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# Crystal and Molecular Structure of $\pi$-$C_5H_5Fe(CO)_3PF_6$, a Cationic Iron Carbonyl Complex

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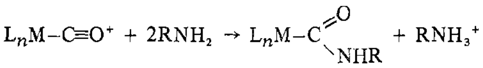
The crystal structure of $\pi$-$C_5H_5Fe(CO)_3PF_6$ has been determined by three-dimensional single-crystal X-ray analysis. The compound crystallizes in the orthorhombic space group *Pbca* with $a = 15.235$ (9), $b = 12.672$ (5), and $c = 12.422$ (12) Å. Least-squares refinement of 2662 reflections resulted in a final agreement factor of $R = 0.083$. The coordination around the iron atom is essentially octahedral with three carbonyl monodentate ligands and one $C_5H_5^-$ tridentate ligand. The $PF_6^-$ ions are also essentially octahedral. The positively charged iron carbonyl complex exhibits C–O distances that are significantly shorter and Fe–C distances that are longer than in the neutral species. The C–O distances were also found to be shorter than those in isoelectronic $\pi$-$C_5H_5Mn(CO)_3$; moreover, there is a 12° rotation of the carbon monoxide ligands about the Fe–($C_5H_5$) axis of the molecule relative to the cyclopentadienyl ring.

## Introduction

Angelici and coworkers have extensively studied reactions of metal carbonyls with primary and secondary amines to form carboxamido complexes[1-3]



$$L_nM{-}C{\equiv}O^+ + 2RNH_2 \rightarrow L_nM{-}C\begin{matrix}{\scriptstyle\nearrow} O\\ {\scriptstyle\searrow} NHR\end{matrix} + RNH_3^+$$

In particular, for iron cyclopentadienyl cations $[C_5H_5Fe(CO)_2L^+]$ where L = CO or $P(C_6H_5)_3$, they found that carboxamido complexes readily formed. In contrast, $\pi$-$C_5H_5$-$Mn(CO)_3$ which is isoelectronic with $\pi$-$C_5H_5Fe(CO)_3^+$ will not react under the same conditions. We felt it would be worthwhile to carry out the structure investigation of $\pi$-$C_5H_5Fe(CO)_3PF_6$ as this would be the first structure determination of an iron carbonyl cation and the results could be compared with those from the isoelectronic manganese species.

## Experimental Section

Crystals of the compound were obtained from Dr. Angelici and their preparation is discussed elsewhere.[1] Preliminary examination *via* precession photographs exhibited *mmm* diffraction symmetry indicating an orthorhombic space group. Systematic absences for $0kl$ ($k \neq 2n$), $h0l$ ($l \neq 2n$), and $hk0$ ($h \neq 2n$) uniquely determine the space group to be *Pbca*. The unit cell parameters obtained with chromium radiation ($\lambda(K\alpha)$ 2.2909, $\lambda(K\beta)$ 2.0848 Å) at 24° are $a = 15.235 \pm 0.009$, $b = 12.672 \pm 0.005$, and $c = 12.422 \pm 0.012$ Å. These parameters were obtained by a least-squares fit of 14 $2\theta$ values measured from zero-level Weissenberg films calibrated with superimposed aluminum powder lines ($a_0 = 4.0410$ Å). The calculated density of 1.93 g/cm³ for 8 molecules per cell agrees well with the observed density of $1.83 \pm 0.08$ g/cm³ determined by flotation techniques.

For data collection, a crystal of dimensions 0.30 × 0.32 × 0.32 mm and nearly cubic was mounted on the end of a glass fiber using Duco cement.

