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MOLECULAR AND CRYSTAL STRUCTURE OF 1,5-CYCLOÖCTADIENE-BIS(IRON TETRACARBONYL)

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SUMMARY

The structure of 1,5-cyclooctadienebis(iron tetracarbonyl) has been determined from a three-dimensional X-ray analysis. The compound crystallizes in a triclinic unit cell of symmetry $P\bar{1}$ and dimensions: $a = 10.2627$, $b = 7.0824$, $c = 6.4583$ Å; $\alpha = 99.39$, $\beta = 95.76$, $\gamma = 96.21°$.

The unit cell contains one molecule, the molecular symmetry being $2/m$ (C_{2h}). 1409 three-dimensional counter data (Zr-filtered Mo-$K\alpha$-radiation), collected with a computer-controlled Siemens–Hoppe diffractometer, were refined anisotropically to a final discrepancy factor $R = 8.3\%$ ($R_w = 3.3\%$). A description of the automatic data collection procedure is given. The structure was solved by automatic phase determination through symbolic addition procedure, and successive Fourier-syntheses.

A final difference synthesis revealed all the hydrogen positions. The 1,5-cyclooctadiene molecule is bonded to two $Fe(CO)_4$-units through its double bonds in the *chair*-conformation. The C=C distance is 1.400 Å, the double bond being exactly in the trigonal plane of the dsp^3-hybridised iron. Some slight distortions from ideal symmetry within the organometallic entity are observed.

INTRODUCTION

Koerner von Gustorf and Hogan[1] have recently reported the photochemical preparation of various cyclooctadiene complexes of iron carbonyls. In the course of our studies on the geometry and bonding in olefinic transition metal complexes, one of the described compounds, 1,5-cyclooctadienebis(iron tetracarbonyl), $C_8H_{12}[Fe(CO)_4]_2$ (I) was chosen for a detailed single crystal X-ray investigation. Preliminary space group considerations indicated that the COD-ring was complexed in the chair conformation (symmetry $2/m$, C_{2h}), whereas in all the 1,5-COD transition metal complexes previously described[2] the COD molecule is in the boat form; in the free COD molecule neither form seems to be energetically or sterically favored[3].

EXPERIMENTAL

Description of unit cell and collection of intensity data

The orange crystals were recrystallized from pentane, and mounted under dry argon in capillaries. They melt at 85–88° and are elongated along {001}. Weissenberg- and precession photographs- taken at room temperature with Cu-$K\alpha$-radiation (λ 1.5418 Å) show that the crystal is triclinic, the space group being either $P1$ or $P\bar{1}$. The unit cell contains one molecule of the species $[Fe(CO)_4]_2COD$, assuming a density of 1.61 g/ml. (The sensitivity of the compound prohibited the experimental measurement of the density by conventional means.) A crystal of the dimensions 0.29×0.06×0.58 mm was selected for the determination of exact cell data and for subsequent intensity data collection. It was mounted along [001] on a Siemens–Hoppe Automatic Diffractometer, which was equipped with a PDP-8s-computer (4 K), IBM-card-punch, and connected via the small computer to a large time-sharing PDP-10-system for program loading and data interchange. The teletype of the diffractometer-computer may also be used as the time-sharing terminal of the full-scale computing system[4].

38 high-order reflections were measured with Zr-filtered Mo-$K\alpha$-radiation (λ 0.71069 Å) by a scanning procedure in Θ, using a narrow counter slit. Most of the reflections showed well resolved $K\alpha_1$, $K\alpha_2$-splittings.

A least-squares procedure revealed the cell-dimensions, given in Table 1.

TABLE 1

CELL DIMENSIONS

a=10.2628±0.0006 Å	α=99.400±0.001°
b= 7.082 ±0.002 Å	β=95.766±0.001°
c= 6.458 ±0.001 Å	γ=96.216±0.001°
V=458.014 Å^3	

Omega-scans of some low order reflections, taken with a low take-off angle, showed the crystal to have a satisfactory mosaic spread.

