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Studies of some Carbon Compounds of the Transition Metals. I. The Crystal Structure of Dicyclopentadienyldi-iron Tetracarbonyl

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Dicyclopentadienyldi-iron tetracarbonyl, $Fe_2(CO)_4(C_5H_5)_2$, is monoclinic with $a = 7{\cdot}07 \pm 0{\cdot}03$, $b = 12{\cdot}46 \pm 0{\cdot}05$, $c = 7{\cdot}99 \pm 0{\cdot}04$ Å, $\beta = 108^\circ\ 25' \pm 25'$, $Z = 2$ and space group $P2_1/c$. The structure has been determined from two-dimensional data estimated visually from Weissenberg photographs taken with Co $K\alpha$ radiation.

The molecule consists of two bridging and two non-bridging carbonyl groups with the cyclopentadienyl rings bonded to the iron atoms in a manner similar to, but with greater interatomic separation than, that in ferrocene, $Fe(C_5H_5)_2$. The proximity of the iron atoms indicates an iron–iron bond. The average bond lengths are Fe–Fe $2{\cdot}49 \pm 0{\cdot}02$ Å, Fe–C (ring) $2{\cdot}11 \pm 0{\cdot}03$ Å, Fe–C (non-bridging) $1{\cdot}75 \pm 0{\cdot}03$ Å, Fe–C (bridging) $1{\cdot}85 \pm 0{\cdot}03$ Å, C–O (non-bridging) $1{\cdot}12 \pm 0{\cdot}04$ Å, C–O (bridging) $1{\cdot}21 \pm 0{\cdot}04$ Å, and C–C (ring) $1{\cdot}41 \pm 0{\cdot}04$ Å, where the limits given are estimated standard deviations. The R factors for the $0kl$ and $hk0$ zones are 12·8 and 13·3% respectively.

Introduction

In recent years many new organic compounds of the transition metals have been described, and particular attention has been given to those related to ferrocene. In the latter compounds the novel 'sandwich' type of structure has been confirmed in a number of cases, but only for the parent compound, ferrocene, has a detailed crystallographic investigation been published (Dunitz, Orgel & Rich, 1956). The present paper contains a study of one of the related cyclopentadienyl iron carbonyls.

The reaction of iron pentacarbonyl with cyclopentadiene to yield ferrocene has been shown to proceed through a dark-purple intermediate isolatable compound if low temperatures (100–200 °C.) are used. This compound has been shown to have the formula $Fe_2(CO)_4(C_5H_5)_2$, (Hallam, Mills & Pauson, 1955), and it was of basic interest to solve the structural geometry of the molecule.

Experimental

Suitable small crystals, from a sample kindly prepared by Mr B. F. Hallam, were obtained by recrystallization from ligroin (40–60 °C.). The characteristic habit is of [011] prism faces terminated by {100} pinacoids. Oscillation and Weissenberg photographs showed that the system was monoclinic. Refinement of the reciprocal-lattice parameters by the method described by Lipson (Farquhar & Lipson, 1946), together with a value of β determined by the method of angular lag (Buerger, 1942), gave the following direct lattice parameters (for Co $K\alpha$ radiation the wavelengths used were $\lambda K\alpha_1 = 1{\cdot}7889$ Å, $\lambda K\alpha_2 = 1{\cdot}7928$ Å):

$$a = 7{\cdot}07,\quad b = 12{\cdot}46,\quad c = 7{\cdot}99 \text{ Å},\quad \beta = 108^\circ\ 25',$$

within an accuracy of 0·4%. These values are in excellent agreement with those published recently (Wilson & Shoemaker, 1956). The systematic absences are $0k0$ when $k = 2n+1$ (observed up to $k = 13$), $h0l$ when $l = 2n+1$ (observed up to $h = 7$, $l = 8$). Tests for piezo-electricity showed no detectable asymmetry and the distribution of intensities of the $hk0$ and $0kl$ zones both fitted centric curves (Howells, Phillips & Rogers, 1950). These observations are consistent with the space group $P2_1/c$. From the density, $\varrho = 1{\cdot}77 \pm 0{\cdot}01$ g.cm.$^{-3}$, $Z = 2$ (the calculated density is 1·76 g.cm.$^{-3}$) and therefore the molecules are inherently centrosymmetric in the solid.

