spinning at the same speed, was used for both the acidified and unacidified solutions. In addition both signals were recorded at the same spectrum amplitude. It was found that if these precautions were taken, the spectra were highly reproducible and quite satisfactory for the purposes of this research.

At −31° the line width of the signal from the acidified solution is approximately five times that from the unacidified solution. Hence, different sweep widths were used, but this causes no difficulty since the A-60A sweep widths can be very precisely calibrated.

Spectra were recorded for both solutions at 59 and −31°. The 59° measurements were made in order to check the suitability of the acidified solution as the standard. It was shown above that limit B and eq 4 apply to both solutions at this temperature, and hence the product of peak height times line width should be porportional to the total proton concentration in each case, and it must prove to be so experimentally if the acidified solution is to be an acceptable standard.

The integrated intensity values were converted to a value of n_e, an "effective" primary hydration number through eq 11, derived from the slow exchange limit,

$$I_u/I_a = ([H]_u - 2n_e[Ni^{2+}])/[H]_a \qquad (11)$$

where u and a refer to acidified and unacidified, and [H] is the total proton concentration. At 50°, I_u/I_a is 1.015, $[H]_a$ = 94.7 g-atom/l., $[H]_u$ = 95.6 g-atom/l., $[Ni^{2+}]$ = 1.483 g-ion/l., and n_e is calculated to be −0.2. This result is quite satisfactory and the acidified nickel solution proved to be an excellent standard.

At −31°, I_u/I_a is 0.836, $[H]_a$ = 98.7 g-atm/l., $[H]_u$ = 98.6 g-atom/l., $[Ni^{2+}]$ is 1.525 g-ion/l., and n_e is calculated from eq 11 to be 5.3. From eq 10, this corresponds to an actual hydration number of 6.0. Had the actual hydration number been 4, n_e would have been measured as 3.6.

This determination was repeated several times and the measured primary hydration number of Ni^{2+} is 6.0 ± 0.2. Twelve protons on each Ni^{2+} exchange with the bulk at the same rate, and this rate is identical within experimental error with the rate of oxygen exchange.[7]

The method employed here for hydration number determination is potentially applicable to other ions such as vanadyl.[11] However, an acidified vanadyl solution cannot be used as the external standard because T_{2B}^{-1} is much too large to permit this, and this limitation may certainly limit the application of the technique to the study of other ions.

Acknowledgment. We wish to acknowledge the financial support of the National Science Foundation in the form of a research grant to T. J. S.

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(11) T. J. Swift, T. A. Stephenson, and G. R. Stein, *J. Am. Chem. Soc.*, **89**, 1611 (1967).

Stereochemically Nonrigid Organometallic Molecules. XIV.[1] The Crystal and Molecular Structure of (1,3,5,7-Tetramethylcyclooctatetraene)diiron Pentacarbonyl[2]

F. A. Cotton and Marie D. LaPrade[3]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received September 23, 1967*

Abstract: A three-dimensional, X-ray diffraction study of the fluxional molecule $[(CH_3)_4C_8H_4]Fe_2(CO)_5$ has been completed employing the conventional sequence of Patterson maps, Fourier maps, and least-squares refinement. The crystals belong to the monoclinic system, space group $P2_1/n$, with the dimensions a = 15.126 Å, b = 13.374 Å, c = 8.587 Å, β = 101.17°. The observed density is 1.601 g cm^{-3}, that calculated assuming $Z = 4$ is 1.605 g cm^{-3}. The final value of the usual discrepancy index is 0.088 for 1142 independent nonzero reflections measured at 25° with a manually operated General Electric counter diffractometer. The least-squares refinement employed the full matrix and used isotropic temperature factors for all atoms except the two iron atoms, the five oxygen atoms, and the carbon atom of the bridging carbonyl group. The structure is essentially the same as that of $(C_8H_8)Fe_2(CO)_5$; the methyl groups occupy the 1 and 3 positions of the two intraannular, coordinated allyl groups. The relatively long Fe–Fe distance of 2.72 Å and the relatively long distances (2.33–2.50 Å) from the iron atoms to the nonallyl carbon atoms of the ring support the postulate that in this set of two iron atoms and two carbon atoms there are six electrons so delocalized as to provide five bonds of fractional order.

As noted in an earlier paper,[1] among the products obtained by treating the carbonyls of iron with 1,3,5,7-tetramethylcyclooctatetraene, hereafter abbreviated TMCOT, was a compound believed to be analogous to the compound $(COT)Fe_2(CO)_5$ prepared by Keller, Emerson, and Pettit[4] and formulated by them as I. $(TMCOT)Fe_2(CO)_5$ exhibits an nmr spectrum both at room temperature and at −60° consisting of only one ring proton resonance and one methyl proton resonance. Thus it appeared to be a fluxional molecule, like its COT

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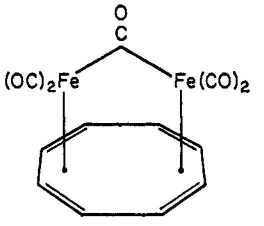
(1) Part XIII: F. A. Cotton and A. Musco, *J. Am. Chem. Soc.*, **90**, 1444 (1968).