1409 intensity data (hkl–$\bar{h}\bar{k}l$) were collected by Θ–2Θ technique (5-value measurements), giving for each reflection two background counts on either side of the peak, two halves and one full integrating scan over the reflection. The number of scanning steps is selected automatically as a function of Θ, and range in this case from 0.54 to 0.80°. The maximal counting time was set to be 480 msec for 1/100°Θ, the minimum measuring time of the instrument was 60 msec. Strong reflections were handled automatically by the computer by selecting shorter stepping times and, if necessary, inserting 5 Ni-filters of different thickness to reduce the primary beam intensity. Misalignment (and decomposition) of the crystal was taken into account by measuring one monitoring reflection twice, once with and once without a half-slit inserted in front of the counter, every 25 measurements. Thus, missetting was corrected for eventually by changing the setting matrix of the data collection program. This procedure is carried out by a second program, which computes the necessary changes of the setting matrix. The collected intensity data were screened automatically for peak-centering, or erroneous measurements by comparing all collected data for one reflection, according to the rules given by the 5-value-method (program DIKAP). In this way, some poor reflections were excluded from the subsequent data-processing. 84 reflections were below the statistical noise level of the counter and were regarded as unobserved. As a PHI-Scan at CHI 90° had indicated no stronger absorption effects (μ_0=16.67 cm^{-1}), the data were corrected for Lorentz- and polarisation-factors only, and multiplied by a scale factor, which was computed by comparing the monitoring reflections*.

SOLUTION AND REFINEMENT OF THE STRUCTURE

A statistical test showed the space group to be $P\bar{1}$, with a statistic of E's being specific for centrosymmetric space groups. The solution of the structure was straightforward by direct methods, using the program set FAME–MAGIC[6], which was adapted to our computer-system. The reflections given in Table 2 were chosen as starting reflections and assigned the given symbolic signs. A corresponding E-map, computed with E's and the signs given in Table 2, showed clearly the heavy atom

TABLE 2

h	k	l	E	Symbol	Interactions	Sign
1	−2	4	2.373	A	18	−
4	3	0	2.037	B	21	+
2	4	1	2.861	C	22	+
−2	7	3	2.385	D	12	−
3	2	5	2.261	E	19	+
7	5	0	2.527	F	10	+
1	−5	3	2.145	G	20	−

position and some atoms of the carbonyl groups; the structure was subsequently completed by two Fourier-syntheses. In order to check the automatic program, a sharpened Patterson-systhesis was computed. The heavy atom vectors were in accordance with the iron position as found.

The model refined isotropically within 5 cycles of full-matrix least squares using a flat weighting scheme, from 38% to a conventional R of 13.7%. The atomic scattering factors for Fe, C, and O where taken from the calculaton of Cromer[7], for hydrogen, the form factors given by McWheeny[8] were used. Five more cycles of weighted least squares, with all atoms refined anisotropically and minimizing R_w, lowered the R-factor to 9.3%. At this stage a difference-Fourier-synthesis clearly showed all hydrogen atoms at reasonable positions. 3 more cycles of anisotropic refinement of the atoms other than hydrogen, keeping the latter fixed, reduced the discrepancy factors to**:

$$R=[\Sigma K(F_o)-|F_c|/\Sigma K(F_o)] \quad : 8.5\% \text{ (unobserved included)}$$
$$: 8.39\% \text{ (unobserved excluded)}$$

and

$$R_w=[\Sigma_N(K^2\cdot F^2 -|F_c|^2)^2/\Sigma_N K^4\cdot F_o^4] \quad : 3.5\%$$

A final difference map did not show any extra electron density. It is worthwhile to mention that only two of the 121 signs determined initially were found by the symbolic addition procedure to be incorrect***. Final atomic and thermal parameters and their standard deviations are given in Table 3.

* A modified version of DATAP was used for data reduction (see ref. 5).

