1 week at 5° producing three crops (410 mg) of (−)-*cis*-dichloro-(*trans*-cyclooctene)-(*S*)-(α-phenethylamine)platinum(II). When the olefin was recovered from the recrystallized levorotatory diastereoisomer, (+)-COT was obtained, with an optical purity of more than 95%.

Chemical Properties of the Complexes I. From all the complexes I, the olefin can be removed by reaction with cyanide aqueous solutions, or triphenylphosphine, or α,α′-bipyridine. By reduction with H_2 of the complexes I and II, either in solution or in the absence of solvents we obtained platinum metal and the saturated hydrocarbon corresponding to the olefin within a short period of time. Treatment of the (−) diastereoisomer of the ethyl α-chloroacrylate in acetone solution with H_2 at 50 psi led to the formation of racemic ethyl α-chloropropionate. This behavior supports the observation that the hydrogenation,[13] even if occurring with a stereospecific mechanism, is followed by a rapid racemization process with a rate of the same order as that of the hydrogenation reaction. With regard to this argument other experiments are in progress.

Acknowledgment. We wish to acknowledge many fruitful discussions with and the continuous support of Professor P. Corradini and the assistance of Dr. B, Pispisa in the gas chromatographic analyses.

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Structure of the Hexapyridineiron(II) Salt of the Tetranuclear Iron Carbonyl Anion, $[Fe_4(CO)_{13}]^{-2}$, with Comments Concerning the Nonisolation of the Corresponding Neutral Tetranuclear Iron Carbonyl, $Fe_4(CO)_{14}$

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Abstract: A three-dimensional single-crystal X-ray examination of the salt $[Fe(C_5H_5N)_6]^{2+}[Fe_4(CO)_{13}]^{2-}$ not only has shown a new type of molecular configuration for the diamagnetic tetrameric anion, $[Fe_4(CO)_{13}]^{2-}$, but also has produced definite stereochemical information concerning the nonexistence of the corresponding neutral iron carbonyl, $Fe_4(CO)_{14}$. The triclinic crystals of $[Fe(C_5H_5N)_6][Fe_4(CO)_{13}]$ contain two formula species in a unit cell of symmetry $P\bar{1}$ and of reduced-cell parameters $a = 10.09$, $b = 14.86$, $c = 15.61$ A, $\alpha = 90°\ 00'$, $\beta = 90°\ 00'$, $\gamma = 103°\ 12'$. Isotropic least-squares refinement carried out with a specially written full-matrix rigid-body program, in which the six pyridine rings were constrained to a fixed geometry, yielded final discrepancy factors of $R_1 = 10.9\%$ and $R_2 = 12.7\%$. The $[Fe_4(CO)_{13}]^{2-}$ anion of pseudo-threefold symmetry consists of four tetrahedrally oriented iron atoms in which an apical $Fe(CO)_3$ group is symmetrically coordinated by only iron–iron bonds to a basal $Fe_3(CO)_9$ fragment containing three identical $Fe(CO)_3$ groups located at the corners of an equilateral triangle and bonded to one another by iron–iron bonds. The thirteenth carbonyl group triply bridges the three basal iron atoms. As a result of weak interactions with neighboring basal iron atoms, three of the essentially terminal basal iron carbonyl groups are slightly deformed toward a doubly bridging carbonyl configuration. The chemical significance of these highly unsymmetrical doubly bridging groups is indicated. To a first approximation the carbonyl carbon atoms lie at the vertices of a polyhedral fragment which is related to an icosahedron. The criteria necessary for the possible formation of the polynuclear metal carbonyls and their derivatives are discussed, and the little appreciated importance of the stereochemical compatibility requirements of the ligands about the metal cluster in determining the compound's stoichiometry is stressed. The hexapyridineiron(II) cation, which has a regular octahedral array of six nitrogen atoms about the central iron(II) with the pyridine molecules oriented in three mutually perpendicular planes such that each pair of *trans* pyridine rings is coplanar, is one of the few known species belonging to the centosymmetric cubic point group T_h.

While no neutral tetranuclear carbonyl of iron has been prepared, the anion $[Fe_4(CO)_{13}]^{2-}$ is well known, having first been synthesized by Hieber and co-workers[2,3] in 1930. Initially, the products of the reactions of $Fe(CO)_5$ and $Fe_3(CO)_{12}$ with pyridine were formulated as $Fe_2(CO)_4(C_5H_5N)_3$[2] and $Fe(CO)_3$-(C_5H_5N),[3] respectively; Hieber and Werner[4] later recognized that only one product of stoichiometry $Fe_5(CO)_{13}(C_5H_5N)_6$ is formed from either of these two reactions. Their formulation of this complex as $[Fe(C_5H_5N)_6]^{2+}[Fe_4(CO)_{13}]^{2-}$ was based on conductance measurements which established its ionic character and on identification of one of the five iron atoms per formula unit as an iron(II) by its precipitation as $Fe(OH)_2$. The magnetic moment of 5.47 BM for this salt was of the magnitude expected for a single high-spin iron(II), thereby indicating that the anion is diamagnetic.[4] Reactions of the iron carbonyls with other bases have yielded a large number of additional salts containing the tetrameric anion.[4-8] All of the salts containing this anion are air sensitive, and many are

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[1] National Science Foundation Predoctoral Fellow, 1961–1964; this article is based in part on a dissertation by R. J. Doedens in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin, 1965.

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[4] W. Hieber and R. Werner, *ibid.*, **90**, 286, 1116 (1957).

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[6] W. Hieber and N. Kahlen, *ibid.*, **91**, 2223 (1958).

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pyrophoric. The reported infrared spectra of several ionic substances containing the $[Fe_4(CO)_{13}]^{2-}$ anion show considerable variation in the absorption band frequencies in the carbonyl stretching region.[7] For only one salt was an absorption band detected below 1900 cm^{-1} (*viz.*, at 1875 cm^{-1});[7] however, a very weak absorption band at 1829 cm^{-1} has recently been listed[9] for the anion in DMF solution.

Without the use of bridging carbonyls it is impossible to devise a probable structure in which each iron atom of the tetranuclear iron anion attains a closed-shell electronic configuration. Because of the lack of structural information on the $[Fe_4(CO)_{13}]^{2-}$ anion, a single crystal X-ray structural determination of $[Fe(C_5H_5N)_6][Fe_4(CO)_{13}]$ has been carried out. The salt of the hexapyridineiron(II) cation was chosen because of its relative stability (in the absence of air), its availability in crystalline form, and its amenability to a rigid-body least-squares refinement.

Experimental Section

Large, black, air-sensitive crystals of $[Fe(C_5H_5N)_6][Fe_4(CO)_{13}]$ were generously supplied by Professor Dr. Dr. W. Hieber and Dr. W. Beck of the Anorganisch-Chemisches Laboratorium der Technischen Hochschule, Munich, Germany. Considerable difficulty was encountered in obtaining a good single crystal, and a number of crystals (selected initially by optical inspection) were examined by X-ray photographs before a suitable one was found. A crystal of approximate dimensions 0.35 × 0.25 × 0.25 mm was used for gathering intensity data. This crystal was mounted about the 0.35-mm direction in a thin-walled glass capillary which was subsequently evacuated, filled with argon, and then sealed.

