iron distances from a mean value of 2.520 Å to a mean value of 2.484 Å. The cubic-deformed geometry of the monocation may be ascribed to a Jahn–Teller distortion upon which there is superimposed crystal-packing effects. The average C–O bond length of 1.188 Å in the monocation is 0.015 Å shorter than that in the neutral molecule, whereas the average Fe–CO bond length of 1.984 Å is virtually identical with that in the neutral molecule. These observed changes in molecular parameters along with an increase of 80 cm^{-1} in the carbonyl stretching frequency on oxidation of the parent tetramer to give the PF_6^- salt are rationalized with an MO correlation diagram. This energy-level diagram emphasizes for a completely bonding organometallic cluster system which has *no* electrons in the *strongly antibonding* metal symmetry orbitals that little change in the metal–metal distances may be expected on oxidation but that a large increase in metal–metal distances should be observed on reduction. Crystals of $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ are orthorhombic with symmetry *Pnma* and lattice parameters $a = 18.717$ (4), $b = 9.721$ (2), $c = 13.760$ (3) Å; $d_{obsd} = 1.94$ *vs.* $d_{calcd} = 1.965$ g cm^{-3} based on four formula species per unit cell. The structure was solved with 1745 independent nonzero diffraction maxima (*i.e.*, $I > 2.0\cdot\sigma(I)$), collected with an automated diffractometer. The space group necessitates that each $[Fe\cdot(h^5\text{-}C_5H_5)(CO)]_4^+$ monocation and each PF_6^- anion in the unit cell possess C_s-*m* crystallographic site symmetry with the octahedral-like PF_6^- anion randomly disordered in one of two crystal orientations. Evidence is presented that two of the three independent C_5H_5 rings are also distributed among two crystal orientations. Least-squares refinements by one model involving anisotropic thermal parameters for all nonhydrogen atoms and by a second model involving D_{5h} idealized rigid pentagons for the disordered C_5H_5 rings yielded unweighted R_1 values of 5.9 and 7.7%, respectively, with all corresponding atomic coordinates and calculated molecular parameters for the central $Fe_4(CO)_4$ core being equivalent for both models within statistical error (*viz.*, <2.0 esd's).

As part of our continuing effort to monitor the influence of valence electrons on the molecular geometries of polynuclear organometallic clusters in order to obtain more definitive information concerning the metal–metal bonding of such complexes, structural studies of cationic systems formed by oxidation of the corresponding neutral species have been carried out and compared with those of the neutral species having the same basic structure.[1–3] We wish to report here the X-ray crystallographic characterization of a tetrameric metal cluster cation, $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$, whose structure together with the previously determined structure of the neutral $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule[4] enable a bonding analysis concerning the consequences of the removal of a valence electron from a complex containing a tetrahedrally bonded framework of metal atoms (*viz.*, one in which each metal atom is linked to the other three metal atoms by direct metal–metal interactions as well as by triply bridging ligands).

The paramagnetic $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ cation was first reported by King[5] as the tribromide salt from the reaction of excess bromine with the neutral diamagnetic $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ complex. The chloride and pentaiodide salts were subsequently prepared by Greatrex and Greenwood[6] in connection with their Mössbauer spectral measurements of both the neutral and cationic species. In addition, the neutral molecule has been characterized by mass[5,7] and Raman[8] spectroscopy; the latter method was utilized[8] to estimate an Fe–Fe force constant of 1.3 mdyn $Å^{-1}$. Abnormal electrochemical behavior of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ has also been reported.[9] Recent cyclic voltammetric measurements by Ferguson and Meyer[10] have shown that $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ not only undergoes electrochemically reversible oxidation to both the monocation and dication but also reduction to the monoanion.

Our preliminary attempts to grow single crystals of the halide salts were unsuccessful, since the cation is easily reducible to the neutral tetramer. Crystalline

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$[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ was finally obtained by us from the reaction of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ with $AgPF_6$. It is noteworthy that the $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ salt was also produced by Ferguson and Meyer[10] in 85% yield by controlled-potential electrolysis of the neutral molecule at a platinum electrode in an $[n\text{-}Bu_4N][PF_6]$–dichloromethane solution.

Experimental Section

Preparation and Properties. The neutral $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ complex was prepared by King's method.[5] The cationic species was formed by oxidation of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ dissolved in CH_2Cl_2 with an equimolar amount of $AgPF_6$ (Ozark-Mahoning Co.) in CH_2Cl_2 solution. The almost black precipitate was filtered off, washed with a CH_2Cl_2–ether mixture, and extracted in a Soxhlet apparatus with methanol for several days. Since metallic silver is also formed in the redox reaction, it was necessary to use glass extraction thimbles with fritted disks in order to keep the reduced silver powder from mixing with the extracted solution. Alternatively, a solution of the product in methanol or acetone–methanol was first filtered through a fritte packed with cellulose powder and then evaporated to dryness followed by an extraction in a Soxhlet apparatus with methanol for 3–4 days. After this period, dark green crystals which were formed in the slowly cooled flask were recrystallized from acetone solution to yield single crystals of size suitable for X-ray diffraction analysis.

The above reactions were carried out under nitrogen and with nitrogen-saturated solvents in order to exclude moisture because, although the complexes are relatively stable to air, some reagents such as $AgPF_6$ are easily hydrolyzable. CH_2Cl_2 was first treated consecutively (a) with an aqueous solution of $NaHCO_3$, (b) with dilute H_2SO_4, and (c) with distilled water; it was then predried with anhydrous Na_2SO_4 and refluxed over P_2O_5 for 2–3 days under a nitrogen atmosphere before distillation. CH_3OH was dried by its being refluxed over CaH_2 under nitrogen.

Anal. Calcd for $C_{24}H_{20}F_6Fe_4O_4P$: C, 38.91; H, 2.72; Fe, 30.15; P, 4.18. Found: C, 38.95; H, 2.77; Fe, 29.94; P, 4.03.[11]

For the paramagnetic $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ salt a magnetic moment of $\mu_{eff} = 2.2$ BM was obtained at 23° by the Faraday method,[12] while a magnetic moment of $\mu_{eff} = 1.91$ BM was determined at 35° by the nmr method in acetone. These values are comparable with magnetic moments of 2.13 and 2.03 BM reported by King[5] for two samples of $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]Br_3$ at room temperature by the Faraday method.

A KBr pellet infrared spectrum of $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ gives one single carbonyl band at 1700 (vs) cm^{-1}, in close agreement with the single peak reported[6] at 1695 cm^{-1} for both the chloride and tribromide salts[13] and at 1700 cm^{-1} for the pentaiodide salt. Most of the other absorption bands for the PF_6^- salt at 3120 (w), 1425 (m), 1355 (w), 1010 (w), 945 (w), 855 (s), 840 (s), 820 (s), and 550 (m) cm^{-1} are in accord with those of the KBr pellet spectrum obtained by King[5] for the tribromide salt. One or more peaks in the 820–855-cm^{-1} region and the one at 550 cm^{-1} may be ascribed at least partially to the vibrational modes of the PF_6^- anion, since the KPF_6 salt as a mineral oil mull shows ir-active bands at 830 (s) and 558 (m) cm^{-1} attributed[14] to normal vibrational modes of the PF_6^- anion.