** All calculations and drawings were performed using a PDP-10 time-sharing computer.

*** A final list of F_o and F_c may be obtained on request from the author.

TABLE 3

FINAL ATOMIC AND THERMAL PARAMETERS AND THEIR STANDARD DEVIATIONS ($\times 10^4$)

Atom	x	$\sigma \cdot x$	y	$\sigma \cdot y$	z	$\sigma \cdot z$
Fe	1999	1	2166	1	2907	1
C(1)	2606	6	1332	9	5268	10
C(2)	466	7	2429	10	3924	11
C(3)	1383	7	3069	10	582	11
C(4)	2072	7	−155	9	1398	10
C(5)	6357	6	4388	9	3716	10
C(6)	5139	6	2830	8	3355	10
C(7)	3890	6	3650	8	2647	9
C(8)	3223	6	4892	8	3955	10
O(1)	2980	6	784	8	6779	8
O(2)	−527	6	2567	10	4568	9
O(3)	994	6	3654	9	−902	9
O(4)	2134	8	−1644	8	467	10
H(1)	7142		3607		3003	
H(2)	6170		5411		3062	
H(3)	4884		2525		4875	
H(4)	5157		1804		1534	
H(5)	3759		3968		1258	
H(6)	2808		5771		2843	

Atom	$b_{1,1}$	$\exp[-(h^2 \cdot b_{1,1} + \ldots 2k \cdot l \cdot b_{2,3})]$										
		$\sigma \cdot b_{1,1}$	$b_{2,2}$	$\sigma \cdot b_{2,2}$	$b_{3,3}$	$\sigma \cdot b_{3,3}$	$b_{1,2}$	$\sigma \cdot b_{1,2}$	$b_{2,3}$	$\sigma \cdot b_{2,3}$	$b_{1,3}$	$\sigma \cdot b_{1,3}$
Fe	472	7	345	5	377	6	15	4	20	3	−23	3
C(1)	556	40	428	30	490	37	61	28	71	27	83	26
C(2)	539	38	604	38	487	38	−14	32	82	30	−110	29
C(3)	531	41	540	35	512	39	38	30	50	30	33	28
C(4)	781	50	458	36	464	37	5	33	19	29	24	30
C(5)	479	37	431	30	490	36	65	26	−52	26	77	25
C(6)	485	38	366	28	573	38	51	26	−115	26	28	26
C(7)	521	36	367	28	437	34	−13	25	37	24	−15	24
C(8)	400	33	342	27	533	35	−3	24	55	24	−15	23
O(1)	917	40	729	33	621	34	154	29	298	27	13	26
O(2)	542	36	1149	49	803	39	109	31	172	34	89	26
O(3)	891	40	948	41	601	33	206	32	263	30	−52	26
O(4)	167	66	510	31	714	40	133	35	−106	28	76	36

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The cyclooctadiene ring

The molecule shows, as result of the crystallographic symmetry of the unit cell, ideal $2/m$ (C_{2h}) symmetry, with a *chair* conformation of the COD-moiety (Fig. 1).

To our knowledge, this is the first structure in which a COD-ring is bonded to a transition metal in this manner. Free 1,5-COD is said to exist predominantly in the boat form[9]. In agreement with this, in all COD-transition metal complexes examined so far[2], the COD molecule adopts the boat conformation. However, taking into account Pitzer strains and non-bonded interactions within the ring both forms