Multiple-film equiinclination Weissenberg data were taken with Zr-filtered Mo Kα radiation for reciprocal levels $0kl$ through $12kl$. In order to eliminate errors due to spot compaction on the lower half of the film,[10] a full 360° rotation range consisting of two separate sets of film data was taken for all levels except $0kl$. Reflections common to both sets of films were utilized in a least-squares merging program[11] which placed the two upper halves of each level on a common scale. The intensities were estimated visually by comparison with a calibrated set of intensities taken from the same crystal. Lattice constants were determined from $hk0$ and $h0l$ precession photographs which were calibrated by the superposition of a zero-level NaCl exposure on the same film. Corrections for Lorentz polarization effects and spot extension[12] were made, but absorption corrections were neglected due to the small absorption coefficient ($\mu R_{\max} = 0.4$). Atomic scattering factors were taken from the International Tables.[13] The standard deviations of the individual structure factor amplitudes were estimated as follows. If $I(hkl)_0 < \sqrt{10 I_{\min}}$, $\sigma(F(hkl)_0) = [|F(hkl)_0|/20][\sqrt{10}\, I_{\min}/I(hkl)_0]^2$; if $I(hkl)_0 \geq \sqrt{10}\, I_{\min}$, $\sigma(F(hkl)_0) = |F(hkl)_0|/20$.

Results

Crystal Data. Crystals of $[Fe(C_5H_5N)_6][Fe_4(CO)_{13}]$ are triclinic with reduced cell parameters $a' = 10.09 \pm 0.025$, $b' = 14.86 \pm 0.04$, $c' = 15.61 \pm 0.04$ A, $\alpha' = 90°\ 00' \pm 10'$, $\beta' = 90°\ 00' \pm 10'$, $\gamma' = 103°\ 12' \pm 10'$. The intensity data were taken with respect to a nonreduced primitive triclinic cell related to the above cell by the following transformation: $\mathbf{a}' = -\mathbf{c}$; $\mathbf{b}' = \mathbf{a} + \mathbf{c}$; $\mathbf{c}' = \mathbf{b}$. All results are reported in terms of this nonreduced cell, the lattice constants of which are $a = 15.95 \pm 0.04$, $b = 15.61 \pm 0.04$, $c = 10.09 \pm 0.025$ A, $\alpha = 90°\ 00' \pm 10'$, $\beta = 114°\ 50' \pm 10'$, $\gamma = 90°\ 00' \pm 10'$. The calculated density of 1.58 g/ml agrees with the observed density, which because of the instability of the crystals was only determined to lie in the range 1.58–1.66 g/ml. The centrosymmetric space group $P\bar{1}$ was inferred from the vector distribution of the Patterson function and later confirmed by the satisfactory refinement of the structure. The crystallographically independent unit thus contains one formula species composed of 5 iron, 13 oxygen, 6 nitrogen, 43 carbon, and 30 hydrogen atoms. All atoms were found from the structural analysis to occupy the general twofold set of positions (2i): $\pm(x,y,z)$.[14]

Determination of the Structure. Although the expected tetrahedral arrangement of the four iron atoms of the anion and the relative orientation of this tetrahedron in the unit cell were apparent from the three-dimensional Patterson function, initial attempts to locate this tetrahedron in the unit cell were unsuccessful. No self-consistent set of atomic coordinates based on the tetrahedral iron–iron vectors was found from the presumed single-weight Patterson vectors. In this connection the 20 strongest Patterson peaks were assumed to correspond to the 20 centrosymmetric double-weight, nonorigin vectors required for the five independent iron atoms in the space group $P\bar{1}$. A trial set of coordinates for three atoms was chosen and used together with an estimated isotropic thermal parameter of 1.5 A^2 as a model for calculation of structure factors, from which the discrepancy factors $R_1 = [\Sigma ||F_o| - |F_c|| / \Sigma |F_o|] \times 100$ and $R_2 = [\Sigma w ||F_o| - |F_c||^2 / \Sigma w |F_o|^2]^{1/2} \times 100$ yielded values of 58 and 63%, respectively. A Fourier synthesis based on these structure factors revealed distinct peaks, two of which were interpreted as the other two independent iron atoms whose positions were consistent with the double-weight vectors of the Patterson map. However, no single-weight Patterson vectors corresponding to these positions were present. Attempts to determine the light-atom positions by means of Fourier synthesis phased on these five tentative iron positions failed, and the discrepancy factors did not fall below 50%, thereby indicating that the model being used was incorrect.

The key to the solution of the structure was found when it was noted that the five strongest peaks (other than those for the five input iron atoms) on one of these Fourier maps formed an image which was related to the five trial iron positions by a nonimposed center of symmetry at $x = -0.125$, $y = 0.340$, and $z = 0.320$. The new atomic parameters obtained by a shift of the origin of the centrosymmetric unit cell to this point were observed to be in excellent agreement with the vectors of the Patterson map. These coordinates had not been found initially because of the coincidence of one of the single-weight vectors with a double-weight vector and because of the peak-height enhancement of another single-weight vector at $v = w = 1/2$, which thereby originally was assigned as a double-weight vector.

Based on the new coordinates of the five iron atoms as a starting point, the light-atom positions were obtained by means of successive Fourier syntheses.

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After location of all 67 nonhydrogen atoms in the asymmetric unit, the discrepancy factors R_1 and R_2 stood at 18 and 22%, respectively.

Rigid-Body Least-Squares Refinement. The large number of parameters and the presence of six pyridine rings made this structure a logical candidate for a rigid-body least-squares refinement.[15–20] In a rigid-body refinement certain subunits of the structure (in this case each of the pyridine rings) are constrained to a fixed geometry; the position of each such subunit (or group) in the unit cell is defined by six parameters, three fractional coordinates and three angles, which relate the origin and orientation of the internal group coordinate system to an external orthogonal system. An over-all group thermal parameter may be used[15–18] or the individual atomic temperature factors may be retained for the group atoms.[19,20]

The reduced number of parameters permits full-matrix least-squares refinement to be applied to problems which otherwise would be too large to permit such a refinement on existing computers. Group refinement sometimes is preferable to refinement of individual atoms even if the latter is possible. This is particularly true in cases in which insufficient data are available to justify refinement of individual atoms, although it should be emphasized that whenever possible it is desirable to remove the constraint of fixed-group geometries and observe the effect on the whole structure. The convergence properties of group refinement including both increased rate and range of convergence[15,16] make it extremely useful in the early stages of any refinement to which it is applicable. Recently this technique was successfully utilized[18b] in the refinement of a disordered structure for which a conventional least-squares refinement was impossible.

