neighbors within 3·2 Å and it is not involved in any hydrogen bonding. The short S–O(3) distance suggests a double bond. If there were no such double bond and the sulfur atom were actually shifted 0·078 Å from the center of the tetrahedron, a spontaneous polarization of 3·0 microcoulomb.cm^{-2} in the direction of the c axis should be observed. This is an order of magnitude larger than the observed value for σ_s measured at room temperature. Atom O(1), on the other hand, has two nitrogen nearest neighbors, N(1) and N(2′), at 2·915 and 3·046 Å, which suggests a bifurcated hydrogen bond.

A study of a three-dimensional electron density map and a difference Fourier synthesis was made in order to locate, if possible, the hydrogens and the lithium atoms. In the neighborhood of N(2), six positive peaks were observed in the difference map corresponding to about 0·5 e.Å^{-3}. One set (A) of three of these peaks may correspond to three half hydrogens, two of which are positioned between N(2) and O(1) and O(1′). The remaining peaks form a second set (B) of half hydrogen atoms, two of which are located between N(2) and O(2), and between N(2) and O(2) in the cell immediately (in the **c** direction), as shown in Fig. 5.

The positional coordinates of the lithium ion as obtained from the final electron density map are $x=0·433$, $y=0·339$, $z=0·271$.

The present work was started at the Crystal Research Laboratory of the Pennsylvania State University under contracts with the Solid State Sciences Division of the Air Force Office of Scientific Research and with the Signal Corps Engineering Laboratories. The authors wish to thank Professor Ray Pepinsky for suggesting the problem and for his keen interest in this study.

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The Crystal Structure of Iron Pentacarbonyl: Space Group and Refinement of the Structure

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(*Received* 15 *July* 1963)

The data from iron pentacarbonyl reported by Hanson have been refined, both in the space group Cc assumed by Hanson, and in $C2/c$. The results indicate the correct space group to be $C2/c$. The required molecular symmetry is only 2, but deviations from an ideal trigonal bipyramid are not significant, within the limits of error of this determination. The bond lengths are Fe–C = 1·79 ± 0·02, and C–O = 1·12 ± 0·02 Å.

Additional calculations confirm that the bonding is Fe–C–O rather than Fe–O–C: with the latter structure worse agreement between the F_o and the F_c resulted, and highly unreasonable temperature factors were obtained.

Introduction

In the report by Hanson (1962) on the structure of iron pentacarbonyl the space group assignment was mentioned but once, namely, that it was 'probably Cc'. The alternate possibility, $C2/c$, which is also consistent with the observed absences, was apparently not considered. The required molecular symmetry (for $Z=4$) is none for Cc, and 2 (or $\bar{1}$) for $C2/c$. Upon examination of Hanson's Fig. 1 and his Table 1 it appeared that within experimental error the molecule does contain a twofold axis, and that the space group is thus $C2/c$. The deviations of Hanson's coordinates from the restrictions of $C2/c$ are given in Table 1; the average value of 0·07 Å is less than two standard deviations. Thus, it was felt that further examination of this structure was indicated in order to decide with more certainty which of the two space groups is the correct one.

There is, moreover, additional interest for reexami-

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* This situation was brought to our attention by Prof. A. W. Adamson.

Table 1. *Atomic coordination in space groups Cc and C2/c*

Values under *Cc* are those of Hanson, and those under *C*2/*c* represented the best fit of these to *C*2/*c*. The deviations of the *Cc* values from *C*2/*c* are given under Δx, Δy, and Δz

	x		y		z				
	Cc	*C*2/*c*	*Cc*	*C*2/*c*	*Cc*	*C*2/*c*	Δx	Δy	Δz
Fe	0	0	0·1663	0·1663	0	0	0 Å	0 Å	0 Å
C(1)	0·0800	0·0850	0·3271	0·3099	0·1572	0·1638	0·06	0·02	0·06
C(3)	−0·0899		0·2927		−0·1704				
C(2)	0·1293	0·1284	0·1530	0·1650	−0·0675	0·0673	0·01	0·08	0·00
C(4)	−0·1276		0·1769		0·0671				
C(5)	0·0037	0	−0·1020	−0·1020	0·0135	0	0·04	0	0·13
O(1)	0·1283	0·1372	0·4204	0·3918	0·2607	0·2685	0·01	0·19	0·07
O(3)	−0·1462		0·3633		−0·2763				
O(2)	0·2106	0·2096	0·1367	0·1600	−0·1082	0·1101	0·01	0·16	0·02
O(4)	−0·2086		0·1832		0·1120				
O(5)	0·0055	0	−0·2705	−0·2705	0·0173	0	0·06	0	0·16

nation of this structure because it does not appear to be generally appreciated* that the question of whether in metal carbonyls the structures are $M(-C-O)_n$ or $M(-O-C)_n$ has not often been subjected to direct test. As Cotton & Wilkinson (1962) remark 'only for $Ni(CO)_4$ is there definite X-ray evidence that the metal atom is bound to carbon, but it is commonly assumed and seems likely that this is quite generally true'. We have therefore made calculations on the $Fe(CO)_5$ structure with the specific purpose of testing these alternate possibilities.