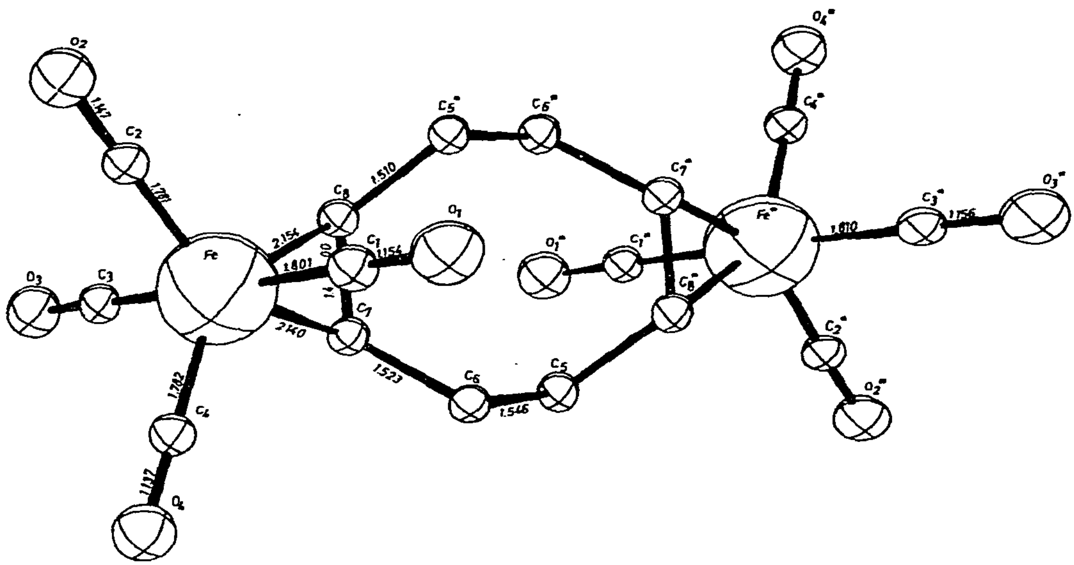

Fig. 1

are energetically equally favored[3]. It seems plausible that in our example the bulky iron–carbonyl groups prevent the adoption of *mm*2 symmetry and that of 2/*m* is adopted for steric reasons. Bond length and angles between the ring atoms, including hydrogen atoms, are found in Table 4. The lengthening of the complexed double

TABLE 4

BOND DISTANCES (Å) AND ANGLES (°) OF THE COD RING

C(5)–C(6)	1.546±0.008
C(6)–C(7)	1.523±0.009
C(7)–C(8)	1.400±0.009
C(8)–C(5)	1.510±0.008
C(5)–H(1)	1.12
C(5)–H(2)	1.06
C(6)–H(3)	1.08
C(6)–H(4)	1.09
C(7)–H(5)	1.12
C(8)–H(6)	1.11
C(5)–C(6)–C(7)	111.1±0.5
C(6)–C(7)–C(8)	125.2±0.5
C(7)–C(8)–C(5)	124.7±0.5
C(8)–C(5)–C(6)	111.2±0.5

bond from 1.34 Å found in free 1,5-COD[10] to 1.400 Å is in accordance with the results from similar compounds. A shift of the double bond stretching frequency from 1655 cm^{-1} to 1450 cm^{-1}, and a shift of the olefin proton absorption in the NMR, from τ 4.52 to 6.3, could correspond to a pronounced sp^3-character of the double bond C-atoms. This is also shown by the positions of the hydrogen atoms, for which the bonding angles are in the region of 109° rather than 120°.

The remaining three independent C-distances in the COD-ring, 1.510 Å, 1.523 Å, and 1.546 Å, are very close to those found for equivalent positions in compounds containing the boat conformation. The hydrogen atoms on C(5) and C(6) are found at positions which correspond to sp^3-hybridisation (see Fig. 2). Two NMR-