The only generally available rigid-body program, that of Scheringer,[15] did not have sufficient storage capacity to handle a problem of this size, primarily because Scheringer's program stores the full symmetric matrix of the normal equations. Since the widely used Busing–Martin–Levy least-squares program[21] stores only half of the matrix, it was used as a starting point for writing a new rigid-body refinement program in FORTRAN 63 for the CDC 1604 and 3600 computers. The basic features of the Scheringer program were incorporated into the framework of the local version of the Busing–Martin–Levy program. Changes included the generalization of Scheringer's transformation equations to make the procedure applicable to triclinic crystals and the replacement of provisions for over-all anisotropic group temperature factors with a provision for the optional use of individual isotropic atomic temperature factors for group atoms. The latter change was desirable because it has been found[19,20] in cases such as σ-coordinated phenyl rings, in which the amplitudes of thermal motion of the individual atoms in a group differ widely, that the use of individual isotropic atomic temperature factors for the atoms in a group leads to a better structural model than is obtained with one over-all group isotropic or anisotropic thermal parameter.

In this refinement the parameters used for each of the pyridine rings were constrained to those of pyridine in the vapor phase as determined from microwave spectroscopy by Bak, *et al.*[22] Recent X-ray structural investigations[23–25] have shown no significant variations in the geometry of metal- and hydrogen-coordinated pyridine rings from that of the free gaseous pyridine molecule. Refinement was first carried out with an over-all isotropic thermal parameter for each rigid group and individual atomic isotropic temperature factors for the nongroup atoms together with the group and atomic positional parameters and the 13 interlayer Weissenberg scale factors. Thus, the total number of parameters refined was 179, as opposed to the 268 parameters which would have been required for individual-atom refinement. Convergence was attained in four cycles with no parameter shifting by more than one-half of its standard deviation in the last cycle. At the conclusion of the fourth cycle the discrepancy factors R_1 and R_2 stood at 11.2 and 13.2%, respectively. Two additional cycles of refinement were carried out with individual temperature factors assigned to the group atoms. These two cycles lowered the discrepancy factors slightly to 11.0 and 13.0%. Because even the group refinement program did not have sufficient storage capacity to vary the 209 parameters involved in the last two cycles, the heavy-atom positional parameters were held constant in the first of these cycles, and the scale factors were not varied in the second. In the last cycle only four parameters, all of them atomic temperature factors for group atoms, shifted by more than one-half of their standard deviations with the largest shift being 0.8 standard deviation. Correction of two minor errors in the data further reduced R_1 and R_2 to their final values of 10.9 and 12.7%, respectively. A difference Fourier map based on the final parameters verified the correctness of the structure.

Although the decrease in the R values with the change to individual atomic thermal parameters was very small, the temperature factors of the atoms in a group do show the expected deviations from the value of the over-all group isotropic thermal parameter, with the temperature factors of the two *ortho* carbon atoms in general having been lowered and that of the *para* carbon atom raised. The rather small differences among the temperature factors for the atoms in a given ring presumably result from steric hindrances to group motion due to the relatively close packing of six pyridine rings about the iron(II). The final parameters listed in Tables I, II, and III are those from the refinement with individual isotropic atomic temperature factors for the group atoms. Calculated and observed structure factors are given in Table IV. Bond lengths and angles

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Table I. Positional and Thermal Parameters with Standard Deviations for Nongroup Atoms from Rigid-Body Least-Squares Refinement

Atom	x	$10^4\sigma(x)$	y	$10^4\sigma(y)$	z	$10^4\sigma(z)$	B, A^2	$\sigma(B)$
Fe(1)	0.2032	2	0.2503	2	0.2470	4	3.09	0.07
Fe(2)	0.6159	2	0.2466	2	0.2471	4	3.60	0.08
Fe(3)	0.7307	3	0.3267	3	0.1732	4	5.02	0.09
Fe(4)	0.7912	3	0.2561	3	0.4185	4	4.56	0.09
Fe(5)	0.7397	3	0.1667	3	0.1922	4	4.84	0.09
C(2–1)	0.5212	22	0.2312	19	0.0789	34	6.16	0.70
O(2–1)	0.4561	15	0.2171	12	−0.0332	22	6.47	0.46
C(2–2)	0.5740	22	0.3406	20	0.3055	32	6.46	0.72
O(2–2)	0.5346	13	0.3923	12	0.3327	21	5.58	0.36
C(2–3)	0.5876	16	0.1696	15	0.3502	25	3.54	0.49
O(2–3)	0.5656	13	0.1217	12	0.4149	20	5.60	0.41
C(3–1)	0.7858	15	0.3790	14	0.0907	24	3.33	0.49
O(3–1)	0.8235	15	0.4193	13	0.0257	22	7.19	0.49
C(3–2)	0.6266	19	0.3725	17	0.0689	29	4.94	0.59
O(3–2)	0.5590	15	0.4127	13	−0.0023	22	6.93	0.48
C(3–3)	0.7559	26	0.3901	25	0.3345	39	8.08	0.87
O(3–3)	0.7669	14	0.4588	14	0.3957	21	6.71	0.48
C(4–1)	0.9048	20	0.2724	17	0.5448	30	5.13	0.61
O(4–1)	0.9820	14	0.2822	12	0.6283	20	6.13	0.44
C(4–2)	0.7408	26	0.2815	22	0.5277	40	8.10	0.89
O(4–2)	0.7219	21	0.3020	18	0.6285	31	10.98	0.73
C(4–3)	0.7853	25	0.1412	23	0.4348	39	7.82	0.86
O(4–3)	0.7990	14	0.0729	13	0.5013	21	6.35	0.45
C(5–1)	0.8108	19	0.1011	16	0.1524	28	4.82	0.59
O(5–1)	0.8647	16	0.0550	14	0.1363	22	7.77	0.53
C(5–2)	0.6600	21	0.0897	19	0.1673	31	5.81	0.67
O(5–2)	0.6062	17	0.0315	14	0.1478	22	7.76	0.53
C(5–3)	0.6866	20	0.2139	17	0.0064	35	5.41	0.64
O(5–3)	0.6539	15	0.2155	12	−0.1213	25	6.90	0.49
C(345)	0.8430	20	0.2537	16	0.2698	28	4.95	0.59
O(345)	0.9190	14	0.2549	11	0.2730	19	5.99	0.43

Table II. Final Group Positional and Thermal Parameters for Six Pyridine Rings in Rigid-Body Least-Squares Refinement[a,b]