Single-Crystal X-Ray Data Collection. For the collection of intensity data, an approximately cubic-shaped crystal of dimensions 0.35 × 0.32 × 0.34 mm was selected by optical examination from the available crystals and mounted on a glass fiber with epoxy cement. Precession and Weissenberg photographs displayed $D_{2h}-2/m2/m2/m$ Laue symmetry characteristic of the orthorhombic system. The crystal was optically aligned about the rotation axis (corresponding to the *a* axis) on a General Electric full-circle, Datex-controlled diffractometer and then centered in the X-ray beam.[15] After 26 representative diffraction maxima were carefully centered, lattice and orientation parameters and instrument constants were calculated from the angle settings and refined by the program ANGSET.[16] These constants and parameters were used to generate the angle settings for all data reflections.[17] Intensity data for three symmetry-equivalent octants (*viz.*, hkl, $\bar{h}kl$, $\bar{h}k\bar{l}$) were collected for $2\theta \leq 45°$ with Zr-filtered Mo Kα radiation (λ 0.7107 Å) at a takeoff angle of 2.0°. Since some of the peaks were broad, variable symmetrical scan ranges for 2θ were used: 2.2° for $2\theta \leq 6°$, 1.9° for $6° < 2\theta \leq 9°$, and 1.5° for $2\theta > 9°$. Intensities were monitored by the θ-2θ scan technique at a 2.0°/min rate with stationary crystal–stationary counter background counts of 15 sec taken on each side of the scan. Three standard reflections sampled at intervals of every 80 reflections revealed no indications of either electronic instability or crystal decay.

The treatment of intensity data including correction for background and Lorentz-polarization effects has been described previously.[18] Calculated transmission coefficients, based on the linear absorption coefficient for Mo Kα radiation of 24.7 cm^{-1}, ranged from 0.45 to 0.52 (corresponding to 3.6% fluctuation in F_o's), and therefore absorption corrections were performed.[19] No extinction corrections were made. After merging[20] of the equivalent reflections for the three octants, 1745 independent reflections were obtained (corresponding to one reciprocal lattice octant of intensities for D_{2h} symmetry) with $|F_o| > 4\sigma(F_o)$.

Unit Cell and Space Group. The $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ salt crystallizes to give an orthorhombic unit cell of dimensions a = 18.717 (4), b = 9.721 (2) and c = 13.760 (3) Å;[21] the cell volume is 2503.6 A³. The observed density of 1.94 g cm⁻³ (flotation method) agrees well with the calculated value of 1.965 g cm⁻³ based on four formula species per cell. The total number of electrons per unit cell, $F(000)$, is 1476.

Systematic absences of $\{0kl\}$ for $k + l$ odd and of $\{hk0\}$ for h odd denote the probable space group as either $Pn2_1a$ (nonstandard axial orientation of $Pna2_1$ (C_{2v}^9, no. 33)) or $Pnma$ (D_{2h}^{16}, no. 62). The choice of the latter centrosymmetric space group was suggested by the distribution of the normalized structure factor magnitudes calculated from the program FAME.[22] These statistical averages of $\langle E\rangle = 0.830$, $\langle |E|^2\rangle = 1.000$ (rescaled), and $\langle |E|^2 - 1\rangle = 0.935$ with $|E| > 1$, 31.1%; $|E| > 2$, 4.4%; and $|E| > 3$, 0.2% are reasonably consistent with those expected from a centrosymmetric crystal structure.[23] This choice was subsequently confirmed by the crystallographic analysis and successful refinement of the structure. The space group $Pnma$ necessitates that each of the four cations and anions possess crystallographic site symmetry C_s-m. For this space group the crystallographically independent atoms occupy either the eightfold set of general positions ($8d$) or the fourfold set of special positions ($4c$) on mirror planes. These positions are as follows: $8d, \pm(x, y, z;\ {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 - z;\ \bar{x}, {}^1/_2 + y, \bar{z};\ {}^1/_2 - x, \bar{y}, {}^1/_2 + z)$; $4c, \pm(x, {}^1/_4, z;\ {}^1/_2 - x, {}^3/_4, {}^1/_2 + z)$.[24]

Determination and Refinement of the Structure. Initial coordinates for three independent iron atoms under $Pnma$ symmetry were obtained from a vector analysis of a three-dimensional sharpened Patterson function[25] by the use of the computer program PHASE.[26]

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[11] Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921.

[12] We wish to acknowledge Dr. Michael Camp for carrying out this measurement for us.

[13] A somewhat lower carbonyl frequency of 1675 (s) cm^{-1} is recorded by King[5] from an infrared KBr pellet spectrum of the tribromide salt.

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[15] T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1966.

[16] A. S. Foust, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1970.

[17] Local version of Argonne National Laboratory "Orientation and Angle Setting Generation Program," Program B-101, 1965.

[18] *Cf.* V. A. Uchtman and L. F. Dahl, *J. Amer. Chem. Soc.*, **91**, 3756 (1969). In the calculation of $\sigma_i^2(F)$, the so-called "ignorance" factor, E, was empirically assigned a value of 0.0016.

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[20] J. C. Calabrese, SORTMERGE, a Fortran program for sorting and merging crystallographic intensity data, University of Wisconsin (Madison), 1968.

[21] The uncertainties of the lattice parameters obtained from least squares[16] are estimates of precision and are unrealistically small due to the large number of reflections used in the determination.

[22] R. B. K. Dewar and A. L. Stone, "Fame and Magic, Fortran Computer Programs for Use in the Symbolic Addition Method," University of Chicago, 1966; *Cf.* E. B. Fleischer, R. B. K. Dewar, and A. L. Stone, Abstracts of Papers, American Crystallographic Association, Winter Meeting, Atlanta, Ga., 1967, p 20.

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[25] The Patterson and Fourier maps were computed with the Blount

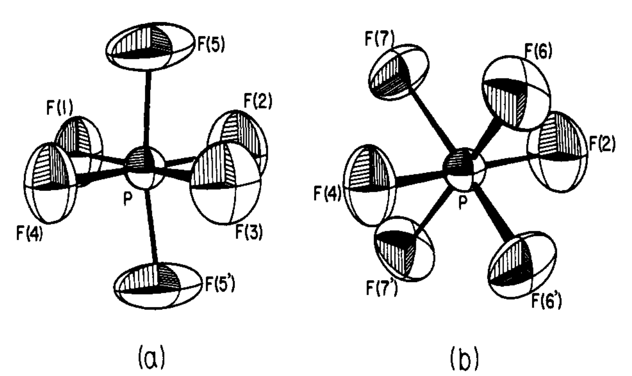

Figure 1. Each octahedral-like PF_6^- anion is randomly distributed in one of two orientations about a crystallographic site of C_s-m symmetry such that only the P, F(2), and F(4) atoms (which lie on a crystallographic mirror plane) are whole-weighted (owing to the superposition of the two orientations for these three atoms). The other four fluorine atoms are statistically distributed in one of two orientations with F(1), F(3), F(5), and F(5') corresponding to half-weighted atoms in the orientation a and F(6), F(6'), F(7), and F(7') representing the half-weighted atoms in the other orientation (b). The 20% probability thermal ellipsoids of the atoms are shown for both PF_6^- orientations which are approximately related to each other by a 45° rotation about the F(2)–F(4) axis.

This program revealed a tetrahedron of four iron atoms, of which two (*viz.*, Fe(1) and Fe(2)) reside on the crystallographic mirror plane at $y = {}^1/_4$, while the other two (*viz.*, Fe(3) and Fe(3')) are related to each other by the mirror plane. The Fe–Fe distances calculated from these initial positions ranged from 2.44 to 2.55 Å. The program PHASE also correctly assigned the position of the phosphorus atom on the mirror plane, but this position was not used in the initial refinement process but instead was obtained from the subsequent Fourier synthesis. The coordinates and assigned isotropic temperature factors of the three independent iron atoms were refined by one least-squares cycle[27–29] to R_1 and R_2 values[30] of 39.8 and 42.1%, respectively.

Further determination and refinement of this structure was not straightforward owing to both a crystal disorder of the PF_6^- anion (Figure 1) and a crystal disorder of two of the three independent C_5H_5 rings. Successive Fourier syntheses coupled with least squares eventually led to the assignment of coordinates for all nonhydrogen atoms (with each of the C_5H_5 rings initially assumed to be ordered). After several cycles of least-squares refinement with anisotropic thermal parameters utilized for all nonhydrogen atoms, convergence was obtained with $R_1 = 5.9$ and $R_2 = 6.8\%$. During the last cycle, no individual positional parameter changed by more than 0.2σ except for one fluorine parameter which changed by 0.44σ and several cyclopentadienyl carbon parameters which still varied by 1.4σ–1.9σ.