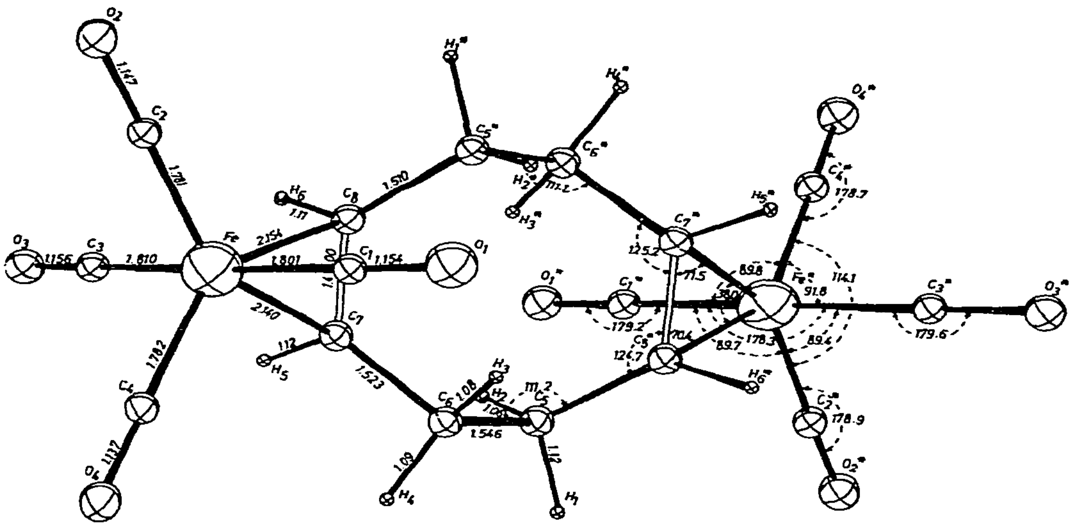

Fig. 2

peaks at τ 8.2 and 7.3 account for the H-atoms which point towards the ring and for those pointing away from the ring. The bond angles at these 4 ring atoms are practically identical (111°) and somewhat lower than that found for the boat conformation (113–116°), whereas the two angles at the coordinated double bond are slightly different (see Table 4).

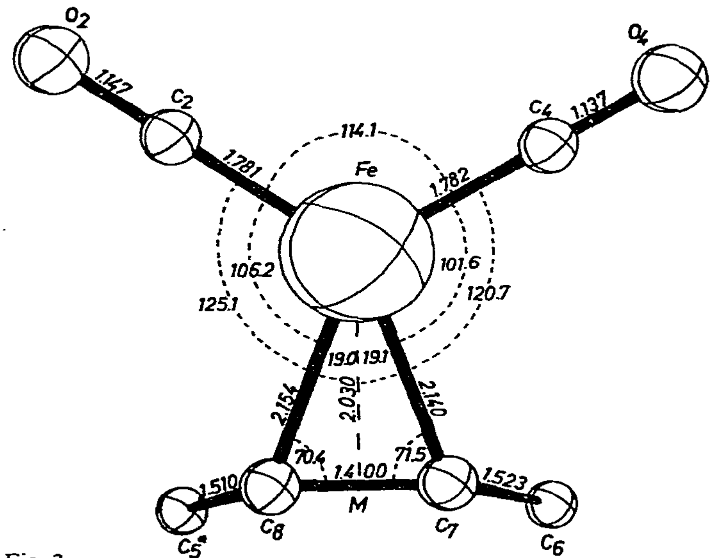

Fig. 3

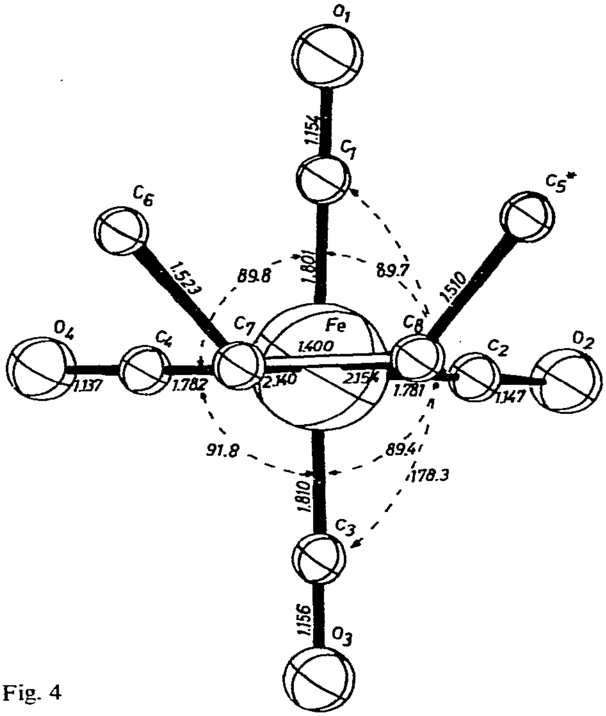

Fig. 4

Coordination around the iron atom

As Fig. 3 and Fig. 4 show, the coordination around the heavy atom only slightly deviates from being ideally trigonal bipyrimidal.