	Pyridine group					
	1	2	3	4	5	6
x_b	0.2753 (9)	0.0668 (9)	0.1730 (13)	0.1314 (10)	0.3346 (9)	0.2330 (12)
y_b	0.1326 (8)	0.2032 (10)	0.1795 (10)	0.3695 (9)	0.2954 (11)	0.3195 (10)
z_b	0.2170 (17)	0.0702 (14)	0.4203 (18)	0.2721 (18)	0.4243 (15)	0.0759 (16)
φ, degrees	−142.4 (5)	116.3 (8)	126.1 (8)	36.7 (6)	−63.3 (9)	−55.6 (7)
θ, degrees	−4.6 (5)	−47.6 (6)	44.8 (6)	2.8 (6)	48.2 (6)	−42.4 (6)
ρ, degrees	−38.6 (6)	169.0 (9)	76.3 (9)	38.7 (7)	−170.4 (10)	−87.6 (8)
B_g[c]	4.63 (24)	4.75 (24)	5.92 (27)	5.41 (26)	5.56 (27)	5.11 (25)

[a] Standard deviations of the last significant figures are given in parentheses. [b] The internal orthogonal axial system x',y',z' for *each* pyridine ring is defined as follows: The origin x_b,y_b,z_b is at the nitrogen atom; the $+x'$ direction is the C(5)–C(1) vector; the $+y'$ direction is the nitrogen–*p*-carbon vector; and z' is the vector product of y' and x'. The three angles φ, θ, and ρ refer to the orientation of the internal axial system with respect to an external orthogonal system by rotations about y', x', and z', respectively. In our program the orthogonal axes a_0, b_0, and c_0 for a right-handed system are defined relative to the crystal axes as: $a_0 = a, b_0 = c_0 \times a_0, c_0 = a \times b$. Since the crystal angles must be defined in the opposite sense than if a right-handed system were chosen (*i.e.*, a positive rotation in a left-handed system is defined as a clockwise rotation relative to the observation down the rotation axes from the positive direction), the definitions used in this case are $a_0 = a, b_0 = a_0 \times c_0, c_0 = b \times a$. [c] Values of B_g are taken from the final cycle of refinement in which group thermal parameters were employed. All other parameters are those from the refinement with individual temperature factors for the group atoms.

were calculated with the Busing–Martin–Levy function and error program[26] and are summarized in Tables V and VI, respectively. All Fourier summations were carried out with the Blount program.[27]

Discussion

As expected, crystalline $[Fe(C_5H_5N)_6]^{2+}[Fe_4(CO)_{13}]^{2-}$ is composed of discrete cations and anions. The tetrameric $[Fe_4(CO)_{13}]^{2-}$ anion shown in Figure 1 consists of four tetrahedrally situated iron atoms in which an apical $Fe(CO)_3$ group is symmetrically coordinated by only iron–iron bonds to a basal $Fe_3(CO)_9$ fragment containing three identical $Fe(CO)_3$ groups located at the corners of an equilateral triangle and bonded to one another by iron–iron bonds. The thirteenth carbonyl group bridges the three basal iron atoms. The resulting *idealized* configuration possesses C_3-3 symmetry with the pseudo-threefold axis (Figure 2) defined by the triply bridging carbonyl group and the apical iron atom, Fe(2). The iron–iron distances in the tetrahedron fall into two distinct groups. The average of the three distances to the apical iron atom, Fe(2), is 2.58 A, while the mean value of the iron–iron distances for the three basal iron atoms is 2.50 A. This variation in iron–iron distances is not uncommon[28,29]

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Table III. Positional and Thermal Parameters for Individual Atoms of the Six Pyridine Rings from the Rigid-Body Least-Squares Refinement

Atom	x	y	z	B, A^2	σ(B)
RN(1)	0.275	0.133	0.217	4.25	0.45
RC(1–1)	0.279	0.059	0.288	5.39	0.61
RC(1–2)	0.328	−0.013	0.280	5.17	0.59
RC(1–3)	0.376	−0.010	0.192	5.10	0.60
RC(1–4)	0.373	0.066	0.117	4.31	0.57
RC(1–5)	0.322	0.135	0.133	3.75	0.53
RN(2)	0.067	0.203	0.070	4.09	0.44
RC(2–1)	0.061	0.130	−0.002	4.40	0.58
RC(2–2)	−0.020	0.100	−0.116	5.25	0.61
RC(2–3)	−0.100	0.149	−0.157	5.38	0.61
RC(2–4)	−0.095	0.226	−0.082	5.23	0.61
RC(2–5)	−0.011	0.250	0.030	4.82	0.59
RN(3)	0.173	0.179	0.420	5.52	0.52
RC(3–1)	0.090	0.145	0.388	5.31	0.64
RC(3–2)	0.065	0.107	0.491	6.19	0.68
RC(3–3)	0.129	0.104	0.637	6.17	0.67
RC(3–4)	0.216	0.140	0.672	6.08	0.68
RC(3–5)	0.235	0.176	0.560	6.62	0.71
RN(4)	0.131	0.370	0.272	5.06	0.49
RC(4–1)	0.129	0.441	0.198	5.10	0.62
RC(4–2)	0.080	0.515	0.202	6.47	0.68
RC(4–3)	0.030	0.514	0.287	5.92	0.65
RC(4–4)	0.032	0.439	0.365	5.57	0.66
RC(4–5)	0.083	0.370	0.354	4.99	0.61
RN(5)	0.335	0.295	0.424	4.45	0.48
RC(5–1)	0.340	0.369	0.495	6.42	0.70
RC(5–2)	0.420	0.399	0.609	6.19	0.67
RC(5–3)	0.500	0.349	0.653	5.78	0.66
RC(5–4)	0.496	0.272	0.580	5.85	0.67
RC(5–5)	0.412	0.249	0.468	5.27	0.63
RN(6)	0.233	0.319	0.076	4.75	0.47
RC(6–1)	0.312	0.364	0.116	5.36	0.63
RC(6–2)	0.341	0.402	0.018	5.27	0.62
RC(6–3)	0.285	0.395	−0.131	5.70	0.64
RC(6–4)	0.203	0.349	−0.175	5.40	0.63
RC(6–5)	0.180	0.313	−0.068	4.70	0.59

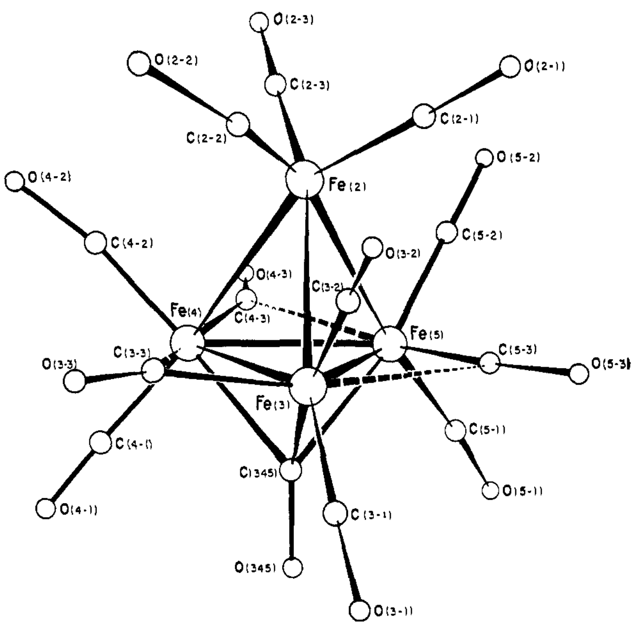

Figure 1. Configuration of the $[Fe_4(CO)_{13}]^{2-}$ anion.