Intensity data for the $hk0$ and $0kl$ zones were obtained from Weissenberg photographs using the multiple-film technique. Throughout these measurements Co radiation was used to avoid fluorescent scattering by the Fe atoms. The data were put on an absolute scale and the overall temperature factor was determined by Wilson's method. Less accurate data were also obtained for the $h0l$ zone.

Solution of the structure

Patterson syntheses projected on the (001) and (100) planes, Fig. 1, gave a set of coordinates consistent with the expected Fe–Fe distance (about 2·5 Å). Fourier syntheses were then calculated using signs from the Fe contribution alone. For the $0kl$ zone, owing to the fact that the z coordinate was approximately $\frac{1}{8}$, signs could not be assigned to the cosine terms with $l = 2, 6, 10$, etc. nor to sine terms with $l = 4, 8, 12$, etc. The electron-density map thus obtained showed spurious detail but allowed the signs of the remaining reflexions to be calculated from the

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light-atom structure, which is almost completely resolved in this projection. At this stage no distinction was made between carbon and oxygen atoms but the resultant Fourier syntheses unambiguously showed two peaks of magnitude substantially greater than the remaining light peaks, and these were thus subsequently treated as oxygen atoms. At this stage the agreement index, R, was decreased to 20%, an overall B of 4·5 Å^2 being used. Difference maps now clearly showed the necessity of using different isotropic temperature factors for the iron and light atoms. With B_{Fe} = 3·9 Å^2 and $B_{O \text{ and } C}$ = 8·0 Å^2, the value of R was improved to 15%. The scattering factors used for carbon and oxygen were those published by Berghuis *et al.* (1955) and for iron those published in *International Tables* (1935), an allowance being made for the proximity of the incident radiation to an absorption edge in iron by subtracting 3·8 electrons over the whole range of the scattering curve (Henry, Lipson & Wooster, 1953).

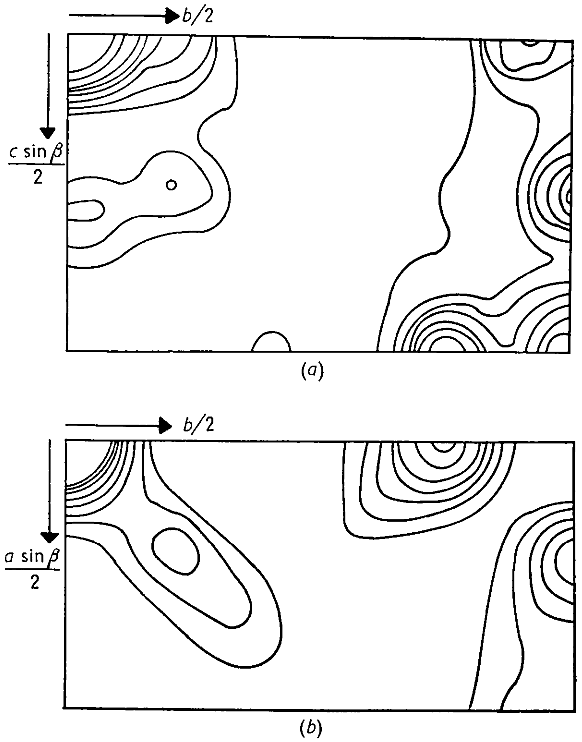

Fig. 1. Patterson synthesis projected (*a*) down [100], (*b*) down [001]. Contours at equal but arbitrary intervals, except round origin.