Intensity data were taken at room temperature (24°) using Zr-filtered Mo K$\alpha$ ($\lambda$ 0.7107 Å) radiation on a fully automated Hilger-Watts four-circle diffractometer equipped with a scintillation counter and interfaced to an SDS-910 computer in a real-time mode. One octant of data was collected within a $\theta$ sphere of 30°. Intensities were measured by counting at the peak center ($\theta_{hkl}$) for 10 sec with two 5-sec background counts at $\theta_{hkl} \pm (0.25 + 0.01\theta_{hkl})$. For conversion of peak height to integrated data, some integrated intensities were taken by the step-scan (moving-crystal, moving-counter) technique,[4] and the integrated-peak height ratios were plotted as a function of $\theta$ (0–30°). (No dependence on $\chi$ or $\phi$ was observed.) The intensities of three standard reflections which were remeasured periodically showed no decrease in intensity during data collection.

All intensity data were corrected for background and Lorentz-polarization effects. Because the linear absorption coefficient was small ($\mu = 15.2$ cm$^{-1}$), no absorption correction was made. Minimum and maximum transmission factors were 0.61 and 0.63. Standard deviations ($\sigma_I$) in the intensities were estimated from the total count (TC) and background count (BC) values by $(\sigma_I)^2 = TC + BC + (0.05TC)^2 + (0.05BC)^2 + (0.05I)^2$. The last three factors represent estimates for nonstatistical errors in the total count, background count, and the net intensity, respectively. The estimated standard deviation in the structure factor ($\sigma_F$) was found by the finite difference method.[5] Of the 4175 reflections measured, 2662 had $F_o > 2.5\sigma_F$ and were considered observed.

## Solution and Refinement of the Structure

The coordinates of the iron and phosphorus atoms were readily determined from an unsharpened Patterson map, and subsequent structure factor and electron density map calculations revealed the positions of the other atoms. The structure was refined by a full-matrix least-squares procedure using a local modification of Busing, Martin, and Levy's ORFLS.[6] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ where $w$ is the weight defined as $1/\sigma^2(F_o)$. Isotropic refinement resulted in a conventional discrepancy factor ($R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$) of 0.154 and a weighted discrepancy factor ($R_w = [\Sigma w \cdot (|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$) of 0.214.

After conversion to anisotropic temperature factors, final convergence was reached at $R = 0.083$ and $R_w = 0.111$, with the average shift per error for the last cycle of 0.04. A final electron density difference map showed no peaks greater than 1.1 e/Å³; there were some small peaks between fluorine atom positions, suggesting some rotational disorder of the $PF_6$ group.

Addition of hydrogen atom positions at calculated C–H distances of 1.07 Å and further refinement of the original structure resulted in $R = 0.082$ and $R_w = 0.111$.

The relativistic Hartree–Fock scattering factors of Doyle and Turner[7] for $Fe^{2+}$, P, F, O, and C were used, with those of iron and phosphorus modified for the real and imaginary parts of anomalous dispersion.[8] Hydrogen scattering factors are from the tables by Hanson, *et al.*[9] The observed and calculated structure factors are available.[10] The final positional and thermal parameters and their standard deviations as derived from the inverse matrix of the final least-squares cycle are given in Table I. In Table II are listed the calculated positions of the hydrogen atoms in the cyclopentadienyl ring. Interatomic distances and angles and their deviations as cal-

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(4) L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, 15, 983 (1962).

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(6) In addition to ORFLS, the authors wish to acknowledge the use of ORFFE (Busing, Martin, and Levy), ORTEP (C. K. Johnson), and LSP, a least-squares plane program by D. E. Williams.

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(8) K. Lonsdale, Ed., "International Tables for X-Ray Crystallography," Vol. III, 2nd ed, Kynoch Press, Birmingham, England, 1968, p 215.