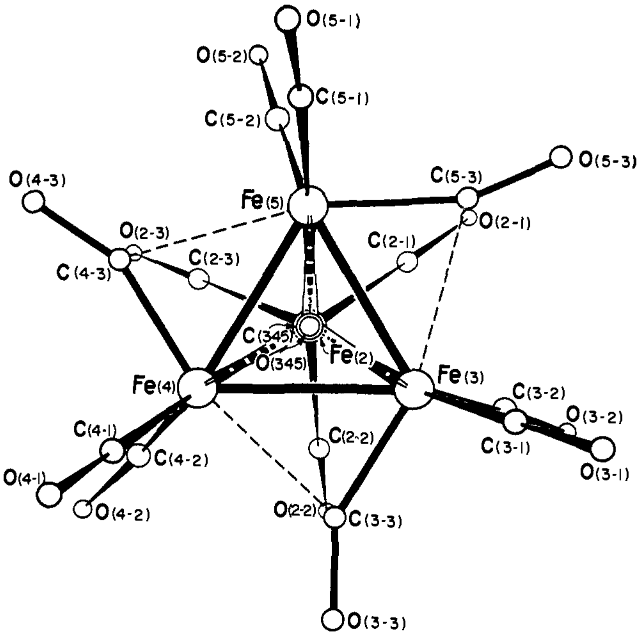

Figure 2. View of the $[Fe_4(CO)_{13}]^{2-}$ anion projected down its pseudo-threefold axis.

and no doubt is a consequence of the different character of the orbitals involved in the iron–iron bond formation, the effective iron charge, the iron coordination number, and steric and electronic factors imposed by the other iron-coordinated ligands.

The triply bridging carbonyl group equidistant from the three basal iron atoms is analogous to the triply bridging carbonyl groups found by X-ray diffraction studies in $(C_5H_5)_3Ni_3(CO)_2$,[30] $Rh_6(CO)_{16}$,[31] and $[C_5H_5FeCO]_4$.[32] The average Fe–CO distance of 1.96 A in the latter compound is in good agreement with the average Fe–(bridging carbonyl) distance of 2.00 A in the $[Fe_4(CO)_{13}]^{2-}$ anion. The average Fe–C–O angle of 134° for the bridging carbonyl group agrees closely with the corresponding angles of 134° in $(C_5H_5)_3Ni_3(CO)_2$,[30] 132° in $Rh_6(CO)_{16}$,[31] and 132° in $[C_5H_5FeCO]_4$.[32] The average value of 1.72 A for the distances for the nine "pure" terminal carbonyl groups (*vide infra*) is normal; the average terminal C–O distance of 1.18 A is similar to the single C–O distance of 1.20 A in the bridging carbonyl group. Other triply bridging carbonyl groups have been reported to give rise to infrared absorption bands at 1800 cm^{-1} in $Rh_6(CO)_{16}$,[33] 1625 cm^{-1} in $[(C_6H_6)_3Co_3(CO)_2]^+$,[34] and 1620 cm.$^{-1}$ in $[C_5H_5FeCO]_4$.[32] The infrared spectrum of $[Fe(C_5H_5N)_6][Fe_4(CO)_{13}]$ shows, in addition to a broad band in the terminal carbonyl region, a sharp but weak band at 1600 cm^{-1}. However, any attempt to assign unambiguously this band to the triply bridging carbonyl is precluded, since free pyridine has a number of strong absorption bands in the same region. In $[Fe(C_4H_8NH)_6][Fe_4(CO)_{13}]$

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(28) *Cf.* (a) C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966); (b) C. H. Wei, G. R. Wilkes, P. M. Treichel, and L. F. Dahl, *Inorg. Chem.*, **5**, 900 (1966); (c) J. F. Blount, L. F. Dahl, C. Hoogzand, and W. Hübel, *J. Am. Chem. Soc.*, **88**, 292 (1966), and references cited therein.

(29) J. Lewis and R. S. Nyholm, *Sci. Progr.*, **52**, 557 (1964); J. Lewis, in "Plenary Lectures of VIIIth International Conference on Coordination Chemistry," Butterworths, London, 1965, pp 11–36.

(30) A. A. Hock and O. S. Mills in "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, pp 640–648.

(31) E. R. Corey, L. F. Dahl, and W. Beck, *J. Am. Chem. Soc.*, **85**, 1202 (1963).

(32) M. A. Neuman, L. F. Dahl, and R. B. King, to be published; R. B. King, "Abstracts of Papers," 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 22-O.

(33) W. Beck and K. Lottes, *Chem. Ber.*, **94**, 2578 (1961).

(34) P. Chini and R. Ercoli, *Gazz. Chim. Ital.*, **88**, 1171 (1958).

Table IV, Calculated and Observed Structure Factors

an absorption band reported[7] at 1644 cm^{-1} and attributed to the presence of a ketonic impurity might be due to the stretching mode of the triply bridging carbonyl group.

Table V. Bond Lengths with Standard Deviations

Bond	Distance, A	Std dev, A	Bond	Distance, A	Std dev, A
Fe(2)–Fe(3)	2.57	0.006	Fe(5)–C(5–3)	1.85	0.03
Fe(2)–Fe(4)	2.60	0.005	Fe(3)–C(345)	2.00	0.03
Fe(2)–Fe(5)	2.58	0.005	Fe(4)–C(345)	1.99	0.03
Fe(3)–Fe(4)	2.50	0.006	Fe(5)–C(345)	2.02	0.03
Fe(3)–Fe(5)	2.50	0.006	C(2–1)–O(2–1)	1.19	0.03
Fe(4)–Fe(5)	2.50	0.006	C(2–2)–O(2–2)	1.12	0.03
Fe(2)–C(2–1)	1.75	0.03	C(2–3)–O(2–3)	1.14	0.02
Fe(2)–C(2–2)	1.81	0.03	C(3–1)–O(3–1)	1.23	0.03
Fe(2)–C(2–3)	1.77	0.03	C(3–2)–O(3–2)	1.19	0.03
Fe(3)–C(3–1)	1.66	0.02	C(3–3)–O(3–3)	1.21	0.03
Fe(3)–C(3–2)	1.70	0.03	C(4–1)–O(4–1)	1.17	0.03
Fe(3)–C(3–3)	1.80	0.04	C(4–2)–O(4–2)	1.22	0.04
Fe(4)–C(4–1)	1.74	0.03	C(4–3)–O(4–3)	1.23	0.03
Fe(4)–C(4–2)	1.66	0.04	C(5–1)–O(5–1)	1.18	0.03
Fe(4)–C(4–3)	1.81	0.04	C(5–2)–O(5–2)	1.21	0.03
Fe(5)–C(5–1)	1.70	0.03	C(5–3)–O(5–3)	1.17	0.03
Fe(5)–C(5–2)	1.69	0.03	C(345)–O(345)	1.20	0.03
Fe(1)–N(1)	2.25	[a]	Fe(1)–N(4)	2.26	[a]
Fe(1)–N(2)	2.28	[a]	Fe(1)–N(5)	2.22	[a]
Fe(1)–N(3)	2.29	[a]	Fe(1)–N(6)	2.25	[a]

[a] An esd value of 0.03 A is presumed on the basis of individual standard deviations of Fe–C bonds.