Fig. 4 is a view down the trigonal plane, Fig. 3 is seen perpendicular to it.

Bond angles and distances for the carbonyl groups and the organometallic bonds are given in Tables 5–7, where M denotes the midpoint of the olefinic bond. The bond distances and angles of the iron tetracarbonyl-grouping are in agreement with previous results.

TABLE 5

BOND DISTANCES (Å) TO THE HEAVY ATOM

Fe–C(1)	1.801 ± 0.007
Fe–C(2)	1.781 ± 0.008
Fe–C(3)	1.810 ± 0.007
Fe–C(4)	1.782 ± 0.006
Fe–C(7)	2.140 ± 0.006
Fe–C(8)	2.154 ± 0.005
Fe–M	2.030 ± 0.006

TABLE 6

BOND DISTANCES (Å) IN THE CARBONYL GROUPS

C(1)–O(1)	1.154 ± 0.009
C(2)–O(2)	1.147 ± 0.009
C(3)–O(3)	1.156 ± 0.009
C(4)–O(4)	1.137 ± 0.008

The slight shortening (0.01–0.03 Å) of the C–O as well as the Fe–C bonds in the trigonal plane, compared to the CO-groups perpendicular to it along the polar axis is noteworthy. This effect has also been observed by Truter[10] in tetracarbonyl(acrylonitrile)iron, which has essentially the same structural framework around the iron atom, and has also been observed[11] in $Fe(CO)_5$. It is in accord with the predic-

TABLE 7

BOND ANGLES (°) AT THE HEAVY ATOM

C(1)–Fe–C(2)	89.7±0.3	C(4)–Fe–C(7)	101.6±0.3
C(1)–Fe–C(3)	178.3±0.3	C(4)–Fe–C(8)	139.6±0.3
C(1)–Fe–C(4)	89.8±0.3	C(4)–Fe–M	120.7±0.2
C(1)–Fe–C(7)	92.7±0.3	C(7)–Fe–C(8)	38.1±0.2
C(1)–Fe–C(8)	90.4±0.3	C(7)–Fe–M	19.1±0.2
C(1)–Fe–M	91.6±0.2	C(8)–Fe–M	19.0±0.2
C(2)–Fe–C(3)	89.4±0.3	Fe–C(7)–C(8)	71.5±0.3
C(2)–Fe–C(4)	114.1±0.3	Fe–C(8)–C(7)	70.4±0.3
C(2)–Fe–C(7)	144.2±0.3	Fe–C(1)–O(1)	179.2±0.6
C(2)–Fe–C(8)	106.2±0.3	Fe–C(2)–O(2)	178.9±0.7
C(2)–Fe–M	125.1±0.2	Fe–C(3)–O(3)	179.6±0.6
C(3)–Fe–C(4)	91.8±0.3	Fe–C(4)–O(4)	178.7±0.7
C(3)–Fe–C(7)	87.2±0.3	M–C(7)–Fe	71.5±0.5
C(3)–Fe–C(8)	88.5±0.3	M–C(8)–Fe	71.5±0.5
C(3)–Fe–M	87.7±0.2		

tions for *dsp*^{3}-hybridisation[12], which demands shortening along the polar axes. All four predicted IR-carbonyl-stretching frequencies are observed. As Fig. 4 shows the C=C group lies almost exactly in the trigonal plane. Deviations from the best plane, through Fe, C(2)–O(2), C(4)–O(4), and C(7)–C(8), are 0.07 Å for C(7) and −0.02 Å for C(8). The equation of this plane is given by:

$$3.126x-3.484y+5.595z-1.495=0$$

The two olefinic carbon atoms are not bonded symmetrically to the iron atom. The bond lengths differing by 0.02 Å while the angle from the midpoint of the double bond to the adjacent CO-group is 125.1° in one case and 120.7° in the other.