Refinement

Hanson's intensity data (three zones) were treated together by full-matrix least-squares (Palenik, 1962), assuming both *Cc* and *C*2/*c* symmetry. Individual isotropic *B*'s were included as variables. The scattering factor curves used were those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon and oxygen and that of Freeman & Watson (1961) for iron. The weighting scheme was that of Hughes (1941) with $4F_{\min}=32$. The initial parameter values were those of Hanson for *Cc* refinement and the same values modified or averaged to conform to the *C*2/*c* symmetry requirements as given in Table 1.

After four and six cycles for the centric (*C*2/*c*) and acentric (*Cc*) refinements, respectively, the maximum value of the ratio parameter shift/e.s.d. was less than 0·3, and convergence was judged adequate. At that stage, the respective *R* values were 11·1 and 9·5%, while the sums of the weighted square residuals, $\Sigma w\Delta F^2$, were 3523 and 2818. Although the refinement of the coordinates was completed, the agreement of the structure factors was further improved by graphically adjusting the overall temperature and scale factors of each zone for both refinements. The resulting final values of *R* and $\Sigma w\Delta F^2$ may be found in Table 2.

Alone, these results might be considered to favor the *Cc* space group. The number of parameters is, for *Cc*, 31 positional and 11 thermal, and for *C*/2*c*, 15 positional and 7 thermal. A consequent reduction of both *R* and $\Sigma w\Delta F^2$ is expected in *Cc*, but whether the observed reductions in these two numbers alone can be used to direct the choice of the correct space group must remain open in the absence of a quantitative theory relating them to the number of variables. However, examination of the final parameters and their standard deviations in Tables 3 and 4 reveals that during the *Cc* refinement those atoms which otherwise would be related by a twofold axis in *C*2/*c* of course strongly interact with each other. In particular, the temperature factors seem to have lost all physical significance. Thus, it is unreasonable for nearly chemically equivalent atoms to have *B* values varying from 0·7 to 7·6 Å² (carbon atoms) or from 2·3 to 4·3 Å² (oxygen atoms). It may be noted further that the carbon atoms C(1) and C(3) with the extreme *B* values are closest to being related by a twofold axis. Even more indicative is the fact that the standard deviations of the acentric parameters are appreciably larger than those of the centric ones (2·5 times as great, on the average) and that out of 31 positional parameters only 6 deviate by more than three e.s.d.'s from the centric values. We feel, therefore, that there is little doubt that the correct space group is *C*2/*c*.

Table 2. *Cc vs. C*2/*c refinement*

	[010] at −80 °C			[001] at −70 °C			[110] at −110 °C			Final Overall	
	Cc	*Cc*	*C*2/*c*	*Cc*	*Cc*	*C*2/*c*	*Cc*	*Cc*	*C*2/*c*		
	Hanson	This work		Hanson	This work		Hanson	This work		*Cc*	*C*2/*c*
B (Å²)	2·0	1·9	1·8	2·3	2·0	1·9	1·7	1·1	1·2	1·4	1·4
R (%)	8·0	5·4	7·4	10·0	6·8	9·4	12·0	12·4	11·4	8·8	9·6
$\Sigma w\Delta F^2$	—	278	626	—	208	369	—	1871	1888	2357	2883

Table 3. *Final atomic coordinates for the Cc and C2/c refinements*

All values $\times 10^4$, except the last three columns. Standard deviations in parentheses. The *c* origin has been changed to conform with the conventional *C*2/*c* origin