Examination of Figure 2 clearly shows a small but highly significant Fe–C–O angular distortion of each of the three carbonyl groups which lie essentially in the plane of the three basal iron atoms. This deformation can be interpreted as resulting from a weak interaction of the carbonyl carbon atom with a second basal iron atom. The evidence that these threefold-related carbonyl groups form highly unsymmetrical doubly bridging groups is based on the following three geometric features: (1) the deviation from linearity toward a doubly bridging configuration for the three Fe–C–O bond angles which possess significantly smaller angles (151, 155, and 158°) than the other nine terminal Fe–C–O angles for which the smallest angle is 167°; (2) distances from each of the three basal carbonyl carbon atoms to the second basal iron atom of only 2.24, 2.28, and 2.33 A, as contrasted with the other closest intramolecular nonbonding Fe···CO distances of 2.72, 2.74, and 2.76 A observed for the three (basal iron)-coordinated carbonyl carbon atoms nearest the apical iron atom; (3) longer bonding Fe–CO distances of 1.80, 1.81, and 1.85 A compared to the average Fe–CO distance of 1.72 A for the other nine terminal carbonyl groups. A similar small deformation of a terminal carbonyl group toward a doubly bridging group has been noted by Hock and Mills[35] in $(CH_3C_2OH)_2Fe_2(CO)_6$, in which a second Fe–CO distance of 2.48 A and a corresponding Fe–C–O angle of 168° were observed. Two asymmetrically doubly bridging carbonyl groups, with Fe–CO distances of 1.84 and 1.99 A to the first and 1.77 and 1.99 A to the second, have been reported by Dodge and Schomaker[36] for the black isomer of $(C_6H_5C_2C_6H_5)_2Fe_3(CO)_8$. These structural results demonstrate that carbonyl groups in metal carbonyl complexes may take on a number of configurations which are intermediate between the terminal and symmetrical doubly bridging cases.

The structural features given above in these highly unsymmetrical doubly bridging metal carbonyl complexes not only indicate the mechanistic pathway in the conversion of a terminal carbonyl group to a symmetrical doubly bridged carbonyl group but also provide indirect support of the proposed mechanistic route involving methyl group migration to a terminal carbonyl carbon atom in reactions of methyl–transition metal–carbonyl complexes such as $CH_3Mn(CO)_5$ and $C_5H_5Fe(CO)_2CH_3$ with a variety of nucleophiles which give acetyl derivatives.[37] The presumed analogous structural change no doubt involves an interaction of the terminal carbonyl carbon atom with the migrating methyl group together with a concomitant weakening of the metal–CO bond (as evidenced in the $[Fe_4(CO)_{13}]^{2-}$ anion by the observed longer metal–CO terminal distance as the carbonyl group interacting with the second metal becomes in the limiting case a symmetrical bridging group) to give the metal–COR group without any metal–carbonyl bond-breaking.

The long iron–carbon interaction completes a distorted octahedron about each basal iron atom in the $[Fe_4(CO)_{13}]^{2-}$ anion. These six octahedral-type sites are occupied by three terminal carbonyl carbon atoms, the carbon atom of the triply bridging carbonyl group, the apical iron atom, and the weakly interacting carbonyl carbon atom. The other two basal iron atoms are located somewhat above the midpoint of one octahedral-type edge and along a threefold axis of the octahedron, respectively. Thus, the basal iron atoms are either seven- or eight-coordinated, depending on whether the weak iron–carbon interaction is considered in determining the coordination number. A seven-coordinated description corresponds to a distorted version of a 4:3 orientation of ligands.[38] The apical iron atom has a localized trigonal environment about it. A bookkeeping of electrons for the $[Fe_4(CO)_{13}]^{2-}$ anion shows both types of iron atoms to conform to the closed-shell ground-state configuration in agreement with the susceptibility measurements.

A salient feature is that the carbon atoms of the twelve essentially terminal carbonyl groups lie at the vertices of a polyhedral-type geometry which is related to an icosahedron. If four parallel planes, each containing an equilateral triangle of vertices, are drawn through the twelve vertices of a regular icosahedron and labeled A, B, C, and D in sequence, then the twelve carbonyl carbon atoms, beginning with the three bonded to the apical iron atom, Fe(2), define planes in the order A, B, C, B. In other words, it is as if an icosahedron were mirrored about plane C and then truncated at the mirror image of plane B. The triply bridging carbonyl group lies 0.12 A above the center of this mirrored plane B. The nonbinding C···C distances, which correspond to the edges of the polyhedral fragment, vary from 2.45 to 3.11 A and are listed in Table VII. It is noteworthy that these tabulated nonbonding distances show that the directionally significant shifts of the three basal carbonyl carbon atoms from their otherwise undistorted terminal carbonyl positions toward a doubly bridging configuration result in a more nearly regular polyhedral-type fragment.

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

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

(37) *Cf.* J. P. Bibler and A. Wojcicki, *Inorg. Chem.*, 5, 889 (1966), and references cited therein.

(38) C. H. Wei and L. F. Dahl, *ibid.*, 4, 493 (1965); L. F. Dahl and P. W. Sutton, *ibid.*, 2, 1067 (1963).