(2) This study was supported, in part, by a grant from the Petroleum Research Fund administered by the American Chemical Society.

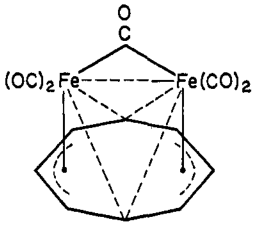
(3) National Science Foundation Summer Predoctoral Fellow.

(4) C. E. Keller, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 1390 (1965).

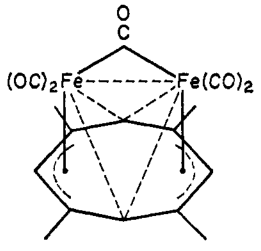
analog, and its structure in the crystal was therefore considered to be of interest. Scarcely had the present investigation begun, however, when the crystal structure of (COT)$Fe_2(CO)_5$ was reported,[5] showing that the molecule had the structure II.



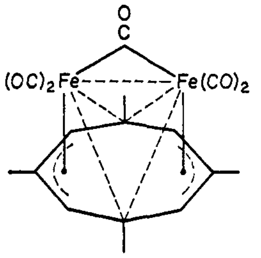
I



II



III



IV

It was decided to continue the present study for several reasons: first, because II is a decidedly surprising structure and it seemed worthwhile to see whether it occurred also in the TMCOT analog; second, assuming that (TMCOT)$Fe_2(CO)_5$ were to have the same basic structure, two isomers are possible, III and IV, and we wished to see which one occurs in the crystal; third, as noted before,[6] the presence of the methyl carbon atoms in TMCOT compounds permits one to estimate the hybridization at four of the ring carbon atoms and thus to analyze more closely than in the COT compounds the electronic structure of the bound olefin and its bonding to the metal atoms.

Procedure

Small, deep red crystals of $[(CH_3)_4C_8H_4]Fe_2(CO)_5$, prepared and chemically characterized as described elsewhere,[1] were grown from pentane solution at about 0°, using material kindly provided by Dr. A. Musco. Weissenberg films of the $h0l$, $h1l$, $h2l$, and $h3l$ nets showed the crystals to be monoclinic with the following systematic absences: $h0l$ for $h + l = 2n + 1$; $0k0$ for $k = 2n + 1$. These absences uniquely identify the space group as $P2_1/n$, with the general (fourfold) positions $x, y, z;\ -x, -y, -z;\ {}^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z;\ {}^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$. The unit cell edges were measured accurately using a General Electric counter diffractometer, manually operated. The angle β was measured on films from a calibrated precession camera. All these measurements were made at 24 ± 1° using Cu Kα radiation (λ 1.5418 Å). The unit cell dimensions are $a = 15.126 \pm 0.003$ Å, $b = 13.374 \pm 0.003$ Å, $c = 8.587 \pm 0.002$ Å, $\beta = 101.17 \pm 0.05°$. The density was measured by flotation as 1.601 g cm^{-3}; assuming that there are four molecules per unit cell, a density of 1.605 g cm^{-3} is calculated. The entire molecule thus constitutes the asymmetric unit.

For collection of intensity data a prismatic crystal with approximate dimensions 0.22 × 0.13 × 0.15 mm was placed in a thin-walled, Lindemann glass capillary. With this capillary mounted in the usual way on the goniometer head, the a^* axis was coincident with the ϕ axis of the eucentric goniometer of the diffractometer. The intensities of 2635 reflections in the range $0 < 2\theta < 120°$ were measured using a $\theta/2\theta$ scan technique. A range of 2.66° in 2θ about the computed 2θ setting was scanned for 40 sec. Counts taken for 20 sec at the start and 20 sec at the end of each scan were added, and the total was assumed to be equivalent to the background through the scan range.

Unfortunately, crystals large enough for the use of Mo radiation were not obtained. Therefore Cu radiation with a nickel foil β-filter was used. The combination of fluorescence and high thermal motion in the crystal resulted in unusually high background. Also, the crystal was observed to decompose slowly in the X-ray beam. Decomposition was monitored by periodic checking of certain reflections, and it was shown that decomposition had proceeded to the extent of about 7% at the time the final reflections were counted. The intensities (scan counts minus background counts) of 1152 of the reflections measured were $\geq 3\sigma$, where σ is (scan counts + background counts)$^{1/2}$. Only these reflections were considered statistically significant and used to solve and refine the structure. After applying Lorentz and polarization corrections and approximately scaling these intensities, they were considered to be approximate values of $|F_o|^2$, suitable for the initial stages of solving the structure. Absorption corrections were later applied to give more accurate $|F_o|^2$ values for final refinement.