	x		*y*		*z*		Differences*			Ratios of σ's†		
	Cc	*C*2/*c*	*Cc*	*C*2/*c*	*Cc*	*C*2/*c*	*x*	*y*	*z*	*x*	*y*	*z*
Fe	0 —	0 —	1655 (6)	1656 (6)	2500 —	2500 —	0	1	0	—	1·0	—
C(1)	0771 (84)	0829 (17)	3065 (161)	3055 (30)	4040 (92)	4122 (19)	58	−10	82	4·9	5·4	4·8
C(3)	−0836 (22)	— —	3051 (35)	— —	0862 (23)	— —	7	4	16	1·3	1·2	1·2
C(2)	1280 (54)	1299 (16)	1738 (73)	1572 (33)	1815 (61)	1830 (18)	19	−166	15	3·4	2·2	3·4
C(4)	−1318 (43)	— —	1488 (60)	— —	3159 (47)	— —	19	84	11	2·7	1·8	6·3
C(5)	0132 (28)	0 —	−0927 (37)	−0937 (50)	2726 (26)	2500 —	−132	10	−226	—	0·7	—
O(1)	1395 (31)	1364 (15)	4062 (58)	3922 (27)	5170 (33)	5165 (17)	−31	−140	−5	2·1	2·1	1·9
O(3)	−1315 (50)	— —	3699 (73)	— —	−0203 (49)	— —	−49	123	38	3·3	2·7	2·9
O(2)	2068 (31)	2097 (15)	1379 (45)	1578 (28)	1382 (33)	1427 (16)	29	199	45	2·1	1·6	2·1
O(4)	−2117 (36)	— —	1805 (50)	— —	3534 (40)	— —	20	−227	39	2·4	1·8	2·5
O(5)	0070 (43)	0 —	−2557 (40)	−2557 (44)	2746 (31)	2500 —	70	0	−246	—	0·9	—

* Differences between the centric and acentric parameters. † Ratios of the acentric to centric standard deviations.

Table 4. *Final temperature factors for the Cc and C/2c refinements*

	B			
	Cc	*C*2/*c*	$\sigma_{Cc}/\sigma_{C2/c}$	*B**
Fe	1·4 (0·1)	1·4 (0·1)	1·0	1·4 (0·1)
C(1)	7·6 (2·3)	2·7 (0·3)	7·8	6·6 (0·6)
C(3)	0·7 (0·7)		2·3	
C(2)	2·6 (0·9)	2·5 (0·2)	3·7	4·4 (0·4)
C(4)	1·7 (0·6)		2·6	
C(5)	1·2 (0·4)	2·8 (0·5)	0·9	5·2 (0·8)
O(1)	2·3 (0·5)	3·5 (0·3)	1·8	2·1 (0·3)
O(3)	4·3 (1·0)		3·6	
O(2)	2·4 (0·6)	3·6 (0·3)	2·2	2·2 (0·3)
O(4)	3·2 (0·7)		2·8	
O(5)	2·7 (0·5)	4·0 (0·5)	1·0	2·3 (0·5)

* Isotropic temperature factors and their standard deviations for the *C*2/*c* refinement with the carbon and oxygen positions interchanged.

The average *B* value of 2·7 Å² for the carbon atoms from the centric refinement is smaller than the corresponding average of 3·8 Å² for the oxygen atoms. This result could have arisen if the carbon and oxygen atoms had been mistakenly interchanged, but it is much more reasonable that atomic bending motions and molecular librations cause the atom temperature factors to increase with the radial distance of the atoms from the molecular center, *i.e.* the iron atom.

Additional steps were therefore carried out in order to identify the peripheral atoms: first, the [010] electron density projection was calculated (Fig. 1) and second, the final centric parameters were subjected to four additional least-squares cycles with the carbon positions assigned to oxygen scattering factors and *vice versa*.* The results of both of these tests favor Fe–(C–O)$_5$ over Fe–(O–C)$_5$: in the Fourier synthesis the peaks are higher at the original oxygen positions (12·1 and 11·2 e.Å^{-2} at O(1) and O(2)) than at the carbon positions (9·1 and 9·7 e.Å² at C(1) and C(2)),

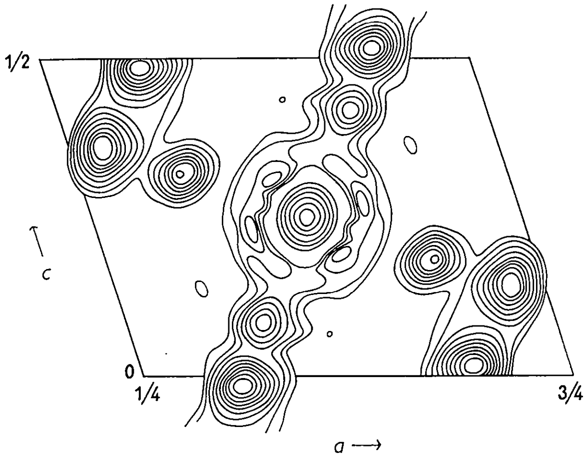

Fig. 1. Electron density projected down *b*. Contours around the iron atom (center of the figure) are at 2, 3, 4, 10, 20, 30 ... 70 e.Å^{-2}; contours around the other atoms are at 2, 3, 4 ... e.Å^{-2}. For identification of the atoms see Fig. 4.