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**Table I.** Final Atomic Coordinates and Thermal Parameters[a]

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Fe | 0.13043 (4) | 0.10282 (5) | 0.20710 (6) | 0.00328 (3) | 0.00464 (5) | 0.00591 (5) | −0.00010 (3) | −0.00012 (3) | −0.00003 (3) |
| P | 0.41234 (10) | 0.24667 (11) | 0.04335 (12) | 0.00517 (7) | 0.00637 (9) | 0.00620 (9) | −0.00033 (6) | −0.00031 (6) | 0.00049 (7) |
| F(1) | 0.31169 (40) | 0.26715 (68) | 0.06988 (63) | 0.00631 (27) | 0.02903 (103) | 0.02124 (79) | −0.00298 (42) | 0.00007 (39) | 0.00197 (70) |
| F(2) | 0.40268 (76) | 0.12625 (40) | 0.05398 (51) | 0.03033 (101) | 0.00677 (32) | 0.01293 (54) | −0.00187 (47) | −0.00283 (60) | 0.00008 (33) |
| F(3) | 0.01264 (45) | 0.22985 (84) | 0.47439 (62) | 0.00766 (34) | 0.03797 (150) | 0.01862 (81) | 0.00589 (57) | −0.00356 (39) | −0.00581 (79) |
| F(4) | 0.42523 (65) | 0.36658 (40) | 0.03427 (48) | 0.02515 (89) | 0.00731 (33) | 0.01273 (50) | −0.00153 (45) | 0.00134 (49) | 0.00024 (33) |
| F(5) | 0.42709 (39) | 0.25105 (41) | 0.17063 (36) | 0.01202 (38) | 0.01419 (48) | 0.00697 (28) | 0.00052 (34) | −0.00135 (28) | −0.00034 (30) |
| F(6) | 0.39918 (44) | 0.25733 (40) | 0.41774 (36) | 0.01437 (43) | 0.01270 (44) | 0.00669 (29) | −0.00057 (36) | −0.00159 (31) | 0.00058 (26) |
| O(1) | 0.09838 (47) | 0.32932 (39) | 0.19661 (47) | 0.01012 (39) | 0.00519 (29) | 0.01690 (66) | −0.00020 (27) | −0.00135 (39) | −0.00037 (32) |
| O(2) | 0.17060 (41) | 0.41128 (51) | 0.47587 (37) | 0.00812 (32) | 0.01585 (61) | 0.00592 (32) | 0.00041 (33) | 0.00087 (26) | 0.00118 (31) |
| O(3) | 0.44832 (27) | 0.03252 (39) | 0.31397 (44) | 0.00360 (18) | 0.00929 (37) | 0.01447 (51) | −0.00106 (20) | 0.00069 (23) | −0.00178 (33) |
| C(1) | 0.10855 (45) | 0.24241 (44) | 0.20005 (52) | 0.00599 (29) | 0.00514 (33) | 0.00938 (51) | −0.00047 (25) | −0.00013 (31) | −0.00009 (30) |
| C(2) | 0.15460 (42) | 0.09397 (49) | 0.06300 (50) | 0.00541 (28) | 0.00804 (43) | 0.00650 (39) | −0.00060 (27) | −0.00018 (27) | −0.00052 (33) |
| C(3) | 0.01693 (36) | 0.06215 (46) | 0.19108 (46) | 0.00395 (22) | 0.00604 (33) | 0.00800 (42) | −0.00057 (22) | −0.00021 (24) | 0.00077 (30) |
| C(4) | 0.24970 (48) | 0.11375 (79) | 0.28654 (75) | 0.00429 (28) | 0.01256 (76) | 0.01319 (80) | −0.00141 (37) | −0.00243 (41) | 0.00388 (64) |
| C(5) | 0.24283 (59) | 0.01811 (95) | 0.23710 (67) | 0.00696 (43) | 0.01720 (107) | 0.00906 (58) | 0.00719 (60) | −0.00082 (42) | 0.00025 (64) |
| C(6) | 0.33144 (78) | 0.46627 (55) | 0.28306 (79) | 0.01133 (67) | 0.00595 (42) | 0.01452 (91) | −0.00074 (43) | 0.00655 (65) | 0.00168 (48) |
| C(7) | 0.13538 (53) | 0.03338 (89) | 0.35893 (62) | 0.00685 (41) | 0.01615 (97) | 0.00772 (53) | 0.00072 (50) | −0.00036 (37) | 0.00521 (60) |
| C(8) | 0.18542 (71) | 0.12173 (65) | 0.35947 (69) | 0.00962 (58) | 0.01000 (61) | 0.00985 (66) | 0.00088 (48) | −0.00450 (51) | −0.00175 (49) |

[a] The form of the anisotropic temperature factor expression is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. In this and in subsequent tables, estimated standard deviations are given in parentheses for the least significant figures.