Table 1. *Coordinates*

	$x'=x/a$	$y'=y/b$	$z'=z/c$	Distance from mean plane (Å)*
Fe	0·094	0·063	0·118	0·01 (1)
C non-bridge	−0·085	0·165	0·060	
O non-bridge	−0·199	0·231	0·026	
C bridge	0·092	0·046	−0·108	0·04 (1)
O bridge	0·180	0·080	−0·204	0·02 (1)
C_1 ring	0·350	−0·014	0·257	0·03 (2)
C_2 ring	0·237	0·007	0·375	0·02 (2)
C_3 ring	0·244	0·121	0·377	0·01 (2)
C_4 ring	0·349	0·152	0·260	0·01 (2)
C_5 ring	0·413	0·072	0·175	0·03 (2)

* The distance quoted are those from the atom to mean planes, derived by least squares, defined by

(1) origin, Fe and bridging C and O: equation to plane $5{\cdot}90x'-10{\cdot}49y'+z' = 0$;

(2) the cyclopentadiene ring: equation to plane $1{\cdot}753x'-0{\cdot}053y'+1{\cdot}541z'-1 = 0$.

Table 2. *Observed and calculated structure factors*

h	k	l	F_o.	F_c.
1	0	0	63.4	83.3
2	0	0	28.6	-25.6
3	0	0	22.8	-21.6
4	0	0	29.5	-30.1
5	0	0	17.9	-15.8
6	0	0	19.2	-16.4
7	0	0	8.9	-9.0
0	2	0	75.5	97.9
1	2	0	28.9	30.5
2	2	0	17.9	13.6
3	2	0	u.	0.2
4	2	0	21.8	-19.5
5	2	0	14.3	-15.8
6	2	0	11.7	-11.3
7	2	0	6.4	-3.7
0	4	0	4.8	5.3
1	4	0	3.2	1.7
2	4	0	8.6	8.5
3	4	0	u.	3.3
4	4	0	4.7	1.9
5	4	0	u.	2.1
6	4	0	u.	0.7
0	6	0	33.4	-33.5
1	6	0	32.1	-28.0
2	6	0	5.8	-6.0
3	6	0	21.3	19.3
4	6	0	10.6	9.6
5	6	0	2.6	5.7
6	6	0	5.8	6.5
0	8	0	29.0	-26.5
1	8	0	29.8	-26.6
2	8	0	17.4	-19.9
3	8	0	6.0	6.0
4	8	0	9.1	15.8
5	8	0	13.8	12.5
0,10,		0	17.4	-15.9
1,10,		0	15.2	-12.6
2,10,		0	8.0	-7.4
3,10,		0	u.	1.8
4,10,		0	6.6	7.6
5,10,		0	5.5	6.6
0,12,		0	5.4	3.7
1	1	0	28.6	-28.0
2	1	0	2.8	4.1
3	1	0	17.6	-17.8
4	1	0	9.2	-10.1
5	1	0	u.	-0.2
6	1	0	u.	2.8
7	1	0	3.2	3.6
1	3	0	77.9	101.5
2	3	0	66.6	67.5
3	3	0	35.1	-34.0
4	3	0	u.	-5.2
5	3	0	5.0	-5.0
6	3	0	u.	2.3
7	3	0	6.2	7.0
1	5	0	17.1	-19.5
2	5	0	48.5	-51.9
3	5	0	42.9	-45.1
4	5	0	18.4	-17.1
5	5	0	8.7	-6.0
6	5	0	5.9	6.0
1	7	0	7.4	-6.4
2	7	0	13.0	-12.2
3	7	0	8.7	-9.0
4	7	0	4.9	-3.9
5	7	0	u.	-0.7
6	7	0	u.	1.2
1	9	0	11.2	9.1
2	9	0	12.6	8.7
3	9	0	6.9	7.8
4	9	0	u.	0.5
5	9	0	u.	0.3
1,11,		0	9.6	8.9
2,11,		0	6.6	8.3
3,11,		0	7.4	12.6
4,11,		0	4.8	5.6
1,13,		0	5.3	5.9
2,13,		0	6.5	7.0
0	0	2	25.8	-17.8
0	0	4	38.6	-33.9
0	0	6	7.3	-7.9
0	0	8	11.8	10.6
0	1	1	60.6	71.0
0	1	2	21.0	-24.2
0	1	3	35.8	-34.8
0	1	4	15.8	-16.6
0	1	5	13.0	-14.5
0	1	6	4.5	3.0
0	1	7	43.6	35.2