At the termination of this anisotropic refinement, bond lengths and angles within the $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ salt were completely consistent with expected values except for those of the C_5H_5 rings 2 and 3 (where rings 1, 2, and 3 denote the *pentahapto*cyclopentadienyl ligands attached to Fe(1), Fe(2), and Fe(3), respectively). In this anisotropic refinement each C_5H_5 ring was assumed to be ordered with rings 1 and 2, which are bisected by a crystallographic mirror plane, each comprised of three crystallographically independent carbon atoms with one atom located on the mirror plane (Figure 2). Ring 1 showed almost perfect planarity, with the largest perpendicular displacement of the individual carbon atoms from the idealized plane being only 0.004 Å. Furthermore, for ring 1 the three independent intraring angles of range 105.9 (18)–109.4 (13)° compare favorably with those in other cyclopentadienyl metal complexes. However, for both rings 2 and 3 wide ranges of C–C distances and intraring angles were observed together with pronounced deviations of the rings from planarity.

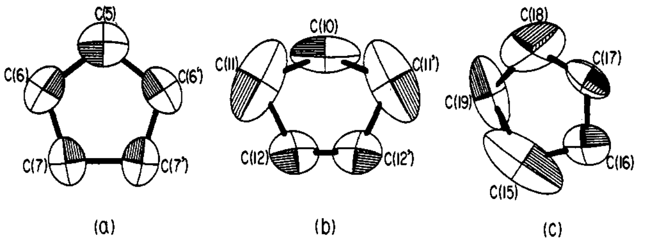

Figure 2. View normal to the mean plane of each of the three crystallographically independent C_5H_5 rings showing the cyclopentadienyl carbon atoms, refined by a crystal-ordered anisotropic least-squares model, as 20% probability thermal ellipsoids: (a) ring 1 (bisected by a crystallographic mirror plane) attached to Fe(1), (b) ring 2 (bisected by the same mirror plane) attached to Fe(2), and (c) ring 3 (whose atoms are all located in general positions) attached to Fe(3). Whereas the thermal ellipsoids of ring 1 are "normal" in accord with expected bond lengths and angles, the "abnormal" thermal ellipsoids (and apparent nonplanarity) of rings 2 and 3 have been interpreted in terms of a crystal-disordered model involving two orientations of D_{5h}-idealized rigid C_5H_5 pentagons.

Definite evidence of crystal disorder rather than high librational ring motion for rings 2 and 3 is shown in Figure 2, which pictures the thermal ellipsoids, calculated from the anisotropic refinement, for three independent C_5H_5 rings. In contrast to the normal thermal ellipsoids in ring 1, the thermal ellipsoids of three carbon atoms in each of the rings 2 and 3 are markedly elongated relative to those of the other two carbon atoms. It would be expected that a librational motion *per se* would uniformly spread the electron density of each carbon atom such to give rise to elongated thermal ellipsoids approximately within the mean plane of the five carbon atoms. In addition, a three-dimensional Fourier difference map showed some residual electron-density peaks between adjacent carbon atoms for rings 2 and 3 but not for ring 1. These observations were interpreted as an indication of crystal disorder for rings 2 and 3. Despite the large variations in C–C distances, the individual Fe–C(cyclopentadienyl) ring distances for rings 2 and 3 as well as for ring 1 were all within 0.04 Å of the average value of 2.09 Å. The distinct nonplanarity of rings 2 and 3 together with the small range of Fe–C(cyclopentadienyl) distances implies that these rings have preferred crystal orientations which are *tilted but not noticeably skewed*[31] with respect to the Fe–(ring centroid) axis. To the extent that this ring tilting (which most likely is due to the molecular packing in the crystal) actually occurs, the crystal-ordered anisotropic model would less adequately represent the actual situation.

In an attempt to provide a better electron-density representation of rings 2 and 3, idealized rigid-body C_5H_5 rings of D_{5h} symmetry (with assumed C–C bond lengths of 1.405 Å and C–H distances of 1.08 Å) were placed in two orientations (which appeared to best fit the anisotropic thermal ellipsoids) and refined by least squares.[32] For this crystal-disordered C_5H_5 ring model a statistical disorder was assumed (corresponding to half-weighted carbon and hydrogen atoms in the two orientations of each disordered ring), with variable isotropic temperature factors for the carbon atoms and fixed ones for the hydrogen atoms. This rigid-body refinement was terminated at $R_1 = 7.7$ and $R_2 = 9.7\%$. A final Fourier difference map showed the highest three peaks of 1.0–1.4 e/Å^3 to be in the vicinity of the ring carbon atoms. Nevertheless, an examination showed the individual isotropic thermal parameters of the carbon atoms (Table I) to be reasonable. Most importantly, a comparison between the corresponding determined atomic coordinates and calculated bond

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program: J. F. Blount, Ph.D. Thesis (Appendix), University of Wisconsin (Madison), 1965.

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(27) 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.

(28) The atomic scattering factors used for all atoms except hydrogen are those based on Hartree–Fock–Slater calculations (H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, 17, 1040 (1964)); for hydrogen the scattering factors 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 were made for the iron atoms (*viz.*, $\Delta f' = 0.4$ and $\Delta f'' = 1.0$ for Mo Kα radiation).[29]

(29) D. H. Templeton in ref 24, Vol. III, 1962, p 215.

(30) $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|]100$ and $R_2 = [\Sigma w_i||F_o| - |F_c||^2/\Sigma w_i|F_o|^2]^{1/2}100$. All least-squares refinements were based on the minimization of $\Sigma w_i \Delta F_i^2$; the weights were assigned according to the relationship $w_i = 1/\sigma_i^2(F_o)$.[18]

(31) *Cf.* J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Amer. Chem. Soc.*, 91, 2528 (1969); F. A. Cotton and G. A. Rusholme, *ibid.*, 94, 402 (1972).

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Table I. Final Positional and Thermal Parameters of $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ (Model II)[a,b]

(i) Individual Atomic Parameters

Atom	x	y	z	B_{11} ($\times 10^4$)	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)	0.47497 (9)	0.25000	0.18960 (14)	21.2 (5)	140.8 (25)	71.6 (13)	0.0^c	5.4 (7)	0.0^c
Fe(2)	0.34439 (10)	0.25000	0.14929 (13)	23.3 (6)	280.8 (42)	45.9 (11)	0.0^c	−4.4 (6)	0.0^c
Fe(3)	0.38864 (7)	0.12224 (12)	0.29201 (10)	30.8 (4)	96.6 (15)	80.5 (10)	−6.3 (7)	−4.1 (5)	14.0 (10)
P	0.35868 (20)	0.25000	0.70775 (29)	34.0 (13)	143.6 (50)	70.0 (25)	0.0^c	9.1 (14)	0.0^c
F(1)	0.3018 (13)	0.2500	0.7839 (16)	49 (9)	425 (66)	70 (14)	0.0^c	25 (8)	0.0^c
F(2)	0.2960 (8)	0.2500	0.6362 (11)	84 (6)	493 (35)	163 (13)	0.0^c	−48 (7)	0.0^c
F(3)	0.4129 (23)	0.2500	0.6230 (36)	69 (13)	466 (146)	175 (32)	0.0^c	43 (15)	0.0^c
F(4)	0.4198 (6)	0.2500	0.7798 (8)	57 (5)	494 (33)	115 (9)	0.0^c	−14 (5)	0.0^c
F(5)	0.3554 (20)	0.0972 (23)	0.6995 (27)	199 (25)	146 (25)	255 (40)	22 (19)	85 (22)	20 (29)
F(6)	0.3966 (15)	0.1416 (31)	0.6470 (21)	112 (16)	352 (83)	159 (26)	68 (28)	40 (14)	−73 (35)
F(7)	0.3267 (15)	0.1368 (24)	0.7722 (17)	111 (13)	283 (45)	132 (18)	−56 (18)	16 (11)	73 (23)
O(1)	0.2486 (5)	0.2500	0.3181 (7)	22 (3)	380 (23)	77 (7)	0.0^c	13 (3)	0.0^c
O(2)	0.5046 (6)	0.2500	0.4004 (9)	43 (4)	329 (24)	108 (9)	0.0^c	−42 (5)	0.0^c
O(3)	0.4216 (5)	−0.0037 (12)	0.1026 (9)	73 (4)	365 (21)	225 (12)	−37 (8)	36 (6)	−240 (15)
C(1)	0.3079 (7)	0.2500	0.2843 (9)	28 (4)	153 (18)	66 (9)	0.0^c	−1 (5)	0.0^c
C(2)	0.4635 (7)	0.2500	0.3352 (11)	30 (4)	176 (20)	83 (10)	0.0^c	−4 (6)	0.0^c
C(3)	0.4149 (6)	0.0979 (15)	0.1485 (10)	45 (4)	263 (23)	115 (10)	−24 (8)	15 (5)	−54 (13)
C(5)	0.5407 (12)	0.2500	0.0621 (20)	44 (8)	526 (83)	161 (24)	0.0^c	61 (12)	0.0^c
C(6)	0.5566 (7)	0.3673 (17)	0.1254 (15)	29 (4)	299 (31)	191 (18)	−9 (10)	34 (7)	77 (18)
C(7)	0.5796 (5)	0.3238 (14)	0.2164 (13)	17 (3)	225 (20)	209 (16)	−13 (6)	14 (6)	−2 (15)