Using the approximate $|F_o|^2$ values, a three-dimensional Patterson function was computed.[7] The iron atoms were located and their coordinates refined by one cycle of least squares, in which the scale factor and an isotropic temperature factor were also permitted to vary. Using phases given by the iron atoms, a three dimensional Fourier map was computed, from which coordinates of the carbon and oxygen atoms were obtained. After several cycles of least-squares refinement,[8a] the residual, $R_1 = \Sigma||F_o| - |F_c||/|F_o|$ was 0.20. Absorption corrections were now applied. The shape of the crystal was roughly that of a right hexagonal prism, and absorption corrections were calculated for this shape, taking the mean diameter as 0.14 mm whence $\mu = 141.5$ cm^{-1} and $\mu r = 0.95$. Also, the 200, 020, 011, 021, $2\bar{1}\bar{1}$, 022, 241, $3\bar{1}2$, and $3\bar{1}\bar{2}$ reflections were

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(5) E. B. Fleischer, A. L. Stone, R. B. K. Dewar, J. D. Wright, C. E. Keller, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 3158 (1966).

(6) M. J. Bennett, F. A. Cotton, and J. Takats, *J. Am. Chem. Soc.*, **90**, 903 (1968).

(7) Computer programs used in this study were: D. P. Shoemaker, MIXG2 (calculates diffractometer settings) and DISTAN (calculates orthogonal cell coordinates, intra- and intermolecular contacts, and angles); R. C. Elder, PDATA2 (corrects MIXG2 output for ϕ_0 and scan width and prints diffractometer setting in convenient format) and PUBTAB (prepares structure factors in proper format for publication); W. G. Sly, D. P. Shoemaker, and J. G. Van den Hende, MIFR-2A, 1962 (Fourier summation for Patterson or Fourier maps); W. C. Hamilton, GONO9 (used for the absorption correction); C. T. Prewitt, SFLSQ3, 1962, and SFLS5, 1967 (least-squares refinement of parameters minimizing $\Sigma(w||F_o| - |F_c||^2)$; D. L. Weaver, WOFF2 (calculates average Δ^2 *vs.* average F_o for weighting); J. S. Wood, MGEOM (calculates intramolecular bond lengths and angles and standard deviations and best least-squares planes).

(8) "International Tables for Crystallography," Kynoch Press, Birmingham, England, 1962: (a) Vol. III, Table 3.3.1A; (b) Vol. III, Table 3.3.2B.

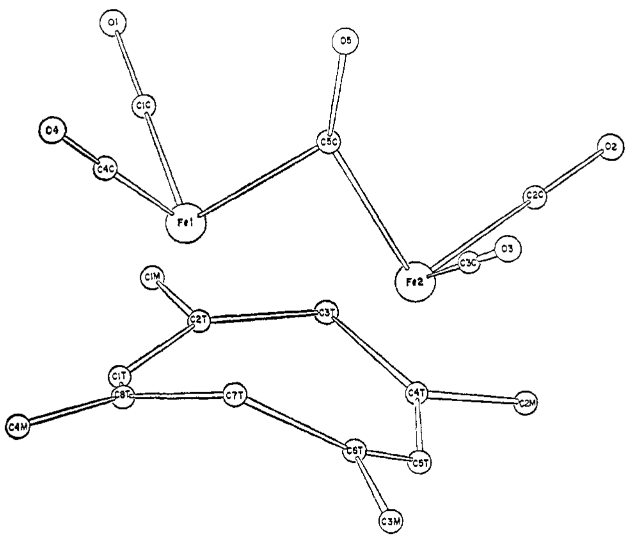

Figure 1. A perspective view of the (TMCOT)$Fe_2(CO)_5$ molecule, showing the numbering scheme for the atoms.

judged to be seriously affected by extinction and were omitted from further cycles of refinement. Anomalous dispersion corrections[8b] were introduced for the iron and oxygen atoms, and anisotropic thermal parameters of the form $\exp(-\beta_{11}h^2 - \beta_{22}k^2 - \beta_{33}l^2 - 2\beta_{12}hk - 2\beta_{13}hl - 2\beta_{23}kl)$ were introduced for the iron atoms, the oxygen atoms, and the carbon atom of the bridging carbonyl group. These choices of atoms to be refined anisotropically were indicated by the appearance of a difference Fourier map. Finally, a weighting scheme was introduced. The weights, $w = \sigma^{-1/2}$, were assigned according to the following prescription (where RLP stands for reciprocal Lorentz-polarization correction): $\sigma = 0.342F_o + 12.6$ for $0 < \text{RLP} < 0.5$; $\sigma = 0.184F_o + 7.5$ for $0.5 \leq \text{RLP} < 1.0$. This corrects σ for Lorentz and polarization effects[9] while satisfying Cruickshank's criterion[10] that data should be so weighted as to make $w\Delta^2$ constant over the entire range of $|F_o|$ values. When refinement was stopped the quantity $[\Sigma\omega\Delta^2/(\text{number of observations} - \text{number of parameters})]^{1/2}$ had reached a value of 0.93.