**Table II.** Calculated Hydrogen Positions

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| H(4)[a] | 0.2978 | 0.1729 | 0.2697 |
| H(5) | 0.2858 | −0.0106 | 0.1758 |
| H(6) | 0.1447 | −0.1109 | 0.2617 |
| H(7) | 0.0784 | 0.0209 | 0.4091 |
| H(8) | 0.1755 | 0.1886 | 0.4121 |

[a] The hydrogen atoms are labeled according to the C atom to which they are bonded. For example, H(4) is bonded to C(4).

culated by ORFFE using the variance-covariance matrix from the final least-squares cycle are given in Table III.

## Discussion

Cyclopentadienyliron tricarbonyl hexafluorophosphate exists as discrete $C_5H_5Fe(CO)_3^+$ and $PF_6^-$ ions in the solid state. The coordination around the iron atom (Figure 1) can best be described as octahedral with coordination to three carbonyl monodentate ligands and a $C_5H_5^-$ tridentate ligand. This configuration is in agreement with the current MO bonding scheme[11] for this type of compound which uses primarily the d orbitals on the metal and includes overlap of the $e_1$ $d_{xy}$ and $d_{yz}$ orbitals with $C_5H_5$ $e_1$ $\pi$ orbitals and involves back-donation of the nonbonding d electrons into the C≡O bond. The $PF_6^-$ group, as expected, has approximately $O_h$ symmetry, although as stated earlier, there exists some degree of rotational disorder in the solid.

A least-squares plane was calculated for $C_5H_5^-$ to show its relationship to the plane described by the three carbonyl carbon atoms (Table IV). The two planes are essentially parallel with a dihedral angle of only 0.01°. A projection (Figure 2) of the cation normal to these planes shows the configuration of the carbonyl groups relative to the cyclopentadienyl ring. Note that one carbonyl carbon atom lies directly below a carbon atom of the ring, with the other two carbonyl carbon atoms at staggered positions. This implies that one orbital, involved in $\sigma$ bonding to C≡O, will be directed toward the midpoint of a C–C bond in the ring.

**Table III.** Selected Distances and Angles

| | | | |
|---|---|---|---|
| (a) Distances, Å | | | |
| Fe–C(1) | 1.802 (6) | P–F(1) | 1.590 (6) |
| Fe–C(2) | 1.831 (7) | P–F(2) | 1.539 (5) |
| Fe–C(3) | 1.815 (6) | P–F(3) | 1.559 (7) |
| C(1)–O(1) | 1.113 (7) | P–F(4) | 1.536 (5) |
| C(2)–O(2) | 1.111 (7) | P–F(5) | 1.598 (5) |
| C(3)–O(3) | 1.112 (7) | P–F(6) | 1.574 (5) |
| C(4)–C(5) | 1.363 (13) | Fe–C(4) | 2.072 (7) |
| C(5)–C(6) | 1.428 (14) | Fe–C(5) | 2.055 (6) |
| C(6)–C(7) | 1.366 (13) | Fe–C(6) | 2.055 (6) |
| C(7)–C(8) | 1.355 (13) | Fe–C(7) | 2.083 (7) |
| C(8)–C(4) | 1.338 (13) | Fe–C(8) | 2.084 (7) |
| (b) Angles, Deg | | | |
| C(4)–C(5)–C(6) | 106.9 (7) | C(1)–Fe–C(2) | 92.9 (3) |
| C(5)–C(6)–C(7) | 106.4 (7) | C(2)–Fe–C(3) | 93.8 (3) |
| C(6)–C(7)–C(8) | 108.0 (8) | C(3)–Fe–C(1) | 95.6 (3) |
| C(7)–C(8)–C(9) | 110.3 (8) | Fe–C(1)–O(1) | 177.3 (7) |
| C(8)–C(9)–C(4) | 108.4 (7) | Fe–C(2)–O(2) | 178.9 (8) |
| | | Fe–C(3)–O(3) | 175.6 (5) |