Table VI, Bond Angles and Standard Deviations

	Angle, degrees	Std dev, degrees		Angle, degrees	Std dev, degrees
Fe(3)–Fe(2)–Fe(4)	57.87	0.15	C(4–1)–Fe(4)–C(4–2)	97.2	1.6
Fe(3)–Fe(2)–Fe(5)	58.10	0.15	C(4–1)–Fe(4)–C(4–3)	99.0	1.5
Fe(4)–Fe(2)–Fe(5)	57.70	0.14	C(4–2)–Fe(4)–C(4–3)	96.8	1.7
Fe(2)–Fe(3)–Fe(4)	61.65	0.15	C(5–1)–Fe(5)–C(5–2)	94.1	1.3
Fe(2)–Fe(3)–Fe(5)	61.19	0.15	C(5–1)–Fe(5)–C(5–3)	93.9	1.2
Fe(4)–Fe(3)–Fe(5)	59.96	0.16	C(5–2)–Fe(5)–C(5–3)	97.9	1.2
Fe(2)–Fe(4)–Fe(3)	60.48	0.15	Fe(2)–C(2–1)–O(2–1)	176.9	2.7
Fe(2)–Fe(4)–Fe(5)	60.81	0.14	Fe(2)–C(2–2)–O(2–2)	168.8	2.9
Fe(3)–Fe(4)–Fe(5)	60.03	0.16	Fe(2)–C(2–3)–O(2–3)	176.9	2.3
Fe(2)–Fe(5)–Fe(3)	60.71	0.15	Fe(3)–C(3–1)–O(3–1)	177.5	2.1
Fe(2)–Fe(5)–Fe(4)	61.50	0.15	Fe(3)–C(3–2)–O(3–2)	172.9	2.4
Fe(3)–Fe(5)–Fe(4)	60.01	0.16	Fe(3)–C(3–3)–O(3–3)	151.1	2.9
Fe(3)–Fe(2)–C(2–1)	102.4	1.0	Fe(4)–C(4–1)–O(4–1)	178.5	2.4
Fe(3)–Fe(2)–C(2–2)	96.1	1.0	Fe(4)–C(4–2)–O(4–2)	166.9	3.4
Fe(3)–Fe(2)–C(2–3)	152.8	0.8	Fe(4)–C(4–3)–O(4–3)	155.0	2.8
Fe(4)–Fe(2)–C(2–1)	154.2	1.0	Fe(5)–C(5–1)–O(5–1)	174.8	2.4
Fe(4)–Fe(2)–C(2–2)	100.3	1.0	Fe(5)–C(5–2)–O(5–2)	176.3	2.8
Fe(4)–Fe(2)–C(2–3)	96.7	0.8	Fe(5)–C(5–3)–O(5–3)	157.6	2.4
Fe(5)–Fe(2)–C(2–1)	98.7	1.0	Fe(2)–Fe(3)–C(345)	100.5	0.8
Fe(5)–Fe(2)–C(2–2)	151.7	1.0	Fe(4)–Fe(3)–C(345)	51.1	0.8
Fe(5)–Fe(2)–C(2–3)	101.8	0.8	Fe(5)–Fe(3)–C(345)	51.9	0.8
Fe(2)–Fe(3)–C(3–1)	167.8	0.8	Fe(2)–Fe(4)–C(345)	99.7	0.8
Fe(2)–Fe(3)–C(3–2)	75.9	0.9	Fe(3)–Fe(4)–C(345)	51.2	0.8
Fe(2)–Fe(3)–C(3–3)	85.4	1.2	Fe(5)–Fe(4)–C(345)	52.0	0.8
Fe(4)–Fe(3)–C(3–1)	130.4	0.8	Fe(2)–Fe(5)–C(345)	99.5	0.8
Fe(4)–Fe(3)–C(3–2)	131.8	0.9	Fe(3)–Fe(5)–C(345)	51.0	0.8
Fe(4)–Fe(3)–C(3–3)	60.0	1.2	Fe(4)–Fe(5)–C(345)	51.0	0.8
Fe(5)–Fe(3)–C(3–1)	120.3	0.8	C(3–1)–Fe(3)–C(345)	88.3	1.1
Fe(5)–Fe(3)–C(3–2)	118.4	0.9	C(3–2)–Fe(3)–C(345)	169.0	1.2
Fe(5)–Fe(3)–C(3–3)	119.7	1.2	C(3–3)–Fe(3)–C(345)	93.3	1.4
Fe(2)–Fe(4)–C(4–1)	172.8	0.9	C(4–1)–Fe(4)–C(345)	85.5	1.2
Fe(2)–Fe(4)–C(4–2)	76.7	1.3	C(4–2)–Fe(4)–C(345)	166.4	1.4
Fe(2)–Fe(4)–C(4–3)	85.5	1.1	C(4–3)–Fe(4)–C(345)	95.9	1.4
Fe(3)–Fe(4)–C(4–1)	120.6	0.9	C(5–1)–Fe(5)–C(345)	88.8	1.2
Fe(3)–Fe(4)–C(4–2)	117.2	1.2	C(5–2)–Fe(5)–C(345)	167.2	1.3
Fe(3)–Fe(4)–C(4–3)	120.9	1.1	C(5–3)–Fe(5)–C(345)	94.4	1.2
Fe(5)–Fe(4)–C(4–1)	126.3	0.9	Fe(3)–C(345)–O(345)	133.9	2.1
Fe(5)–Fe(4)–C(4–2)	132.3	1.3	Fe(4)–C(345)–O(345)	135.5	2.1
Fe(5)–Fe(4)–C(4–3)	61.3	1.1	Fe(5)–C(345)–O(345)	132.2	2.0
Fe(2)–Fe(5)–C(5–1)	171.4	0.9	N(1)–Fe(1)–N(2)	90.1	[a]
Fe(2)–Fe(5)–C(5–2)	77.3	1.0	N(1)–Fe(1)–N(3)	90.6	[a]
Fe(2)–Fe(5)–C(5–3)	87.7	0.9	N(1)–Fe(1)–N(4)	178.4	[a]
Fe(3)–Fe(5)–C(5–1)	127.3	0.9	N(1)–Fe(1)–N(5)	90.0	[a]
Fe(3)–Fe(5)–C(5–2)	133.0	1.0	N(1)–Fe(1)–N(6)	90.0	[a]
Fe(3)–Fe(5)–C(5–3)	62.6	0.9	N(2)–Fe(1)–N(3)	90.3	[a]
Fe(4)–Fe(5)–C(5–1)	123.8	0.9	N(2)–Fe(1)–N(4)	89.6	[a]
Fe(4)–Fe(5)–C(5–2)	118.1	1.0	N(2)–Fe(1)–N(5)	178.8	[a]
Fe(4)–Fe(5)–C(5–3)	122.5	0.9	N(2)–Fe(1)–N(6)	89.5	[a]
C(2–1)–Fe(2)–C(2–2)	98.1	1.4	N(3)–Fe(1)–N(4)	92.1	[a]
C(2–1)–Fe(2)–C(2–3)	98.5	1.3	N(3)–Fe(1)–N(5)	88.3	[a]
C(2–2)–Fe(2)–C(2–3)	98.0	1.3	N(3)–Fe(1)–N(6)	180.0	[a]
C(3–1)–Fe(3)–C(3–2)	93.8	1.2	N(4)–Fe(1)–N(5)	90.3	[a]
C(3–1)–Fe(3)–C(3–3)	102.6	1.4	N(4)–Fe(1)–N(6)	88.5	[a]
C(3–2)–Fe(3)–C(3–3)	96.8	1.5	N(5)–Fe(1)–N(6)	92.0	[a]

[a] These standard deviations are estimated to lie in the range of 1.2–1.5°.