Refinement was considered complete when in one cycle no thermal or positional parameter changed by as much as its estimated standard deviation. After this final cycle of refinement, R_1 was 0.088 and the weighted residual, $R_2 = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, was 0.12. A final difference Fourier synthesis was then computed. It clearly showed six methyl hydrogen atoms and two of the ring hydrogen atoms (those on C3T and C7T). It was possible to locate the remaining hydrogen atoms if some overlapping of peaks was assumed. The quality of the data was not considered good enough to justify an attempt to refine hydrogen atom positions. The standard deviation in the residual electron density,[11] including peaks suspected of being hydrogen atoms, was 0.13 e/Å^3. The highest peak in the difference Fourier map contained about 0.75 electron.

Results

The final atomic positional and thermal parameters are given in Table I. A list of calculated and observed structure amplitudes has been deposited with the American Documentation Institute.[12]

Table I. Final Atomic Parameters[a]

A. Fractional Coordinates and Isotropic Temperature Factors[b]

Atom	x	y	z	B (or B_{eq}) $\times 10^4$
C1T	0.2654 (11)	0.3551 (12)	0.2144 (18)	3.69 (0.36)
C2T	0.3435 (12)	0.3785 (14)	0.3248 (20)	4.55 (0.38)
C3T	0.3535 (12)	0.3848 (14)	0.4966 (20)	4.61 (0.37)
C4T	0.3203 (12)	0.3263 (14)	0.6144 (21)	4.97 (0.40)
C5T	0.2361 (12)	0.2948 (12)	0.6165 (20)	3.86 (0.34)
C6T	0.1584 (12)	0.3298 (13)	0.5224 (20)	4.78 (0.37)
C7T	0.1444 (11)	0.3825 (13)	0.3696 (19)	3.93 (0.34)
C8T	0.1786 (11)	0.3670 (12)	0.2305 (18)	4.00 (0.35)
C1M	0.4354 (16)	0.3850 (17)	0.2651 (25)	7.10 (0.52)
C2M	0.3993 (14)	0.2923 (15)	0.7597 (23)	6.13 (0.46)
C3M	0.0700 (14)	0.2986 (15)	0.5725 (23)	6.45 (0.48)
C4M	0.1079 (14)	0.3627 (15)	0.0748 (23)	6.26 (0.49)
C1C	0.3312 (14)	0.5745 (16)	0.2636 (23)	5.67 (0.48)
C2C	0.3220 (14)	0.5024 (18)	0.7826 (26)	6.70 (0.48)
C3C	0.1504 (16)	0.5029 (18)	0.6925 (25)	6.95 (0.50)
C4C	0.1651 (14)	0.5743 (16)	0.2028 (23)	5.56 (0.45)
C5C	0.2473 (15)	0.5750 (16)	0.5065 (22)	6.57
O1	0.3860 (11)	0.6287 (11)	0.2295 (19)	8.61
O2	0.3723 (14)	0.5302 (14)	0.8867 (19)	11.96
O3	0.0884 (13)	0.5308 (12)	0.7433 (21)	10.18
O4	0.1115 (12)	0.6265 (12)	0.1347 (20)	10.51
O5	0.2519 (14)	0.6627 (10)	0.5343 (15)	9.45
Fe1	0.25061 (19)	0.49792 (20)	0.31198 (28)	3.965
Fe2	0.24162 (20)	0.45221 (20)	0.61766 (32)	4.468

B. Anisotropic Temperature Factors $\times 10^4$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C5C	110 (16)	67 (17)	179 (35)	−39 (13)	35 (18)	−70 (20)
O1	113 (12)	82 (12)	395 (40)	−30 (10)	101 (19)	−40 (18)
O2	172 (16)	166 (20)	221 (31)	−27 (14)	−85 (18)	−57 (19)
O3	129 (14)	122 (16)	416 (44)	38 (12)	116 (21)	30 (20)
O4	117 (15)	97 (15)	420 (43)	21 (11)	−75 (20)	45 (20)
O5	246 (20)	39 (9)	169 (24)	20 (11)	99 (18)	23 (12)
Fe1	62 (2)	41 (2)	118 (4)	1.3 (15)	136 (18)	−7 (2)
Fe2	70 (2)	51 (2)	121 (4)	0.7 (16)	186 (20)	13 (2)

[a] Numbers in parentheses are esd's, occurring in the last significant figure. [b] B_{eq} is an isotropic temperature factor computed for each atom which was refined anisotropically according to the equation $B_{eq} = {}^4/_3(\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 - 2\beta_{13}ac \cos \beta)$.