A similar distortion of the carbonyl groups in the equatorial plane of the same order of magnitude has been observed for tetracarbonyl(acrylonitrile)iron, and explained by repulsion of one CO-group by the cyanide group of the ligand. Here we have a symmetrical environment, and this explanation may not be the only possible one. One possibility is to assume slight twisting of the double bond hydrogens with typical *trans*-effects in the trigonal plane (see Fig. 5). This effect, however, is not revealed

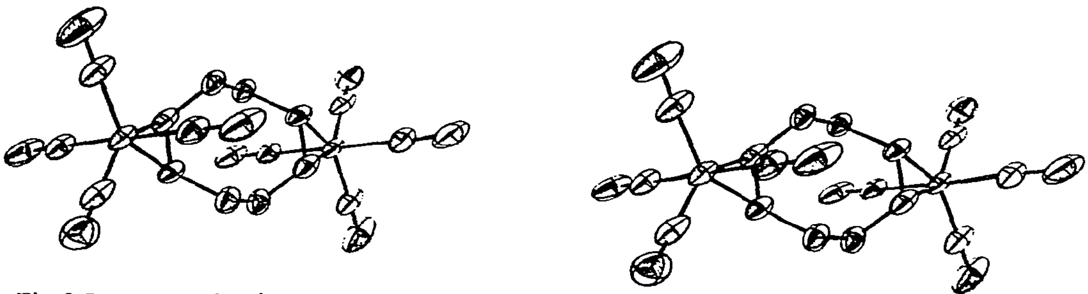

Fig. 5. Stereogram showing the molecule with thermal ellipsoids for non-hydrogen atoms scaled to enclose 50% probability.

in a distortion of the adjacent carbon chains, as the atoms C(5)*, C(6), C(7), C(8) are strictly coplanar. Deviations from the best plane through these atoms are negligble. A qualitative explanation for similar *out-of-plane* distortions in metal(0) complexes, as for instance in tetracarbonyl(fumaric acid)iron[13], has been given recently[14]. It also seems reasonable to invoke small changes in the hybridisation of the central atom to explain the equatorial distortions observed in numerous transition metal complexes.

Intra- and intermolecular contacts

Within the molecule described so far, there are no extraordinary contracts to be observed. The distance between the Fe-atoms of the molecule is 7.008 Å. Fig. 6 shows a stereoscopic representation* of the content of one unit cell. Short intermolecular contacts are given in Table 8. It is obvious from inspection of this table and Fig. 6 that only the carbonyl groups of adjacent molecules are within contact range.

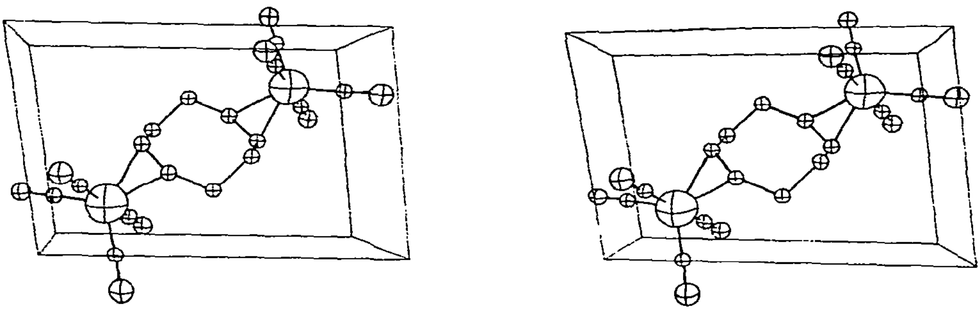

Fig. 6. Stereogram illustrating one unit cell of (I), seen along the *c* axis. The *a* axis is horizontal, the *b* axis vertical

TABLE 8

	Distance (Å)	From lattice point 0 0 0 to		
C(3)–O(1)	3.38	0	0	−1
C(4)–O(1)	3.36	0	0	−1
C(1)–O(3)	3.41	0	0	1
C(2)–O(3)	3.29	0	0	1
O(2)–O(3)	3.11	0	0	1
C(1)–O(2)	3.33	0	0	1
O(3)–O(3)	3.12	0	1	0
C(6)–O(1)	3.36	1	0	1

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* A modified version of program ORTEP[15] was used for preparing the drawings.

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