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* None of the calculated F_{hol} changed sign when carbon and oxygen were interchanged. The electron density projection of Fig. 1 therefore does not depend on any structural assumption.

and in the least-squares refinement a much higher R value of 14·0% resulted, as well as highly unreasonable values for the temperature factors (see Table 4). It is concluded that the carbon atoms are bonded to the iron atom. This conclusion is in line with the findings of several authors in earlier studies of carbonyl metal complexes: in the cases of $Fe_2(CO)_9$ (Powell & Ewens, 1939) and $Ni(CO)_4$ (Ladell, Post & Fankuchen, 1952), this structural feature was explicitly noted, and in the case of $Fe_2(CO)_4(C_6H_5)_2$ (Mills, 1958) the same result is implicit from the published electron density maps.

Since the three sets of Hanson's zonal intensities were collected at different temperatures, and from presumably different crystals, one might question the wisdom of refining all three zones together. However, because after final adjustments the differences between the crystal temperature factors of the zones (see Table 2) are reasonable, it is believed that this procedure did not significantly affect the atomic coordinates. As a further indication of this, it might be added that when the carbon positions were refined with the oxygen scattering factors, and *vice versa*, the atomic coordinates changed by insignificant amounts, as shown in Table 5.

Table 5. *Effect of atom identification on positional parameters*

Column two repeats the values of Table 3; column three gives the values resulting when the identification of the carbon and oxygen atoms is interchanged.
Standard errors (× 10^4) in parentheses

		Fe–C–O	Fe–O–C
Fe	*y*	0·1656 (6)	0·1670 (7)
C(1)	*x*	0·0829 (17)	0·0820 (27)
	y	0·3055 (30)	0·3067 (46)
	z	0·4122 (19)	0·4153 (30)
C(2)	*x*	0·1299 (16)	0·1319 (22)
	y	0·1572 (33)	0·1541 (38)
	z	0·1830 (18)	0·1798 (23)
C(5)	*y*	−0·0937 (50)	−0·1033 (59)
O(1)	*x*	0·1364 (15)	0·1381 (18)
	y	0·3922 (27)	0·3924 (34)
	z	0·5165 (17)	0·5150 (21)
O(2)	*x*	0·2097 (15)	0·2124 (19)
	y	0·1578 (28)	0·1577 (38)
	z	0·1427 (16)	0·1383 (20)
O(5)	*y*	−0·2557 (44)	−0·2613 (54)

Structure

Within experimental error the molecule in the *C*2/*c* space group is a trigonal bipyramid. The bond lengths (Table 6 and Fig. 2) have average values of 1·79 ± 0·02 Å for Fe–C and 1·12 ± 0·02 Å for C–O. There is no apparent distinction between axial and equatorial Fe–C bond lengths, a result different from that reported by Luxmoore & Truter (1962) in the structure of $Fe(CO)_4(CH_2=CH–CN)$. The bond angles (Table 6 and Fig. 2) are quite close to the ideal values of 180°, 120°, and 90°. These results therefore do not provide

Table 6. *Bond lengths* (Å) *and bond angles* (°)

Standard errors × 10^2 in Å and × 1 in degrees in parentheses

Angle	*Cc*	*C*2/*c*
Fe–C(5)–O(5)	171 (3)	180 (—)
Fe–C(1)–O(1)	177 (7)	179 (2)
Fe–C(3)–O(3)	172 (4)	
Fe–C(2)–O(2)	166 (4)	178 (2)
Fe–C(4)–O(4)	165 (4)	
C(2)–Fe–C(4)	178 (1)	176 (2)
C(1)–Fe–C(2)	90 (4)	90 (1)
C(3)–Fe–C(4)	91 (2)	
C(2)–Fe–C(3)	89 (2)	92 (1)
C(1)–Fe–C(4)	92 (4)	
C(2)–Fe–C(5)	91 (2)	88 (1)
C(4)–Fe–C(5)	87 (2)	
C(1)–Fe–C(3)	115 (3)	116 (1)
C(1)–Fe–C(5)	116 (3)	122 (1)
C(3)–Fe–C(5)	129 (1)	