Figure 1 shows the molecule as seen in a projection selected to provide a good view of its main features; the numbering scheme followed in the tables is also indicated in Figure 1. Table II lists the bond distances, interbond angles, and some other significant molecular dimensions. Equations for best mean planes through certain sets of atoms, deviations of individual atoms from the planes, and dihedral angles are given in Table III.

Discussion

It may be seen by comparing Figure 1 with the sketches given by Fleischer, *et al.*,[5] that (TMCOT)$Fe_2(CO)_5$ has essentially the same structure as its (COT)$Fe_2(CO)_5$ analog. Insofar as the published data on the latter

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(9) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(10) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965.

(11) D. W. J. Cruickshank, *Acta Cryst.*, 2, 154 (1949).

(12) This table has been deposited as Document No. 9748 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by an advance remittance ($1.25 for photoprints or $1.25 for 35-mm microfilm) payable to: Chief, Photoduplication Service, Library of Congress.

Table II. Molecular Dimensions

A. Distances, Å			
C1T–C8T	1.36 (2)	Fe1–C8T	2.11 (2)
C1T–C2T	1.40 (2)	Fe1–C1T	2.12 (2)
C4T–C5T	1.35 (3)	Fe1–C2T	2.12 (2)
C3T–C6T	1.37 (3)	Fe2–C4T	2.07 (2)
Mean	1.37 (2)	Fe2–C5T	2.11 (2)
		Fe2–C6T	2.13 (2)
C2T–C3T	1.46 (2)	Fe1–C3T	2.50 (2)
C3T–C4T	1.45 (2)	Fe1–C7T	2.35 (2)
C6T–C7T	1.47 (2)	Fe2–C3T	2.33 (2)
C7T–C8T	1.41 (2)	Fe2–C7T	2.52 (2)
Mean	1.45 (2)		
		Fe1–C1C	1.70 (2)
C2T–C1M	1.58 (3)	Fe1–C4C	1.77 (2)
C4T–C2M	1.62 (3)	Fe2–C2C	1.81 (2)
C6T–C3M	1.54 (3)	Fe2–C3C	1.77 (2)
C8T–C4M	1.54 (3)	Mean	1.76 (2)
Mean	1.57 (2)		
		Fe1–C5C	1.97 (2)
Fe1–Fe2	2.724 (4)	Fe2–C5C	1.91 (2)
C3T–C7T	3.14 (2)		
C1C–O1	1.18 (3)	C5C–O5	1.20 (3)
C2C–O2	1.12 (3)		
C3C–O3	1.17 (3)		
C4C–O4	1.14 (3)		
Mean	1.15 (2)		
B. Angles, Deg			
C2T–C3T–C4T	134 (2)	Fe1–C1C–O1	179 (2)
C6T–C7T–C8T	132 (2)	Fe2–C2C–O2	178 (2)
C1T–C2T–C3T	128 (2)	Fe2–C3C–O3	176 (2)
C3T–C4T–C5T	130 (2)	Fe1–C4C–O4	178 (2)
C4T–C5T–C6T	126 (2)		
C5T–C6T–C7T	131 (2)	Fe1–C5C–O5	132 (2)
C7T–C8T–C1T	129 (2)	Fe2–C5C–O5	139 (2)
C8T–C1T–C2T	128 (2)	Fe1–C5C–Fe2	89 (1)
C1T–C2T–C1M	118 (2)		
C3T–C2T–C1M	114 (2)	C1C–Fe1–C4C	90 (1)
C3T–C4T–C2M	113 (2)	C1C–Fe1–C5C	92 (1)
C5T–C4T–C2M	118 (2)	C4C–Fe1–C5C	
C5T–C6T–C3M	116 (2)		
C7T–C6T–C3M	113 (2)	C2C–Fe2–C3C	92 (1)
C7T–C8T–C4M	116 (2)	C2C–Fe2–C5C	89 (1)
C1T–C8T–C4M	116 (2)	C3C–Fe2–C5C	
C5C–Fe1–C3T	78 (1)	C5C–Fe2–C3T	90 (1)
C3T–Fe1–C7T	81 (1)	C3T–Fe2–C7T	81 (1)

Table III. Some Molecular Planes

Plane *A* through C8T, C1T, C2T, C1M, C4M

$$0.0461x - 0.9978y + 0.0478z - 4.675 = 0$$

Distance of atoms from plane (Å)