A stereochemical implication of this polyhedral-type array of 13 carbonyl groups disposed around the tetrahedron of iron atoms in $[Fe_4(CO)_{13}]^{2-}$ is that this anion cannot add a 14th carbonyl group in place of the two electrons to give a polyhedral-type geometry of carbonyl ligands about the tetrahedral iron cluster which will enable each iron still to conform to a closed-shell electronic configuration. Geometrical considerations of possible scaled molecular models indicate that *no* reasonable arrangement of fourteen carbonyl groups can exist about any cluster of four iron atoms which would conform to realistic molecular parameters and at the same time would satisfy the electronic requirements of each iron atom. This rationalization for the nonisolation of the neutral tetranuclear iron carbonyl, $Fe_4(CO)_{14}$,[39] on the basis of stereochemical considerations of the carbonyl groups can be generalized to other metal cluster systems. Although it is well recognized that the *stoichiometry* of the metal carbonyls and their derivatives is dictated to a large extent by the electronic

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(39) Of interest is that the formula $Fe_4(CO)_{14}$ is in accord with the Sidgwick–Bailey relationship[40] which provides different $M_x(CO)_y$ stoichiometries compatible with the so-called "noble gas configuration" of each of the metal atoms. As noted previously,[41] this rule contains the inherent assumption that each metal forms metal–metal bonds to every other metal.

(40) N. V. Sidgwick and R. W. Bailey, *Proc. Roy. Soc.* (London), **144,** 521 (1934).

(41) E. H. Braye, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Am. Chem. Soc.*, **84,** 4633 (1962).

Table VII. Nonbonding Carbon–Carbon Distances Corresponding to Edges of Icosahedral-Type Fragment in $[Fe_4(CO)_{13}]^{2-}$

	Distance, A	Std dev, A		Distance, A	Std dev, A
C(2–1)···C(2–2)	2.69	0.04	C(5–3)···C(3–1)	2.96	0.04
C(2–2)···C(2–3)	2.70	0.04	C(3–1)···C(3–3)	2.70	0.04
C(2–3)···C(2–1)	2.67	0.04	C(3–3)···C(4–1)	3.05	0.05
			C(4–1)···C(4–3)	2.70	0.05
C(2–1)···C(3–2)	2.80	0.04	C(4–3)···C(5–1)	3.11	0.04
C(3–2)···C(2–2)	2.89	0.04	C(5–1)···C(5–3)	2.60	0.04
C(2–2)···C(4–2)	2.82	0.05			
C(4–2)···C(2–3)	2.92	0.04	C(3–2)···C(3–1)	2.46	0.04
C(2–3)···C(5–2)	2.84	0.04	C(4–2)···C(4–1)	2.55	0.05
C(5–2)···C(2–1)	2.99	0.04	C(5–2)···C(5–1)	2.48	0.04
C(2–1)···C(5–3)	3.03	0.04	C(5–3)···C(345)	2.85	0.04
C(2–2)···C(3–3)	2.90	0.05	C(3–3)···C(345)	2.77	0.05
C(2–3)···C(4–3)	2.93	0.04	C(4–3)···C(345)	2.83	0.05
C(3–2)···C(3–3)	2.62	0.05	C(3–1)···C(345)	2.56	0.04
C(3–3)···C(4–2)	2.67	0.05	C(4–1)···C(345)	2.54	0.04
C(4–2)···C(4–3)	2.60	0.05	C(5–1)···C(345)	2.61	0.04
C(4–3)···C(5–2)	2.72	0.04			
C(5–2)···C(5–3)	2.67	0.04			
C(5–3)···C(3–2)	2.82	0.04			

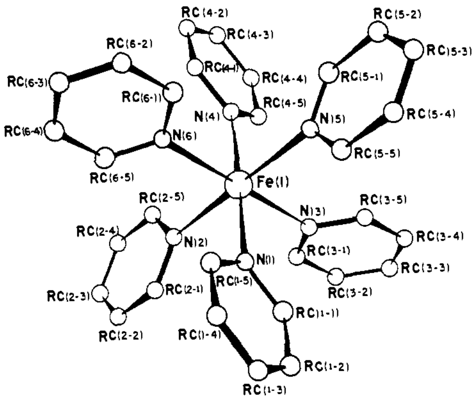

Figure 3. Configuration of the hexapyridineiron(II) cation, $[Fe(C_5H_5N)_6]^{2+}$.

(and orbital) requirements of the metal atoms, the importance of the stereochemical disposition of the ligands about the metal atoms has not been appreciated. As a consequence of the formation to a first approximation of a relatively close-packed polyhedron or polyhedral fragment by the ligand atoms coordinated to the metal cluster, the *idealized* symmetry of the polynuclear metal carbonyls and many of their derivatives is generally high. For example, the twelve carbonyl groups in $Fe_3(CO)_{12}$ and $Co_4(CO)_{12}$ are disposed toward the corners of a regular icosahedron (thereby accounting for the observed crystal disorder of both complexes),[28a] while in $Ir_4(CO)_{12}$ they are directed toward the vertices of a cuboctahedron.[42] The prime importance of this principle of the combined stereochemical and electronic compatibility requirements of the ligands in accounting for the nonexistence of certain neutral analogs of metal carbonyl anions has already been illustrated by the fact that the configuration of the monohydridic anions, $HM_2(CO)_{10}^-$ (M = Cr, Mo, W), does *not* allow further protonation to form the corresponding dihydric dimeric complexes.[43]

The configuration of the $[Fe(C_5H_5N)_6]^{2+}$ cation is shown in Figure 3. The iron(II) has the expected regular octahedral environment of six nitrogen atoms about it with the pyridine molecules lying in three mutually perpendicular planes and with each pair of *trans* pyridine rings coplanar. The over-all *idealized* symmetry of the cation is T_h-2/m$\bar{3}$. Although rather rare, this centrosymmetric cubic symmetry is not unprecedented, having previously been found (but not always recognized) in a series of cubic hexanitrometalate(II) complexes with the anions $[M(NO_2)_6]^{4-}$ (M = Fe, Co, Ni, Cu)[44–47] and in several hexanitrometalate(III) complexes with the anions $[M(NO_2)_6]^{3-}$ (M = Co, Rh, Ir, Bi).[44,45] The pseudo-threefold axis of the anion $[Fe_4(CO)_{13}]^{2-}$ is almost coincident with one of the threefold axes of $[Fe(C_5H_5N)_6]^{2+}$ and is within 3° of being collinear with the *a* axis.

Although the T_h configuration of the $[Fe(C_5H_5N)_6]^{2+}$ cation would be predicted simply on the basis of intraionic packing considerations by which intramolecular nonbonding interactions are minimized, it is also the configuration which maximizes the overlap of the one bonding π orbital (and any existing higher energy antibonding orbitals) for each of the two *trans*-related ligands with the appropriate one of the three d_π orbitals of the metal ion (to the extent that any significant π overlap occurs). Hence, in the absence of distorting forces including hydrogen bonding (as occurs in the case of six H_2O ligands) and/or Jahn–Teller effects, any octahedral-type complex of a transition metal containing six identical ligands of C_{2v} localized ligand symmetry would presumably have T_h molecular symmetry.

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