0	1	8	u.	0.7
0	2	1	56.2	-56.1
0	2	2	36.5	-42.1
0	2	3	38.0	-39.7
0	2	4	37.9	-39.4
0	2	5	8.4	8.6
0	2	6	5.5	-5.5
0	2	7	9.8	8.6
0	2	8	8.4	7.1
0	3	1	1.9	2.3
0	3	2	27.0	-26.3
0	3	3	21.9	-21.3
0	3	4	1.8	-1.8
0	3	5	9.0	-8.6
0	3	6	15.6	18.4
0	3	7	5.0	2.6
0	3	8	u.	2.1
0	4	1	7.1	-10.7
0	4	2	15.3	15.1
0	4	3	29.6	-32.5
0	4	4	3.6	3.5
0	4	5	19.6	21.9
0	4	6	u.	0.7
0	4	7	11.4	9.7
0	4	8	u.	1.0
0	5	1	9.5	-8.6
0	5	2	32.6	-36.1
0	5	3	27.0	24.8
0	5	4	8.0	-1.9
0	5	5	u.	3.4
0	5	6	11.9	13.1
0	5	7	1.2	-1.2
0	6	1	10.2	-6.4
0	6	2	5.2	-4.0
0	6	3	15.2	-17.7
0	6	4	17.8	16.9
0	6	5	6.6	7.0
0	6	6	u.	-2.4
0	6	7	2.9	3.4
0	7	1	36.7	-40.4
0	7	2	13.0	-12.2
0	7	3	25.4	25.1
0	7	4	2.9	0.3
0	7	5	9.0	9.9
0	7	6	u.	3.8
0	7	7	4.6	-4.1
0	8	1	3.9	-3.0
0	8	2	8.4	7.1
0	8	3	6.6	4.0
0	8	4	19.8	18.4
0	8	5	u.	-1.2
0	8	6	2.1	2.0
0	9	1	19.7	-21.3
0	9	2	9.3	11.2
0	9	3	13.7	16.7
0	9	4	4.5	1.4
0	9	5	12.5	12.0
0	9	6	5.9	-5.5
0,10,		1	10.9	8.8
0,10,		2	2.9	-2.9
0,10,		3	8.8	7.6
0,10,		4	8.4	7.8
0,10,		5	3.7	-3.4
0,11,		1	6.4	-6.5
0,11,		2	12.8	16.1
0,11,		3	2.1	1.4
0,11,		4	4.5	2.8
0,11,		5	2.3	3.3
0,12,		1	9.2	10.0
0,12,		2	u.	-1.6
0,12,		3	6.0	6.6
0,12,		4	u.	1.2
0,13,		1	3.8	4.4
0,13,		2	5.6	7.8

Somewhat less satisfactory refinement of the $hk0$ zone was encountered, due to considerable overlap in projection, although the early Fouriers clearly defined the non-bridging carbonyl group and the approximate position of the ring. When this zone had been refined to about 20% further refinement of both zones was achieved by a combination of difference maps and least-squares methods designed for the Manchester University computer. These programmes were designed at first to calculate coordinate shifts only, the offdiagonal terms being computed after experience had shown that their neglect caused very erratic refinement. Later programmes allowed for all possible interactions between coordinates, individual isotropic temperature factors and the overall scale factor. Inspection of the full matrix showed that a number of these cross-interaction terms were not negligible and their inclusion appreciably improved the speed and smoothness of refinement. A fuller description of these and other programmes will be published later (Curtis & Mills).