C8T	−0.023
C1T	0.191
C2T	−0.030
C1M	−0.073
C4M	−0.065

Plane *B* through C2T, C8T, C3T, C7T

$$-0.0080x - 0.9938y + 0.1112z - 4.720 = 0$$

Plane *C* through C3T, C4T, C6T, C7T

$$-0.1753x + 0.8500y + 0.4967z + 5.639 = 0$$

Plane *D* through C4T, C5T, C6T, C2M, C3M

$$-0.1401x + 0.8759y + 0.4618z + 5.655 = 0$$

Distance of atoms from plane (Å)

C4T	0.022
C5T	−0.160
C6T	0.027
C2M	0.056
C3M	0.055

Angle between *A*–*B* = 175°
Angle between *B*–*C* = 143°
Angle between *C*–*D* = 177°

compound permit a quantitative comparison, the resemblances appear to be very close indeed. Thus, in the $Fe_2(CO)_5$ portion of the TMCOT molecule there are mean Fe–C distances of 1.76 and 1.94 Å for terminal and bridging CO groups, respectively, while in $(COT)Fe_2(CO)_5$ the corresponding distances are 1.79 and 1.97 Å. The Fe–Fe distances are 2.724 and 2.742 Å (each with an esd of ~0.004 Å) in the TMCOT and COT compounds, respectively.

In both compounds, there are two distinctly different sets of iron to ring carbon distances: relatively short ones to the members of two sets of three carbon atoms (8, 1, 2 and 4, 5, 6 in TMCOT) and longer ones to the remaining two carbon atoms. The mean value of the six shorter Fe–C bond lengths in $(TMCOT)Fe_2(CO)_5$ is 2.11 Å, while the mean length of the corresponding bonds in $(COT)Fe_2(CO)_5$ is 2.12 Å. In $(COT)Fe_2(CO)_5$ the four longer bonds (two sets of two, related by a crystallographic mirror plane) were equal within experimental error, at 2.50 Å. In $(TMCOT)Fe_2(CO)_5$, where the molecule has no symmetry elements and is, in fact, appreciably distorted from the mm symmetry which might have been expected ideally, the four longer Fe–C distances are 2.33, 2.35, 2.50, and 2.52 Å. Despite this, it can be said that the two molecules resemble each other quite closely.

Turning now to the details of the structure of $(TMCOT)Fe_2(CO)_5$, we observe first that it corresponds to the schematic representation III rather than IV. As it occurs in the crystal, the molecule deviates somewhat from the C_{2v} (mm) symmetry which III would suggest. The distortion consists mainly in a skewing of the $Fe_2(CO)_5$ group relative to the TMCOT. Thus, the plane formed by Fe1, C5C, and Fe2 is not the same as the one defined by C1T, C5T, and the midpoint of a line from C3T to C7T; instead, there is an angle of 5.7° between these planes. This "twist" of one of these planes relative to the other is also observed in the long (~2.50 Å) and short (~2.34 Å) distances from iron atoms to C3T and C7T.

Given the structural relationship between the carbon ring system and the $Fe_2(CO)_5$ moiety, in both $(TMCOT)Fe_2(CO)_5$ and $(COT)Fe_2(CO)_5$, it is evident that an unusual bonding situation exists here. This was recognized by Fleischer, *et al.*,[5] who proposed (1) that each iron atom be considered to form a π-allyl complex with the three carbon atoms to which it is closest, (2) that there exist two three-center, two-electron bonds of the Fe–C–Fe type and, finally, (3) that there is an iron–iron bond. We would agree with this formulation in its essentials, but offer the following amplification and modifications.

First, regarding the existence of two π-allyl-to-iron bonds, certain features of the present structure strongly corroborate this description of the bonding. Thus for a true π-allyl to metal system, one would expect all the bonds formed by the carbon atoms *within* the allyl group to be coplanar, or very nearly so. The presence of methyl carbon atoms on the terminal members of each allyl moiety enables us to test the π-allyl hypothesis closely. Inspection of the bond angles recorded in Table IIB reveals that the three C–C bonds formed by each of the four terminal allyl carbon atoms are almost exactly coplanar since the sum of the angles is in each case 360° within experimental error. Moreover, as

Table III shows, the deviations from coplanarity of all atoms within each allyl moiety are not large, and the entire coordinated TMCOT molecule lies approximately in two planes which make an angle of 143° with each other.

The iron-to-allyl bonding here (and in the COT analog[5]) is a little unusual in that the three Fe–C distances are essentially the same, whereas in other π-allyl complexes[13–16] it has been found that the central carbon atom lies significantly closer to the metal atom. Nevertheless, the concept of each iron atom utilizing one electron and two orbitals to engage in bonding with an intraannular π-allyl group seems to be a valid and useful one.

In addition to the π-allyl-to-iron bonding, each iron atom uses one electron and one orbital to form a bond to the carbon atom of the bridging carbonyl group and two orbitals to form σ bonds to the two terminal CO groups.