Distance	*Cc*	*C*2/*c*
Fe–C(5)	1·77 (3)	1·76 (3)
Fe–C(1)	1·73 (9)	1·80 (2)
Fe–C(3)	1·81 (2)	
Fe–C(2)	1·80 (7)	1·81 (2)
Fe–C(4)	1·83 (5)	
$(Fe–C)_{av}$	1·79 (4)	1·79 (2)
C(5)–O(5)	1·11 (4)	1·10 (4)
C(1)–O(1)	1·28 (9)	1·14 (2)
C(3)–O(3)	1·07 (5)	
C(2)–O(2)	1·14 (6)	1·11 (2)
C(4)–O(4)	1·11 (6)	
$(C–O)_{av}$	1·14 (8)	1·12 (2)

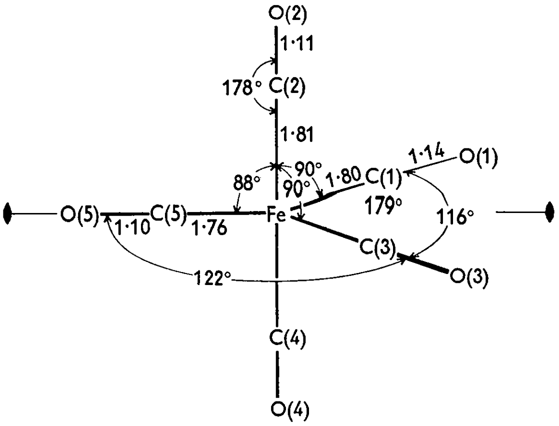

Fig. 2. Bond lengths and angles resulting from refinement in space group *C*2/*c*.

convincing evidence that the molecule 'is slightly distorted in such a way as to allow closer packing' (Hanson, 1962).

Additional evidence that *C*2/*c* is the correct space group is found in Fig. 3, which shows the bond lengths and angles after the refinement in *Cc*. The differences between distances and angles expected to be equivalent are much larger than the corresponding values of Fig. 2.

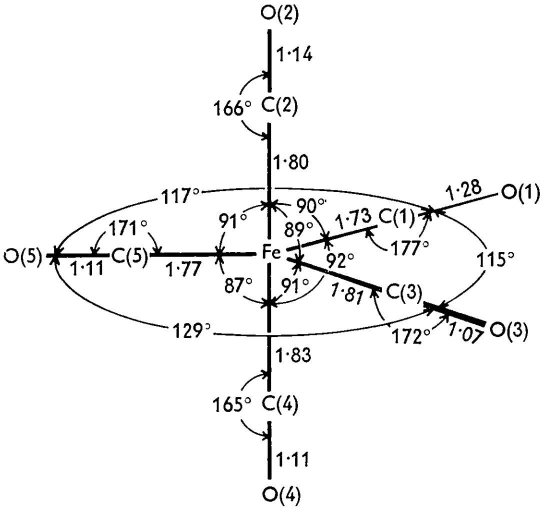

Fig. 3. Bond lengths and angles resulting from the refinement in space group *Cc*.

The intermolecular distances are normal; they are given in Fig. 4, which gives the surroundings of one molecule. The shortest O · · · O distance is 3·15 Å, a value somewhat longer than that of 3·04 Å found in Fe(CO)$_4$(CH$_2$=CH–CN) (Luxmoore & Truter, 1962), about the same as that of 3·1 Å in Fe$_2$(CO)$_9$ (Powell & Ewens, 1939), and shorter than that of 3·24 Å in Ni(CO)$_4$ (Ladell, Post & Fankuchen, 1952). Some of these differences are doubtless due to the different temperatures at which the studies were made.

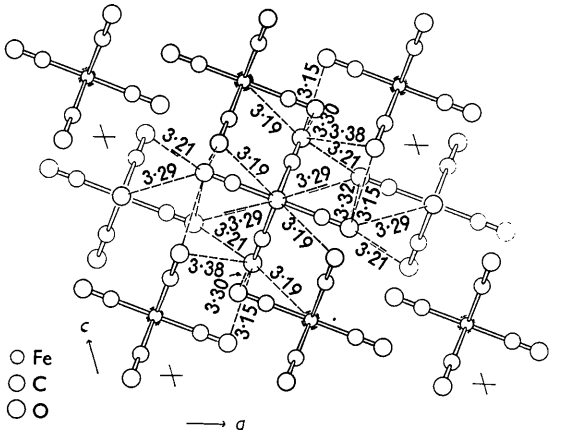

Fig. 4. Projection of the structure down *b*. All intermolecular O · · · O distances less than 3·4 Å involving the central molecule are indicated.

This work was supported by a grant from the National Science Foundation (U.S.A.). Most of the calculations were done at the Western Data Processing Center.

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