**Table IV.** Planes Involving Ligand Atoms[a]

(i) Least-Squares Plane of the Cyclopentadienyl Ring
Equation: $0.5911x - 0.4073y + 0.6962z - 4.1381 = 0$

| Atom | Dist from plane, Å | Atom | Dist from plane, Å |
|---|---|---|---|
| C(4) | −0.006 | C(7) | −0.003 |
| C(5) | 0.004 | C(8) | 0.006 |
| C(6) | 0.000 | | |

(ii) Plane Defined by the Carbonyl Carbon Atoms
Equation: $0.5987x - 0.4009y + 0.6934z - 1.4772 = 0$

[a] Plane coordinates are defined relative to three orthogonal unit vectors.

In two similar structures, $[\pi$-$C_5H_5Fe(CO)_2]_2C_4H_4$[12] and $\pi$-$C_5H_5Fe(CO)_2C_4H_5SO_2$,[13] it was also found that one monodentate ligand was directly below a cyclopentadienyl carbon atom.

The bonding of carbon monoxide ligands has been characterized in numerous compounds as $\sigma$ donation of electron density from the carbon atom accompanied by back-donation of electron density from nonbonding metal orbitals into the C≡O $\pi^*$ orbitals. Structural data for a variety of iron car-

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(10) A listing of observed and calculated structure factor amplitudes 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. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1746.

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**Table V.** Comparison of Structural Results for Iron Carbonyl Complexes

| | C–O bond lengths, Å | Av Fe–C(carbonyl) bond lengths, Å | Fe–C≡O bond angles, deg | C–Fe–C bond angles, deg |
|---|---|---|---|---|
| $[CH_3SFe_2(CO)_6]_2S$[a] | 1.17 (2), 1.16 (2), 1.20 (2), 1.14 (3), 1.23 (2), 1.17 (2), 1.19 (2), 1.17 (2), 1.17 (2), 1.16 (2), 1.20 (2), 1.20 (2) | 1.74 (2) | 174 (2), 173 (2), 178 (2), 178 (2), 176 (2), 176 (2), 174 (2), 177 (2), 177 (2), 175 (2), 175 (2), 175 (2) | 98 (1), 98 (1), 99 (1), 103 (1), 98 (1), 97 (1), 98 (1), 95 (1), 88 (1), 91 (1), 91 (1), 91 (1) |
| $[Fe(h^5\text{-}C_5H_5)(CO)(SCH_3)]_2BF_4$[b] | 1.16 (2) | 1.79 (2) | | |
| $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$[c] | 1.143 (8), 1.146 (9) | 1.75 (1) | 178.2 (7), 179.7 (6) | 86.0 (3), 90.6 (3), 94.1 (3), 89.3 (6) |
| (Vitamin A aldehyde)tricarbonyliron[d] | 1.15 (2), 1.16 (2), 1.15 (2) | 1.78 (2) | 176 (2), 177 (2), 178 (2) | 90 (1), 101 (1), 105 (1) |
| $Fe_2(CO)_6(C_6H_5C_2H)_3$[e] | 1.142 (16), 1.151 (17), 1.144 (20), 1.167 (17), 1.159 (17) | 1.77 (2) | 176.0 (12), 176.8 (12), 176.4 (13), 174.4 (12), 180.0 (12) | 98.6 (6), 91.9 (6), 94.8 (6) |
| $\pi\text{-}C_5H_5Fe(CO)_2Mn(CO)_5$[f] | 1.169 (23) (av) | 1.72 (3) | 170 (2), 173 (2), 174 (2), 174 (2) | 94.9 (11), 94.7 (11) |
| $\pi\text{-}C_5H_5Fe(CO)_2C_4H_5SO_2$[g] | 1.129 (14) (av) | 1.78 (1) | 174.2 (10), 178.8 (10) | 93.0 (4), 88.9 (4), 96.1 (5) |
| $\pi\text{-}C_5H_5Fe(CO)_2(\sigma\text{-}C_5H_5)$[h] | 1.16 (2), 1.15 (3) | 1.70 (2) | 174 (2), 174 (2) | 89 (1), 92 (1), 96 (1) |
| $\pi\text{-}C_5H_5Fe(CO)_3PF_6$ | 1.113 (7), 1.112 (7), 1.111 (7) | 1.82 (1) | 175.6 (5), 177.3 (7), 178.9 (8) | 95.6 (3), 93.8 (3), 92.9 (3) |