(ii) Rigid-Body Cyclopentadienyl Ring Parameters[d]

Rigid-body group	Basis x	Basis y	Basis z	ϕ[e]	θ	ρ
Ring 2	0.2789 (5)	0.2954 (12)	0.0594 (7)	−1.018 (13)	2.515 (10)	−0.498 (14)
Ring 3	0.3757 (8)	−0.0182 (18)	0.3690 (11)	1.890 (26)	2.533 (20)	0.780 (25)
Ring 3P	0.3795 (8)	−0.0372 (14)	0.3502 (8)	1.546 (17)	3.008 (17)	1.082 (14)

(iii) Atoms of Disordered Cyclopentadienyl Rings

Atom	x	y	z	B, Å^2
C(10)	0.2415	0.3536	0.1165	7.1 (5)
C(11)	0.2414	0.2117	0.0974	7.3 (6)
C(12)	0.2931	0.1854	0.0258	8.6 (7)
C(13)	0.3252	0.3111	0.0006	6.3 (5)
C(14)	0.2933	0.4151	0.0567	8.3 (6)
C(15)	0.3370	0.0492	0.4191	8.3 (9)
C(16)	0.4110	0.0328	0.4317	6.6 (5)
C(17)	0.4362	−0.0541	0.3577	7.9 (6)
C(18)	0.3777	−0.0914	0.2992	21.6 (24)
C(19)	0.3164	−0.0275	0.3372	8.4 (9)
C(15P)	0.3727	0.0209	0.4262	7.0 (5)
C(16P)	0.4376	−0.0222	0.3847	10.5 (11)
C(17P)	0.4222	−0.0861	0.2956	6.0 (4)
C(18P)	0.3478	−0.0825	0.2819	5.3 (4)
C(19P)	0.3172	−0.0164	0.3627	8.2 (8)
H(10)	0.2077	0.4063	0.1681	10.0[f]
H(11)	0.2075	0.1360	0.1317	10.0
H(12)	0.3060	0.0860	−0.0046	10.0
H(13)	0.3670	0.3253	−0.0526	10.0
H(14)	0.3063	0.5233	0.0542	10.0
H(15)	0.3021	0.1102	0.4644	10.0
H(16)	0.4430	0.0788	0.4884	10.0
H(17)	0.4908	−0.0866	0.3474	10.0
H(18)	0.3796	−0.1575	0.2362	10.0
H(19)	0.2629	−0.0359	0.3085	10.0
H(15P)	0.3666	0.0734	0.4949	10.0
H(16P)	0.4900	−0.0086	0.4159	10.0
H(17P)	0.4607	−0.1302	0.2462	10.0
H(18P)	0.3192	−0.1234	0.2202	10.0
H(19P)	0.2610	0.0025	0.3739	10.0

[a] Estimated standard deviations of the last significant figure 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. [c] The location of some atoms on a mirror plane ($y = {}^1/_4$) requires the anisotropic thermal coefficients B_{12} and B_{23} to be zero by symmetry. [d] The rigid-group atomic positions are defined relative to an orthonormal coordinate system x', y', z' as follows: the origin of the coordinate system lies on the centroid of the ring, x passes through one atom of the ring, and all atoms lie in the xy plane. The rigid-group angles ϕ, θ, ρ define the orientation of the rigid-group coordinate system with respect to the crystallographic axis system. The hydrogen atoms of the cyclopentadienyl rings lie along vectors extended from the ring centroid through the carbon atoms such that the rings conform to D_{5h} symmetry with C–C = 1.405 Å and C–H = 1.08 Å. [e] ϕ, θ, and ρ are reported in radians. [f] Isotropic thermal parameters of hydrogen atoms were not varied in the course of refinement.

lengths and angles for both the central $Fe_4(CO)_4$ cluster and PF_6^- anion showed all of them to be equivalent for both models within statistical error (*viz.*, <2.0 esd's). Although the R_1 value of 5.9% for the crystal-ordered anisotropic C_5H_5 ring model is expectedly somewhat lower than the R_1 value of 7.7% for this second model, the flexibility of the crystal-disordered C_5H_5 ring model with its allowance for ring tilting causes this model in our opinion to conform slightly more to reality. Hence, only the results from the refinement

Table II. Interatomic Distances[a,b]

(i) Bonding Distances (A) in the $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ Cation			
Fe(1)–Fe(2)	2.506 (2)	Fe(1)–C(5)	2.142 (20)
Fe(1)–Fe(3)	2.478 (2)	Fe(1)–C(6)	2.101 (12)
Fe(2)–Fe(3)	2.467 (2)	Fe(1)–C(7)	2.118 (11)
Fe(3)–Fe(3′)	2.484 (2)		
			2.120 (av)
	2.484 (av)	Fe(2)–C(10)	2.220
Fe(1)–C(2)	2.015 (15)	Fe(2)–C(11)	2.089
Fe(1)–C(3)	1.942 (12)	Fe(2)–C(12)	2.051
Fe(2)–C(1)	1.979 (13)	Fe(2)–C(13)	2.161
Fe(2)–C(3)	1.982 (14)	Fe(2)–C(14)	2.262
Fe(3)–C(1)	1.960 (10)		
Fe(3)–C(2)	1.965 (11)		2.157 (av)
Fe(3)–C(3)	2.048 (13)	Fe(3)–C(15)	2.120
		Fe(3)–C(16)	2.151
	1.984 (av)	Fe(3)–C(17)	2.132
C(1)–O(1)	1.203 (15)	Fe(3)–C(18)	2.089
C(2)–O(2)	1.183 (16)	Fe(3)–C(19)	2.081
C(3)–O(3)	1.179 (14)		
			2.115 (av)
	1.188 (av)	Fe(3)–C(15P)	2.114
		Fe(3)–C(16P)	2.106
		Fe(3)–C(17P)	2.120
		Fe(3)–C(18P)	2.136
		Fe(3)–C(19P)	2.132
			2.122 (av)
(ii) Bonding Distances (Å) in the PF_6^- Anion			
P–F(1)	1.495 (21)		
P–F(2)	1.531 (13)		
P–F(3)	1.546 (40)		
P–F(4)	1.513 (11)		
P–F(5)	1.491 (23)		
P–F(6)	1.520 (23)		
P–F(7)	1.534 (17)		
	1.519 (av)		
(iii) Close Intramolecular Nonbonding Distances (Å)			
C(1)···C(2)	2.996 (19)	O(1)···C(10)	2.954
C(1)···C(3)	3.112 (17)	O(1)···C(11)	3.063
C(2)···C(3)	3.100 (19)	O(1)···C(15)	2.912
C(3)···C(3′)	2.957 (29)	O(1)···C(19)	2.993
O(2)···H(16)	2.359	O(1)···C(19P)	2.955
O(3)···H(18)	2.497	O(2)···C(7)	2.983
O(3)···H(17P)	2.440	O(2)···C(16)	2.777
O(3)···H(14′)	2.266	O(2)···C(16P)	2.937
H(10)···H(19′)	2.527	O(3)···C(18)	2.953
H(14)···H(18P′)	2.495	O(3)···C(17P)	2.773
		O(3)···C(18P)	2.930
		O(3)···C(6′)	2.871
		O(3)···C(13′)	2.955
		O(3)···C(14′)	2.628

[a] Standard deviations of the last significant figures are given in parentheses. [b] Atoms of rings 2, 3, and 3P were refined as rigid-body groups. Standard deviations of bond distances involving these atoms cannot be estimated with our available computer programs.

based on the second model are tabulated and presented in this manuscript.