Up to this point, we have specified the role of five orbitals and two electrons on each iron atom, leaving four valence-shell (3d, 4s, and 4p) orbitals and six electrons to be accounted for.

In order to discuss the utilization of these remaining metal orbitals and electrons as well as the orbitals and electrons on the ring atoms C3T and C7T in bonding, it is advisable to begin by classifying the atomic orbitals—and all molecular orbitals formed—according to the idealized symmetry of the molecule, which is C_{2v} (mm). This symmetry is fully described by specifying the locations of two mutually perpendicular planes, m_1 and m_2, which we do as follows: m_1 contains Fe1, Fe2, C5C, O5, C1T, and C5T; m_2 contains O5, C5C, C3T, and C7T. Molecular orbitals must be classified as either even (+) or odd (−) with respect to reflection in each of these planes, while atomic orbitals can be classified as even or odd only with respect to the plane passing through the atom to which the orbital belongs.

Of the nine valence-shell orbitals on each iron atom, six are even and three are odd with respect to m_1. For the bonding of the π-allyl group, the two terminal CO groups, and the bridging CO group, three even and two odd orbitals are required, thus leaving three even and one odd orbital on each iron atom to be used in constructing the central set of bonds involving the iron atoms and the C3T and C7T atoms and to house electrons which are partly nonbonding and partly used in π-bonding to the terminal CO groups. The C3T and C7T atoms each have available an orbital which is even with respect to m_2 (roughly speaking, these are some species of s–p hybrid directed more or less toward the midpoint of the Fe···Fe line), and each of these orbitals contains one electron.

The symmetry restrictions in this situation are not such as to fix closely the bonding possibilities. They do, however, provide a helpful basis for discussion. Of the six valence-shell electrons of each metal still to be accounted for, four are probably used mainly in π-bonding to the terminal CO groups, but there are no rigid symmetry restrictions concerning what orbital types may be used. Thus, for the central bonding situation, each iron atom supplies two electrons and two orbitals, the latter being either both even or one even and one odd with respect to m_1. Of the four iron atom orbitals and two carbon orbitals, it is possible to construct more or less delocalized molecular orbitals in several ways. Whatever the exact nature of the metal orbitals available, one orbital on each metal atom which is even with respect to m_1 may be used to form a two-center orbital which is Fe–Fe bonding, and two electrons may be placed in this. Considering the great separation (3.14 Å) of the carbon atoms C3T and C7T, no significant direct interaction between these can be postulated. Hence, the remaining two iron atom orbitals, the two carbon atom orbitals, and the remaining four electrons must be used in some sort of delocalized bonding. This cannot be readily formulated as two sets of three-center bonds since there are not sufficient orbitals. It seems likely that only one fairly stable four-center molecular orbital can be formed, into which two more electrons will go. The remaining two electrons must occupy some kind of relatively nonbonding orbital.

The distances from the iron atoms to the C3T and C7T atoms (2.33–2.52 Å) are long enough to be consistent with a bonding picture in which there are only fractional Fe–C bonds. However, it must be noted that the Fe–Fe distance is also unusually long (*cf.* the tabulation by Churchill[15]), thus raising some question as to whether it can really be a full two-center, two-electron bond as suggested in the foregoing analysis. It is entirely possible that by considering more general mixing of orbitals (such as those normally set aside for bonding to the carbonyl groups and to the π-allyl groups), a fractional Fe–Fe bond and perhaps a somewhat more substantial set of Fe to C3T and C7T bonds might be formed.[17]

It is certainly not clear from the foregoing discussion (or any other argument we know of) why the actual structure of this molecule (III) or that of its COT analog (II) is more stable than a structure of type I. That these structures, containing the intraannular allyl systems, are *inherently* more stable than structure I and are not merely consequences of crystal-packing forces is scarcely to be doubted now that *two* compounds differing from each other in their intermolecular contacts have been shown to adopt such a structure. Perhaps the chief advantage in having the present X-ray study of a second compound is the evidence it affords on this point.[17]

It should be noted, finally, that the margin of stability of structures II and III relative to structures of type I cannot be very great, because, presumably, structure I is (or corresponds closely to) the transition state as the molecules manifest their fluxional behavior by passing rapidly form one to another of the equivalent structures of type II or III. The two types of structure probably do not differ in stability by more than 10–15 kcal/mole. Since it would be foolish to pretend that present-day understanding of the complex interactions between metal atoms and olefins is quantitative enough to permit bond-energy estimates accurate to the order of 10 kcal/

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(16) F. A. Cotton and J. Takats, *J. Am. Chem. Soc.*, **90**, 2031 (1968).

(17) NOTE ADDED IN PROOF. The two COT rings in $(C_8H_8)_2Ru_3(CO)_4$ are also bound in the same way to pairs of metal atoms (M. J. Bennett, F. A. Cotton and P. Legzdens, *ibid.*, **89**, 6797 (1967)).

mole, the failure of anyone to anticipate structures II and III should not be considered too surprising. This entire situation is but another indication that present-day understanding of complex metal–olefin interactions is still in a primitive state.