[a] J. M. Coleman, A. Wojcicki, P. J. Pollick, and L. F. Dahl, *Inorg. Chem.*, **6**, 1236 (1967). [b] L. F. Dahl and N. G. Connelly, *J. Amer. Chem. Soc.*, **92**, 7472 (1970). [c] Reference 12. [d] R. Mason and G. B. Robertson, *J. Chem. Soc. A*, 1229 (1970). [e] G. S. D. King, *Acta Crystallogr.*, **15**, 243 (1962). [f] P. J. Hansen and R. A. Jacobson, *J. Organometal Chem.*, **6**, 389 (1966). [g] Reference 13. [h] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

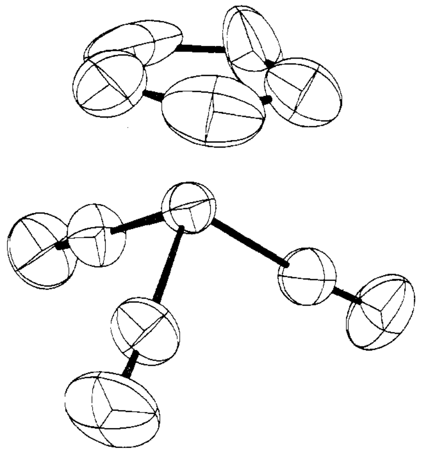

**Figure 1.** $\pi\text{-}C_5H_5Fe(CO)_3^+$ cation in $\pi\text{-}C_5H_5Fe(CO)_3PF_6$.

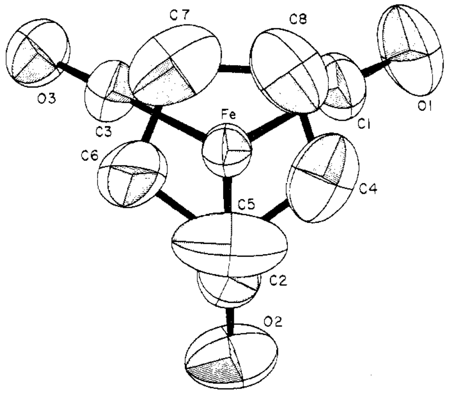

**Figure 2.** Projection of the $\pi\text{-}C_5H_5Fe(CO)_3^+$ cation onto the cyclopentadienyl plane.

bonyl complexes are summarized in Table V. A comparison of bond lengths given in this table shows that the C-O distances in $\pi\text{-}C_5H_5Fe(CO)_3PF_6$ are the shortest found (1.111 (7), 1.112 (7), and 1.113 (7) Å) and the Fe-C(carbonyl) distances are the longest found (1.802 (6), 1.815 (6), and 1.831 (7) Å). Brown and Darensbourg[14] in ir studies of metal carbonyls have shown that for the series $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ the carbon-oxygen stretching frequency increases with higher positive charge on the metal ion. Force constants calculated from C–O stretching frequencies of iron, manganese, and rhenium carbonyl compounds are usually higher when the metal is formally positively charged.[3] The short C-O distances found in this study agree quite well with these observations.