Positional and thermal parameters obtained from the output of the last cycle of the least-squares refinement for the second model are listed in Table I.[33] Interatomic distances and bond angles together with estimated standard deviations, calculated[34] from the full inverse matrix containing the estimated uncertainties in lattice parameters, are documented in Tables II and III. Equations of planes determined by a least-squares method[35] along with perpendicular displacements of atoms from these planes and angles between the normals of these planes are given in Table IV.

Table III. Bond Angles (deg)[a]

(i) $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ Cation			
Fe(2)–Fe(1)–Fe(3)	59.33 (6)	Fe(2)–C(1)–Fe(3)	77.6 (4)
Fe(3)–Fe(1)–Fe(3′)	60.17 (7)	Fe(3)–C(1)–Fe(3′)	78.7 (5)
Fe(1)–Fe(2)–Fe(3)	59.76 (6)	Fe(1)–C(2)–Fe(3)	77.0 (5)
Fe(3)–Fe(2)–Fe(3′)	60.46 (7)	Fe(3)–C(2)–Fe(3′)	78.4 (5)
Fe(1)–Fe(3)–Fe(2)	60.91 (6)	Fe(1)–C(3)–Fe(2)	79.4 (5)
Fe(1)–Fe(3)–Fe(3′)	59.92 (4)	Fe(1)–C(3)–Fe(3)	76.7 (5)
Fe(2)–Fe(3)–Fe(3′)	59.77 (4)	Fe(2)–C(3)–Fe(3)	75.5 (4)
	60.05 (av)		77.6 (av)
C(2)–Fe(1)–C(3)	103.2 (5)	Fe(2)–C(1)–O(1)	133.0 (10)
C(3)–Fe(1)–C(3′)	99.2 (9)	Fe(3)–C(1)–O(1)	133.7 (6)
C(1)–Fe(2)–C(3)	103.6 (5)	Fe(1)–C(2)–O(2)	133.3 (12)
C(3)–Fe(2)–C(3′)	96.5 (7)	Fe(3)–C(2)–O(2)	133.9 (7)
C(1)–Fe(3)–C(2)	99.6 (4)	Fe(1)–C(3)–O(3)	137.1 (10)
C(1)–Fe(3)–C(3)	101.9 (6)	Fe(2)–C(3)–O(3)	134.3 (12)
C(2)–Fe(3)–C(3)	101.2 (6)	Fe(3)–C(3)–O(3)	129.7 (13)
	100.7 (av)		133.6 (av)
		C(5)–C(6)–C(7)	111.2 (18)
		C(6)–C(7)–C(7′)	107.7 (10)
		C(6′)–C(5)–C(6)	102.2 (24)
(ii) PF_6^- Anion			
F(1)–P–F(2)	84.6 (13)	F(4)–P–F(5)	94.7 (15)
F(1)–P–F(3)	175.6 (22)	F(4)–P–F(6)	90.4 (12)
F(1)–P–F(4)	94.5 (11)	F(4)–P–F(7)	85.2 (9)
F(1)–P–F(5)	91.4 (14)	F(5)–P–F(5′)	170.0 (30)
F(1)–P–F(6)	135.9 (13)	F(5)–P–F(6)	44.5 (12)
F(1)–P–F(7)	46.9 (12)	F(5)–P–F(6′)	131.9 (24)
F(2)–P–F(3)	91.0 (20)	F(5)–P–F(7)	46.6 (11)
F(2)–P–F(4)	179.1 (9)	F(5)–P–F(7′)	137.9 (23)
F(2)–P–F(5)	85.4 (15)	F(6)–P–F(6′)	87.7 (26)
F(2)–P–F(6)	90.2 (12)	F(6)–P–F(7)	90.1 (15)
F(2)–P–F(7)	94.2 (10)	F(6)–P–F(7′)	175.1 (16)
F(3)–P–F(4)	89.9 (13)	F(7)–P–F(7′)	91.6 (24)
F(3)–P–F(5)	88.3 (14)		
F(3)–P–F(6)	43.9 (13)		
F(3)–P–F(7)	133.8 (12)		

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

Results and Discussion

General Description of the Crystal Structure. The crystal structure contains discrete $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ cations and PF_6^- anions. Figure 3 displays the configuration of one $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ cation based on the crystal-disordered rigid-body cyclopentadienyl model, while Figure 1 shows the crystal-disordered arrangement of the PF_6^- anion. The $Fe_4(CO)_4$ framework of the cation is sufficiently embodied within the four cyclopentadienyl rings that the shortest *interionic* F···OC and cyclopentadienyl H···OC contacts of 3.50 and 2.89 Å, respectively, are much larger than the expected van der Waals separations. The crystal packing appears to be determined mainly by H···H and H···F interactions, with several H···F distances being up to 0.3 Å shorter than the van der Waals separation of 2.55 Å;[36] however, the two extremely short H(19)···F(7) and H(17)···F(6) distances of 2.01 and 2.18 Å may be rationalized as not being "real" on the basis that when the crystal-disordered C_5H_5 ring 3 is in one of its two crystal orientations (*viz.*, 3

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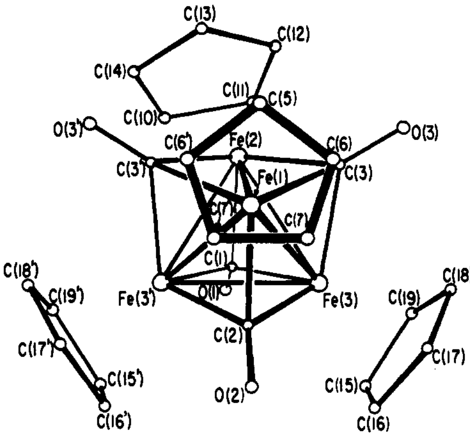
(33) Observed and calculated structure factors for $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4][PF_6]$ will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number JACS-72-3389. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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

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

(36) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.