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The Structure of (1,3,5-Trimethyl-7-methylene-1,3,5-cyclooctatriene)diiron Pentacarbonyl, an Anomalous Reaction Product of 1,3,5,7-Tetramethylcyclooctatetraene with Polynuclear Iron Carbonyls[1]

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Abstract: The structure of a compound with the formula $C_{12}H_{16}Fe_2(CO)_5$, which is obtained by reaction of 1,3,5,7-tetramethylcyclooctatetraene with the polynuclear iron carbonyls and is isomeric with a compound already identified (Cotton and LaPrade, preceding paper) as a true $Fe_2(CO)_5$ derivative of tetramethylcyclooctatetraene, has been determined. The present compound contains an isomer of tetramethylcyclooctatetraene, namely 1,3,5-trimethyl-7-methylene-1,3,5-cyclooctatriene, to which one $Fe(CO)_2$ and one $Fe(CO)_3$ are attached. There is also an Fe–Fe bond. The olefinic macrocycle is bound to the $Fe_2(CO)_5$ group by two π-allyl–metal bonds and an olefin–metal bond. The principal crystallographic data are: space group $A\bar{1}$ (no. 2); unit cell dimensions, $a = 7.394$ Å, $b = 16.87$ Å, $c = 14.19$ Å, $\alpha = 103°\,58'$, $\beta = 91°\,58'$, $\gamma = 96°\,47'$; density 1.60 g/cm³ (measured), 1.61 g/cm³ (calculated for $Z = 4$). The structure was solved from Patterson and electron density maps and refined by least squares to a residual of 0.040. All hydrogen atoms were unambiguously located.

As described in an earlier paper,[2] a study has been made in this laboratory of the reactions of 1,3,5,-7-tetramethylcyclooctatetraene, TMCOT, with the iron carbonyls. A number of distinct products have been isolated and in some cases their identity was postulated with reasonable certainty on the basis of the more routine types of physical data, *e.g.*, nmr and infrared spectra. In some cases, however, an acceptable level of certainty as to structure was not attainable by such means and, thus, for several of the products, the techniques of single-crystal X-ray crystallography were brought to bear.

This paper reports one such study. The compound in question has the empirical formula $C_{17}H_{16}Fe_2O_5$, which was presumed to correspond to (TMCOT)-$Fe_2(CO)_5$. The infrared spectrum of the compound contains five resolved CO stretching bands, and its nmr spectrum is extremely complex. It was not clear from these and similar data whether it was homologous to any known cyclooctatetraene (COT) derivative in the iron[3] or ruthenium[4] systems, though such homology appeared doubtful. As will be seen below, it is not homologous to any COT compound. Instead, it has a novel structure which would not be possible in a COT derivative.

Procedure

The compound $C_{12}H_{16}Fe_2(CO)_5$ was prepared as described elsewhere.[2] Suitable single crystals were grown by slow crystallization from pentane under nitrogen. Although the predominant crystal habit is platelike, a few crystals which were parallelepipeds with appreciable thickness were also found. One of these latter crystals was chosen for X-ray work and sealed in a thin-walled Lindemann glass capillary.

The systematic absences $k + l \neq 2n + 1$, as obtained from precession ($h0l$, $h1l$, $h2l$, $hk0$, $kk1$, and $hk2$ levels) and Weissenberg ($0kl$ and $1kl$ levels) photography, indicated the probable space groups A1 (no. 1) or A1 (no. 2) having the following equipoints, respectively: $x, y, z;\ x, \frac{1}{2} + y, \frac{1}{2} + z;$ and $x, y, z;\ x, y, z;\ x, \frac{1}{2} + y, \frac{1}{2} + z;\ \bar{x}, \frac{1}{2} - y, \frac{1}{2} - z$. The following unit cell dimensions were obtained, at 22°, from the zero level precession photographs and by a method described elsewhere[5] from readings of 2θ made on the General Electric XRD-5 manually operated single-crystal diffractometer with Cu Kα radiation [$\lambda(K\alpha_1)$ 1.5405 Å, $\lambda(K\alpha_2)$ 1.5443 Å]: $a = 7.394 \pm 0.005$ Å, $b = 16.872 \pm 0.008$ Å, $c = 14.185 \pm 0.008$ Å, $\alpha = 103°\,58' \pm 3'$, $\beta = 91°\,58' \pm 3'$, $\gamma = 96°\,47' \pm 3'$. The films were calibrated with a NaCl crystal whose cell dimensions are accurately known.[6] The main source

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(1) This work was supported, in part, by a grant from the Petroleum Research Fund, administered by the American Chemical Society.

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