The C-Fe-C angles appear consistent with other iron carbonyls, as is the deviation from linear Fe-C-O bonds. Kettle[15] has shown that there is no symmetry requirement that the two C≡O π bonds interact equally with the metal orbitals, so that linear bonds are not necessarily expected.

As in most other metal π-bonded cyclopentadienyl complexes there is some variation in the carbon-carbon bond lengths in the cyclopentadienyl ligand. It has been suggested[16-18] that the nonequivalent bond distances are indicative of localization of electron density and that there is unequal overlap of $d_{yz}$ and $d_{xz}$ metal orbitals with the e MO's of $C_5H_5$. In the present study (with variations greater than standard deviations) this appears to be the case. Carbon atoms forming the shortest Fe-C bonds in general exhibit the longest C-C distances. For example, the shortest Fe-C distances are Fe-C(5) and Fe-C(6), both 2.055 (6) Å, and the longest C-C distance in the cyclopentadienyl ring is C(5)-C(6) (1.428 Å).

An X-ray crystal study of $\pi\text{-}C_5H_5Mn(CO)_3$ was carried out by Berndt and Marsh in 1962.[19] The molecular configuration is basically the same as found for the cation in the present study. However, carbon-oxygen bond distances (1.129, 1.142, 1.131 Å) are longer, probably due to increased back-donation of electron density from the neutral Mn compared to the positively charged Fe atom. The C-Mn-C angles are 91, 91, and 94° and the Mn-C-O bond angles are 176, 178, and 180°. The other major difference between the two structures

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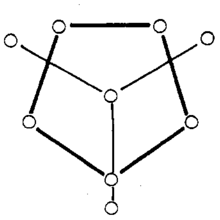
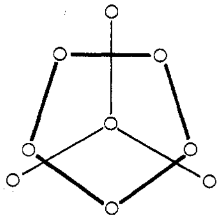


$\pi$-$C_5H_5Fe(CO)_3^+$



$\pi$-$C_5H_5Mn(CO)_3$

is a 12° rotation of the carbon monoxide ligands relative to the cyclopentadienyl ring. This transition, a 12° rotation, which may or may not be the result of packing forces in the crystal, gives the two compounds different geometrical configurations, but it would be difficult to say whether this would affect their relative reactivities.

**Registry No.** $\pi$-$C_5H_5Fe(CO)_3PF_6$, 12079-61-7.

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# Structure of the Ethylenediaminetetraacetatoaquomagnesate(II) Ion in a Crystalline Sodium Salt. Comparative Stereochemistry of the Seven-Coordinate Chelates of Magnesium(II), Manganese(II), and Iron(III)[1]