$[Fe_4(\underline{h}^5\text{-}C_5H_5)_4(CO)_4]^+$

Figure 3. Geometry of the neutral ($n = 0$) and oxidized ($n = 1+$) forms of $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$. The oxidized monocation has crystallographic site symmetry C_s-m in the PF_6^- salt with the mirror plane passing through two iron atoms, Fe(1) and Fe(2), and two carbonyl groups labeled C(1), O(1), C(2), and O(2). The C_5H_5 rings attached to Fe(2) and Fe(3) are disordered; for clarity only one orientation is portrayed for each ring, and all hydrogen atoms are omitted. The oxidized monocation shows a small distortion from quasiregular T_d-$\bar{4}3m$ geometry in the neutral molecule (of crystallographic site symmetry C_1-1) *toward* an idealized D_{2d}-$\bar{4}2m$ geometry.

rather than 3P) the PF_6^- anion cannot be in the crystal orientation b but rather in orientation a. Hence, the crystal-disordered positions of the one cyclopentadienyl ring and the PF_6^- anion are *not independent* of each other. The shortest interionic H···H contacts are 2.26 and 2.27 Å, while all other such contacts are longer than the van der Waals separation of 2.40 Å.[36]

Table IV. Equations of Planes Formed by Different Groups of Atoms in Model II and Angles Between the Normals to these Planes

(i) Equations of Planes[a,b]

(A) Plane of Ring 1 (Composed of C(5), C(6), C(7), C(7′), and C(6′))[c]

$$0.945X - 0.326Z - 9.289 = 0$$

(B) Plane of Ring 2 (Composed of C(10), C(11), C(12), C(13), and C(14))[d]

$$-0.688X + 0.136Y - 0.713Z + 3.779 = 0$$

(C) Plane of Ring 3 (Composed of C(15), C(16), C(17), C(18), and C(19))

$$0.165X + 0.795Y - 0.584Z + 1.938 = 0$$

(D) Plane of Ring 3P (Composed of C(15P), C(16P), C(17P), C(18P), and C(19P))

$$0.085X + 0.880Y - 0.467Z + 1.959 = 0$$

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

$$0.921X - 0.390Z - 5.138 = 0$$

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

$$-0.656X - 0.755Z + 7.793 = 0$$

(G) Plane Containing Fe(1), Fe(2), and Fe(3′)

$$0.129X + 0.812Y - 0.570Z - 1.637 = 0$$

(ii) Angles (deg) between Normals to Planes

A and B	114.7	B and C	65.7
A and C	69.7	B and D	66.8
A and D	76.6	B and F	8.4
A and E	3.9	C and D	9.5
		C and G	2.4
		D and G	7.5

[a] 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. [b] Unit weight was used for all atoms in the application of the Smith least-squares planes program.[35] [c] In ring 1, the distances of component carbon atoms to the mean planes are 0.0010 Å for C(5), −0.0008 Å for C(6) and C(6′), and 0.0003 Å for C(7) and C(7′). All other cyclopentadienyl rings are rigid-body groups, hence perfectly planar. [d] Ring 2 forms an angle of 82.2° with the mirror plane at $y = 1/4$ instead of being perpendicular to the latter.

The $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ Cation. The $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ monocation, which retains the same basic molecular framework of the neutral homolog, possesses a bonding tetrahedron of iron atoms with triply bridging carbonyl ligands situated above the four triangular faces and with each planar cyclopentadienyl ring attached to a given iron atom essentially parallel to the plane formed by the other three iron atoms (Table IV). The bonding tetrahedron of iron atoms together with the interpenetrating, nonbonding tetrahedron of carbonyl ligands gives rise to a cubane-like $Fe_4(CO)_4$ architecture in which the iron atoms and carbonyl groups occupy the alternate corners of a distorted cube. This $Fe_4(CO)_4$ framework in the monocation may be considered to possess an idealized D_{2d}-$\bar{4}2m$ tetragonal geometry. The two opposite Fe–Fe tetrahedral edges (normal to the S_4-$\bar{4}$ axis) of lengths 2.484 (2) and 2.506 (2) Å are slightly longer than the four chemically equivalent (but only two independent) Fe–Fe edges of lengths 2.467 (2) and 2.478 (2) Å. On the other hand, the two opposite OC···CO tetrahedral edges (normal to the S_4-$\bar{4}$ axis) of nonbonding distances 2.957 (29) and 2.996 (19) Å are notably shorter than the four chemically equivalent (but only two independent) OC···CO edges of lengths 3.100 (19) and 3.112 (17) Å compared to the six equivalent OC···CO distances in the neutral $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule of intermediate range 3.028 (8)–3.063 (9) Å. This distortion of the $Fe_4(CO)_4$ core is also reflected in the three Fe(3)–C(1)–Fe(3′), Fe(3)–C(2)–Fe(3′), and Fe(1)–C(3)–Fe(2) bond angles of range 78.4 (5)–79.4 (5)° being somewhat larger than the other four independent Fe–C–Fe bond angles of range 75.5 (4)–77.6 (4)°. The observed deformation from D_{2d} symmetry may be ascribed to crystal-packing forces. The average value for the four independent Fe–Fe distances of 2.484 Å is 0.036 Å shorter than the mean value of 2.520 Å found for the six independent Fe–Fe distances in the neutral molecule. The average Fe–CO distance of 1.984 Å in the monocation is virtually the same as the corresponding average distance of 1.986 Å in the neutral molecule, whereas the average C–O bond length of 1.188 Å (with 1.179 (14)–1.203 (15)-Å range) in the monocation is 0.015 Å less than the average value of 1.203 Å (with 1.197 (7)–1.209 (7)-Å range) in the neutral molecule. These expected bond-length shifts (*vide infra*) are also in accord with the 80-cm^{-1} lower carbonyl stretching frequency of 1620 cm^{-1} (KBr pellet) in the neutral molecule. In harmony with the observed long C–O bond lengths in both $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$ ($n = 0, 1+$), the relative weakness of the C–O bonds and relative strength of the Fe–C bonds for the triply bridging carbonyl groups were also demonstrated by King[7] from electron impact studies which showed an unusual phenomenon for metal carbonyl derivatives of relatively high abundances of species formed by carbon–oxygen fission. The average value of 2.13 Å obtained for the 11 independent Fe–C(cyclopentadienyl) distances in the monocation is comparable to the average value of 2.11 Å found for the 20 independent Fe–C(cyclopentadienyl) distances in the neutral molecule.

The PF_6^- Anion. The geometry of the hexafluorophosphate anion may be described as a slightly distorted octahedron. The P–F bond lengths range from 1.49 (2) to 1.55 (4) Å. The mean value of 1.52 Å is comparable with those found in other PF_6^- salts—*viz.*, 1.55 Å in $[Ru(N_3)(N_2)(NH_2CH_2CH_2NH_2)_2][PF_6]$[37] and 1.57 Å in (+)-4-methylpyridinetrimethylaminebromohydroboron hexafluorophosphate.[38] For the two crystal orientations of PF_6^- (Figure 1), the *cis*-F–P–F bond angles range from 84.6 (13) to 94.7 (15)°, while the *trans*-F–P–F angles vary from 170.0 (30) to 179.1 (9)°. Although these deviations in bond angles from ideal octahedral angles may be primarily the result of the "calculated" models assumed for both the cation and anion, they may also be explained in part by the crystal packing.