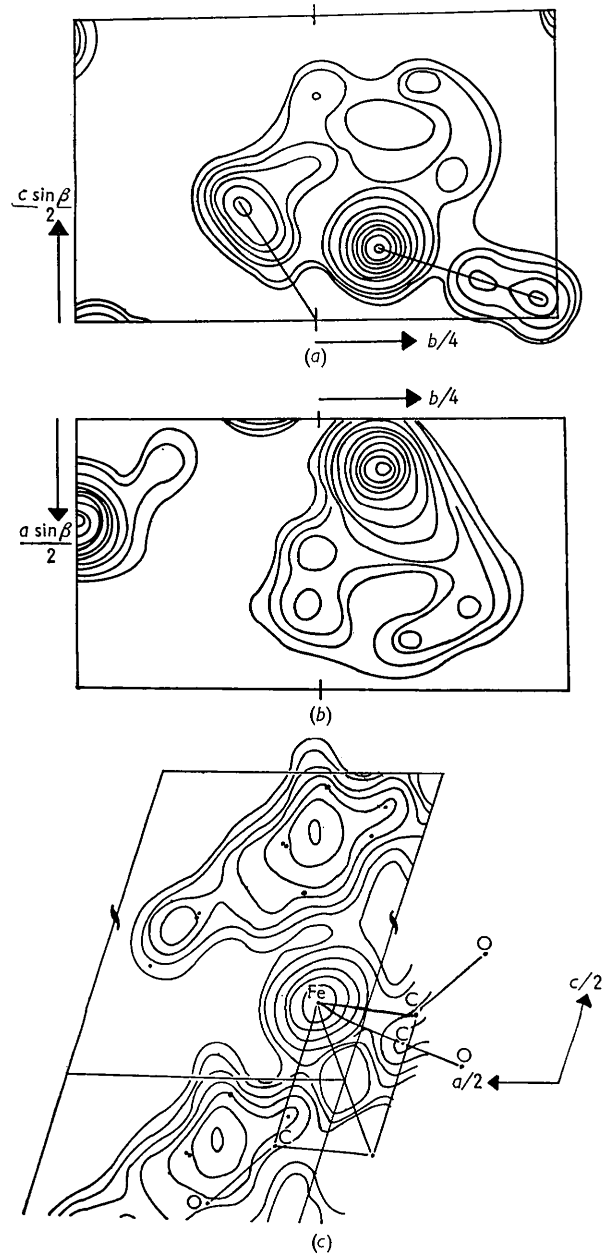

Fig. 2. Fourier synthesis projected (*a*) down [100], (*b*) down [001], (*c*) down [010]. Contours at equal but arbitrary intervals except round Fe.

The final structure, of which the coordinates are given in Table 1 and calculated and observed structure factors in Table 2, gives $R = 11{\cdot}6$–$13{\cdot}9\%$ for the $hk0$ zone and $R = 11{\cdot}9$–$13{\cdot}7\%$ for the $0kl$ zone. In these figures, and in the least-squares treatment, the reflexions 100, 020, 130, 230 and 011 were omitted as being likely to be in error owing to extinction; the smaller values correspond to ignoring all reflexions for which F_o is below the threshold value for observation and the larger value includes all these reflexions with $F_o = 0$. The corresponding values with $F_o = 0{\cdot}75F_{\text{min.}}$ are 13·3% and 12·8%. Reasonable agreement occurs with the unrefined and less accurate $h0l$ data (~ 17%).