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The salt, $Na_2[H_2OMgEDTA] \cdot 5H_2O$ ($EDTA^{4-}$ = ethylenediaminetetraacetate), crystallizes in the monoclinic space group $C_2$ with $a = 11.504$ (3), $b = 9.801$ (3), $c = 8.816$ (3) Å, $\cos\beta = -0.3565$ (3) or $\beta = 110.88°$, and $Z = 2$. Diffracted intensities were recorded with Zr-filtered Mo K$\alpha$ radiation on a computer-controlled four-circle diffractometer. Of the 3800 independent reflections scanned for $(\sin\theta)/\lambda \lesssim 0.98$ Å,$^{-1}$ the 2791 retained as objectively observed gave a data/parameter ratio of 21 for the anisotropic, full-matrix, least-squares refinement of structure. The seven-coordinate $[H_2OMgEDTA]^{2-}$ ion of required $C_2$ symmetry carries two pairs of very long bonds, Mg–N = 2.378 (2) and Mg–O = 2.270 (3) Å, along with a fairly short pair, Mg–O = 2.078 (2) Å, and the unique Mg–$OH_2$ bond at 2.060 (3) Å. All coordination polyhedra in the EDTA chelates of Mg(II), Mn(II), and Fe(III), as also in $[H_2OFeDCTA]^-$ ($DCTA^{4-}$ = 1,2-diaminocyclohexane-*N,N'*-tetraacetate), are $C_2$ hybrids between a $C_{2v}$ pentagonal bipyramid and the $C_{2v}$ monocapped trigonal prism, but with one or the other predominating in the ratio ∿3:1; only $[H_2OFeEDTA]^-$ is better classified as pentagonal bipyramidal. The quantitative differences between the qualitatively similar $[H_2OMgEDTA]^{2-}$ and $[H_2OFeDCTA]^-$ ions may be summed up as follows. The bonding in $[H_2OFeDCTA]^-$ (and in $[H_2OFeEDTA]^-$) enforces very tight packing of the ligands, whereas the bonding pattern in $[H_2OMgEDTA]^{2-}$ is tailored to a pattern of easy packing relations. The large difference in the stability constants of the magnesium and manganese chelates is mostly attributable to the difference in size of the cations; the larger manganese ion is well-adapted to observe the geometrical constraints imposed by the multiply bridged ring system.

## Introduction

The equilibrium reaction in aqueous solution for the complexing of a bivalent cation by the quadruply charged ethylenediaminetetracetate anion ($EDTA^{4-}$) is conveniently written as

$$M(OH_2)_h{}^{2+} + EDTA^{4-} \rightleftarrows [(H_2O)_qMEDTA]^{2-} + (h-q)H_2O$$

For the usual case of sexadentate chelation by the $EDTA^{4-}$ ion, the coordination number of the metal ion in the complexed species becomes 6, 7, 8, 9, · · · accordingly as $q$ = 0, 1, 2, 3, · · · water molecules are retained in the coordination group. Reported values[2] of log $K$ at 20° for the equilibria in which $M^{2+}$ is in turn $Mg^{2+}$, $Ca^{2+}$, and $Mn^{2+}$ are 8.7, 10.6, and 14.0, respectively. The stability constants for the Ca(II) and Mn(II) chelates may appear to be anomalously high relative to that of the Mg(II) complex, but only on the assumption—long since discredited[3,4]—that sexadentate octahedral coordination is freely accessible to, and preferred for, all such species. Existing evidence[4-7] strongly supports a sexadentate seven-coordinate formulation for the manganese chelate, both in crystals and in solution. And, as pointed out elsewhere,[8] a nine-coordinate $[(H_2O)_3CaEDTA]^{2-}$ anion, with a stereochemistry similar to that of the $[(H_2O)_3Ln$-$EDTA]^-$ chelates[9] (Ln = lanthanide), seems likely to be the most characteristic form of the Ca(II) complex. Neither eight- nor ten-coordinate species, however, should be dismissed from consideration.[10]

An abnormally low value for the stability constant of the Mg-EDTA complex is, by contrast, fully consistent with our earlier stereochemical studies of octahedral[3,4] and seven-

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[2] *Cf.* S. Chabarek and A. E. Martell, "Organic Sequestering Agents," Wiley, New York, N. Y., 1959, pp 572-573, for a comprehensive tabulation of stability constants with listed references, predominantly to studies by Schwarzenbach and his collaborators.

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[9] (a) M. D. Lind, B. Lee, and J. L. Hoard, *J. Amer. Chem. Soc.*, 87, 1611 (1965); (b) J. L. Hoard, B. Lee, and M. D. Lind, *ibid.*, 87, 1612 (1965). We note that the terbium chelate has also been shown to be nine-coordinate.

[10] See V. A. Uchtman, Abstracts, 162nd National Meeting of the American Chemical Society, Sept 1971, No. INORG 58, for a brief description of the stoichiometrically constrained structure of crystalline $Ca_2EDTA \cdot 7H_2O$.