Bonding Description of $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$ Species (n = 2+, 1+, 0, 1−). An approach involving directed hybrid metal orbitals has been previously employed for $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$[4a,39] (as well as for $Fe_4(h^5\text{-}C_5H_5)_4S_4$ and $Co_4(CO)_{12}Sb_4$[39]) in order to factorize the metal–ligand interactions from the metal–metal interactions. For the $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule of T_d geometry, symmetry orbital combinations of the atomic basis functions, derived by means of projection operators, are found elsewhere.[4a] In order to extend the bonding picture not only to account for the observational changes determined between the neutral $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule and its corresponding monocation but also to provide stereochemical predictions for the structurally uncharacterized dication and monoanion, a simple MO correlation diagram portraying the assumed relative ordering of the occupied energy levels for a $[M_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$ species of T_d symmetry is given in Figure 4.[40–42] This diagram attempts to convey schematically the following features. (1) For the regular tetrahedral array of four metal atoms the five 3d orbitals per metal atom are transformed to give 20 metal symmetry combinations of ($a_1 + 2e + 2t_1 + 3t_2$) representations which, from reasonable metal orbital overlap considerations, may be qualitatively grouped into three energy categories (relative to the isolated metal orbitals at the same energy) of 6 *bonding* ($a_1 + e + t_2$) combinations, 8 essentially nonbonding ($e + t_1 + t_2$) combinations, and 6 *antibonding* ($t_1 + t_2$) combinations.[43] Similar energy splittings of the tetrametal symmetry combinations compounded from the 4s and 4p metal orbitals will also occur, but these separations are not at all important with respect to the resulting interpretations of this qualitative bonding model. (2) For each of the four cyclopentadienyl rings, the three lowest energy, filled $\pi(C_5H_5)$ orbitals[40] (of $a_1 + e$ representation under localized C_{3v} site symmetry at each metal atom) transform under molecular T_d symmetry as ($a_1 + e + t_1 + 2t_2$). The relevant carbonyl orbitals can be classified as 5σ (CO) electron-pair donors[42] which transform as ($a_1 + t_2$) and 2π (CO) or π* (CO) which transform as ($e + t_1 + t_2$). (3) For the neutral $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule, the available 60 electrons (comprised of 32 electrons from the four iron atoms, 8 electrons from the 5σ orbitals of the four triply bridging carbonyl ligands, and 20 electrons from the four cyclopentadienyl radicals) are distributed among 30 MO's. It is reasonably presumed from our MO diagram that these *filled* energy levels consist of: (a) 4 low-energy metal–5σ (CO) bonding MO's of largely carbonyl character, (b) 12 low-energy metal–C_5H_5 bonding MO's ($a_1 + e + t_1 + 2t_2$) of primarily cyclopentadienyl character, (c) 6 higher energy MO's ($a_1 + e + t_2$) of largely metal d-orbital character that are *strongly bonding* with respect to the metal cluster system, and (d) 8 highest occupied MO's ($e + t_1 + t_2$) which are essentially nonbonding (with the highest one somewhat antibonding)[43] with respect to the metal atoms and strongly stabilized by metal–carbonyl back-bonding with the 2π (CO) orbitals.[44,45] Hence, this

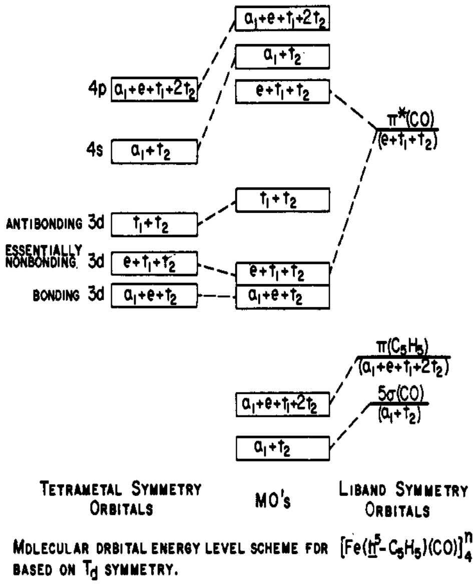


Figure 4. Molecular orbital energy-level scheme (based on cubic T_d symmetry) for $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$ complexes. For the neutral molecule (n = 0), the MO levels arising primarily from the bonding and essentially nonbonding 3d tetrairon orbitals are all filled, while the MO levels arising primarily from the antibonding 3d tetrairon orbitals are completely empty.

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(37) B. R. Davis and J. A. Ibers, *Inorg. Chem.*, **9**, 2768 (1970).

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(40) For simplicity the energy-level diagram in Figure 4 has excluded the very low-energy 3σ (CO), 4σ (CO), and 1π (CO) diagonal terms[41] and resultant filled MO's to which they are the primary contributors. For each cyclopentadienyl ring the symmetry combinations for the highest energy degenerate pair of virtual π orbitals, $\psi_{\pm 2}$, are also omitted from Figure 4, since they lie much higher in energy than the π* (CO) levels and hence do not participate significantly in the bonding.

(41) *Cf.* R. L. DeKock, A. C. Sarapu, and R. F. Fenske, *Inorg. Chem.*, **10**, 38 (1971).

(42) Although the 5σ (CO) orbitals consist predominantly of the carbon AO's, it is noteworthy that these orbitals are antibonding between the carbon and oxygen atoms[41] such that a removal of electron density from these orbitals by greater interaction with the iron orbitals leads to a C–O σ-bond strengthening. Conversely, the composite effect of any charge transfer from the filled 1π (CO) orbitals to the tetrametal orbitals coupled with a charge transfer from the filled tetrametal orbitals to the unoccupied 2π (CO) orbitals will bring about a C–O π-bond weakening.

(43) On the basis of a local Cartesian coordinate system chosen at each metal atom with the positive z axis directed inward toward the center of the metal tetrahedron, the *strongly bonding* and *antibonding* tetrametal symmetry combinations ($a_1 + e + t_1 + 2t_2$) arise under T_d symmetry from the d_{z^2} and d_{xz}, d_{yz} degenerate pair of metal valence orbitals, while each tangential d_{xy}, $d_{x^2-y^2}$ degenerate pair, situated perpendicular to the z direction, gives rise to relatively nonbonding tetrametal symmetry combinations ($e + t_1 + t_2$). The lowest energy level of these latter tetrametal orbitals will be somewhat bonding and the highest one somewhat antibonding relevant to the extent that these d_{xy}, $d_{x^2-y^2}$ orbitals on the four metal atoms overlap with one another.

(44) In order to lower the overall C–O bond order toward a value between 1.0 and 2.0 (as exists in the triply bridging carbonyl groups), there must be a marked increase in back-donation from the metal atoms into the 2π (CO) or π* (CO) ligand orbitals in going from terminal to

delocalized MO picture with the six strongly bonding tetrairon ($a_1 + e + t_2$) orbitals filled and the six strongly antibonding tetrairon ($t_1 + t_2$) orbitals empty corresponds to its localized valence-bond counterpart with electron-pair bonds between each of the six pairs of iron atoms in the neutral $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule. Of prime significance are the principal factors which contribute to an increased energy separation of the empty ($t_1 + t_2$) MO's of *strongly antibonding* tetrametal character from the filled ones—*viz.*, the *direct* metal–metal interactions (which depress the bonding tetrairon energy levels and raise the antibonding tetrairon ones) and the strong stabilization of the essentially nonbonding orbitals of the tetrairon cluster by delocalization of charge into the empty 2π (CO) orbitals of the triply bridging carbonyl ligands.

The observed variations in architecture and in carbonyl stretching frequency due to oxidation of the neutral $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ molecule to the monocation are in accord with this above MO representation in that they provide operational evidence that the electron has been removed from an MO which is somewhat antibonding between the iron atoms and which is also antibonding between the carbon and oxygen atoms. No doubt extensive mixing occurs among orbitals belonging to the same irreducible representation, and indeed such an interaction offers a mechanism by which the highest filled MO in the neutral tetrameric molecule can acquire antibonding tetrairon orbital character, as indicated by the average value for the Fe–Fe distances in the monocation being smaller by 0.036 Å than that for the Fe–Fe distances in the neutral molecule. The small *average* decrease of 0.015 Å in the C–O bond lengths in the monocation compared to those in the neutral molecule represents an expected bond-length change in terms of the triply bridging carbonyl frequency increase of 80 cm^{-1}. A diminution of the electron population of the antibonding 2π (CO) orbitals would strengthen the C–O bond and thereby increase the C–O stretching frequency. It is noteworthy that on oxidation to the monocation a decrease in transfer of electron charge from the metal to the 2π (CO) orbitals may also in part be attributed to a readjustment of the energy levels such that a *net* lowering of the metal orbitals occurs relative to the 2π (CO) orbitals. The virtually identical *average* values of 1.986 and 1.984 Å for the Fe–CO distances in the neutral molecule and monocation, respectively, are also reasonable in light of the Fe–CO bonds being sufficiently strong that a removal of one electron from an MO of even relatively large bonding character between the iron atoms and carbonyl ligands would not be expected to induce any appreciable change in the 12 Fe–CO bond lengths.