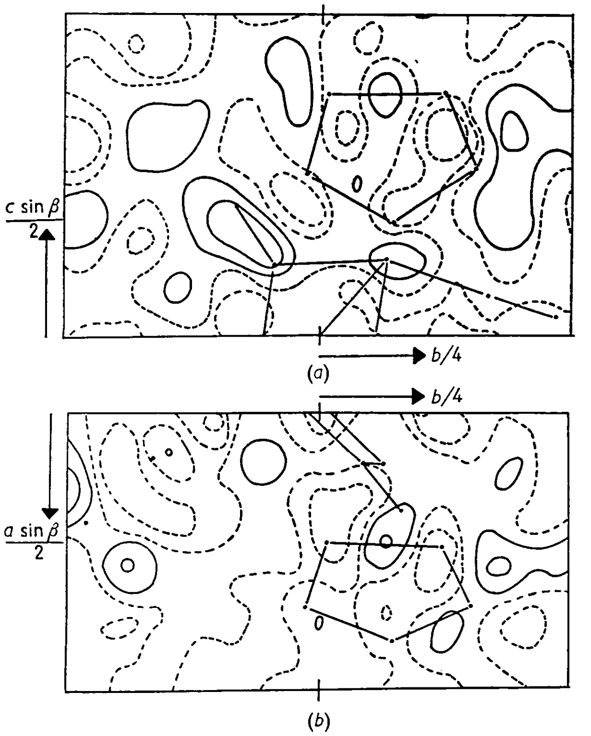

Fig. 3. Difference synthesis, (*a*) $0kl$, (*b*) $hk0$ data. Contours at 0·5 e.Å^{-2}. Zero and negative contours broken.

The final Fourier syntheses are shown in Fig. 2 and difference syntheses in Fig. 3.

Discussion of the structure

The relevant bond lengths and angles are shown in Fig. 4. The Fe atoms are separated by the distance expected from a covalent bond such as is found in iron enneacarbonyl (2·46 Å, Powell & Ewens, 1939). The two C–O bond lengths differ in the order expected for a ketonic double bond in the bridging position to the shorter non-bridging bond, in agreement with the observed infra-red absorptions and comparable with iron enneacarbonyl. The Fe–C bonds (carbonyl) are all appreciably shorter than the sum of covalent radii (single bond), i.e. 2·0 Å, and are of the same order as found in iron enneacarbonyl, although the non-bridging length is shorter. There are two independent estimates of the Fe–C bridging distance. The five-membered ring is arranged geometrically with respect to the Fe in the same way as in ferrocene, i.e. with equidistant Fe–C separations. The mean separation (2·12 Å) is longer than that found by Dunitz but is similar to that found in di-indenyl iron (Trotter, 1958). This increased distance is in accord with the lower stability of both these compounds when compared with ferrocene and with the low stability of nickelocene (2·18 Å). The former compounds are also more intensely coloured than ferrocene.

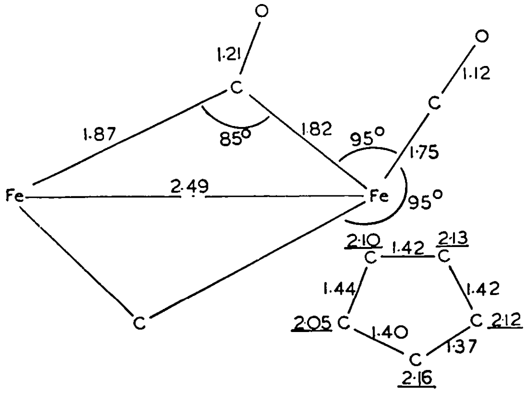

Fig. 4. Angles and bond lengths. The values underlined are Fe–C (ring) distances.

Each iron atom makes three bonds to carbon atoms of carbonyl groups and these bonds are directed to three corners of a distorted octahedron. The structure accounts for the observed diamagnetism with electron pairing of the Fe atoms in the Fe–Fe bond. The packing of the molecules is essentially one involving van der Waals forces between molecules.

As the main object of this investigation was to determine the stereochemistry of the molecule rather than an exact estimation of bond lengths, angles and thermal parameters, the agreement attained is considered sufficient to define the structure. Calculation of standard deviations gives values of 0·02 Å for Fe–Fe, 0·03 Å for Fe–C, and 0·04 Å for C–C and C–O. Within these limits the ring is consistent with a regular planar pentagonal arrangement of the carbon atoms, the maximum deviation of any atom from the least-squares plane being 0·03 Å.

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