The slight but statistically significant distortion of the $Fe_4(CO)_4$ framework of the monocation toward a D_{2d} geometry may be attributed to a composite of two effects—one being a Jahn–Teller distortion from T_d geometry and the other being crystal-packing interactions. A deformation from T_d to D_{2d} geometry is permissible *via* a Jahn–Teller-active vibration[46] if an electron is abstracted from an orbital of e, t_1, or t_2 representation (under T_d symmetry). The continued chemical equivalence of the four iron atoms in the $Fe_4(CO)_4$ core of the monocation under D_{2d} symmetry is compatible with the interpretation by Greatrex and Greenwood[6] from their Mössbauer spectral data that the oxidation of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ to $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^+$ involves the removal of an electron from an MO which affects all iron atoms equally.

Several informative principles are made apparent from this qualitative MO bonding model. First, it emphasizes for a completely bonding organometallic cluster system (*i.e.*, one with no nonbonding metal–metal distances) which has *no* electrons in the *strongly* antibonding metal symmetry orbitals that one may expect little change in the metal–metal distance(s) on oxidation to the monocation or dication owing to the distinct possibility of the electron being removed from an MO which is nonbonding or only somewhat antibonding between the metal atoms. This principle is based on the reasonable premise inferred from the experimental results for $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^n$ (n = 0, 1+) that the MO's comprised of the strongly bonding metal symmetry orbitals are generally lower in energy than the MO's comprised of essentially nonbonding metal symmetry orbitals. Second, it predicts that a reduction of $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ (or any other metal cluster system for which each atom contains a closed-shell electronic configuration) to give the monoanion (or higher negative species) should give rise to a large increase in metal–metal distances in that any additional electrons would occupy MO's containing *strongly antibonding* tetrametal orbitals. In the case of the recently isolated air-sensitive $[Fe_4(h^5\text{-}C_5H_5)_4(CO)_4]^-$ anion,[10] for which ν(CO) = 1576 cm^{-1} and g = 2.013 in CH_3CN, the unpaired electron under T_d symmetry would occupy an MO of either a t_1 or t_2 representation, and hence along with an increase in the Fe–Fe distances a deformation of the tetrairon framework from T_d geometry *toward* a D_{2d} or D_2 geometry may be predicted from the Jahn–Teller effect (along with a further unpredictable kind of superimposed distortion arising from crystal-packing interactions). Further synthetic and structural investigations are in progress to substantiate these conclusions.

Acknowledgment. This research was made possible by financial support from the National Science Foundation (No. GP 4919X). We also wish to thank the Deutscher Akademischer Austauschdienst for a NATO research fellowship for W. P. F. and the Agency for International Development for a predoctoral fellowship

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bridging carbonyls. This increase in the occupation of the 2π (CO) orbitals may be attributed, even in the absence of decreased energy separation between the metal and 2π (CO) orbitals, to the fact that three metal atoms (rather than one) interact *via* direct orbital overlap with a given carbonyl ligand. In accounting for the decreased C–O bond order of a triply bridging carbonyl ligand relative to that for a terminal carbonyl ligand, one would also have to consider the occupancy changes of the 5σ (CO) and 1π (CO) orbitals as well as the 2π (CO) orbitals.[42] In accord with a much higher population of the 2π (CO) orbitals to give a more negatively charged oxygen atom, the expected significant increase in Lewis basicity of a triply bridging carbonyl group relative to that of a terminal carbonyl group has been experimentally demonstrated by Shriver and coworkers,[45] who prepared the oxygen–aluminum adduct $Fe_4(h^5\text{-}C_5H_5)_4(COAl(C_2H_5)_3)_4$ from $Fe_4(h^5\text{-}C_5H_5)_4(CO)_4$ and $Al_2(C_2H_5)_6$.

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(PIO/P No. 730/00239) for T.-T. The use of the UNIVAC 1108 computer at the University of Wisconsin Computing Center was made available by partial financial support from the National Science Foundation and the Wisconsin Alumni Research Foundation administered through the University Research Committee.

Complexes of Iron(II) and Iron(III) with the Tetradentate Macrocycle 5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene

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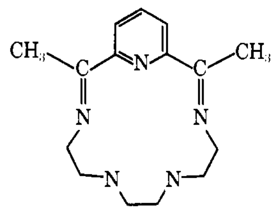
Abstract: A series of iron complexes of the cyclic ligand 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, [14]dieneN$_4$, have been isolated. The coordination number and spin state of the metal atom are dependent on the axial ligands. High-spin, five-coordinate iron(II) complexes were isolated when weak axial ligands were present and low-spin, six-coordinate complexes were isolated with strong axial ligands. One complex has a moment intermediate between the high-spin and low-spin values and has been shown to exist in spin-state equilibrium by the study of the temperature dependence of the magnetic susceptibility. The iron(II) complexes can be oxidized, yielding low-spin, six-coordinate iron(III) complexes.

The uncommon stability of the metal complexes of the new synthetic macrocyclic ligands makes them ideal candidates for studying a great variety of chemical phenomena. For example, they are especially suited to the study of ligand reactions[1,2] and unusual redox behavior.[3,4] It has been shown that oxidation states of copper, nickel, and cobalt which are not normally accessible can be stabilized with macrocyclic ligands. The facile redox behavior of iron, especially in naturally occurring systems, in conjunction with the many favorable characteristics of macrocyclic ligands, makes the study of these systems especially appealing.

Only a few iron complexes of the new nonporphyrin type macrocyclic ligands have been reported. Those iron complexes of 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene (I) form a unique series of seven-coordinate pentagonal-bipyramidal iron(III) complexes.[5] These structures have been confirmed by X-ray analyses.[6] The formation and subsequent stability of this pentadentate 15-membered ring with iron(III) may, in part, be due to special properties related to the d^5 metal ion. The containment of the iron(III) atom in the plane of the pentadentate macrocycle stands in contrast to the behavior of porphyrins. The 16-membered inner ring of porphyrin yields high-spin iron(III) species, in which it appears that the iron atom is too large to fit in the plane of the four nitrogen atoms so that it is significantly (0.5 Å) removed from that plane.[7]

We report here the synthesis and characterization of a variety of iron complexes containing the macrocycle 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (II, abbreviated 5,7,7,12,14,14-Me$_6$-[14]-diene-1,4,8,11-N$_4$ or, more simply, [14]dieneN$_4$).[8]



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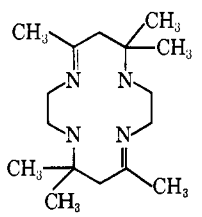

II

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(8) The complexity of the ligands discussed here, and their congeners, requires that the disparate nomenclatures that have been in use be reconciled [compare ref 9 with D. H. Busch, *Helv. Chim. Acta, Fasciculus extraordinarius, Alfred Werner*, 174 (1967)]. Curtis has used a systematic set of abbreviations, while Busch has used a trivial system. Further, the unsaturated ligands can be named according to two possible numbering systems (K. L. Loening, private communication). Since precedence is given to the heteroatoms, the locants for the four nitrogens in structure II are 1, 4, 8, 11 by either sequence. The simplest numbering technique would assign the locants 4, 11 to the two C=N groups. The alternate system, which we have previously used, minimizes the locants for the C=N groups as well as those for the heteroatoms, but it has the disadvantage that one, in effect, counts backward to assign a locant to the first (sequentially) C=N group. These locants become 1, 7 in this system, and to avoid confusion, the locant at the other end of the N=C group should be cited parenthetically 1(14), 7. To avoid the misunderstandings that follow from the use of the more subtle system, we are changing our practice and adopting the convention that always requires numbering in a single direction.

In order to represent these and related ligands by meaningful abbreviations, we are adopting, modifying, and extending Curtis' system. The principle modification involves the use of locants to indicate the positions of unsaturated linkages, rather than the less general cis and trans prefixes. Macrocyclic ring size is still to be indicated by a number in brackets. The complete abbreviation for structure II is 5,7,7,12,-14,14-Me$_6$-[14]-4,11-diene. More often than not, the locants for substituents will not be included when formulas for complexes are written, Ni(Me$_6$-[14]-4,11-diene)$^{2+}$, and upon repetition the substituents will