The Crystal Structure of Racemic Tetracarbonyl(fumaric acid)iron

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The crystal structure of racemic tetracarbonyl(fumaric acid)iron, $Fe(CO)_4(CH.COOH)_2$, has been determined by single-crystal three-dimensional X-ray analysis. The unit cell, of space group *Pccn*, has the dimensions $a = 6.02$, $b = 13.42$, $c = 12.65$ Å. The ligands around the iron atom are arranged according to a trigonal bipyramidal configuration. The fumaric acid group is on the equatorial plane but rotated about 11° around the coordination axis. Furthermore the carbon atoms of the same group deviate significantly from coplanarity.

Introduction

The study of the structure of racemic tetracarbonyl-(fumaric acid)iron is part of a more general investigation on the chemical and structural features of olefin complexes of some transition metals in progress in our laboratory (Paiaro & Panunzi, 1964, 1965).

Experimental

A sample of the compound was prepared in our laboratory following the method described by Weiss, Stark, Lancaster & Murdoch (1963). Crystals suitable for X-ray work were grown by slow evaporation of a solution of racemic tetracarbonyl(fumaric acid)iron in an acetone–hydrochloric acid mixture.

The space group was uniquely determined as *Pccn* by systematic absences observed in Weissenberg photographs for a unit cell having the following dimensions:

$$a = 6.02 \pm 0.03 \text{ Å}$$
$$b = 13.42 \pm 0.05$$
$$c = 12.65 \pm 0.05$$
$$V = 1022 \text{ Å}^3 \quad d_c = 1.84 \text{ g.cm}^{-3} \quad d_{exp} = 1.84 \text{ g.cm}^{-3}.$$

Three-dimensional intensity data ($h0l \ldots h5l$, $0kl \ldots 2kl$) were photographically recorded using the equi-inclination Weissenberg method. Fe $K\alpha$ radiation was used. The intensities of 414 observed reflexions were estimated visually and, after the usual corrections, were placed on a common scale by the method of Rollett & Sparks (1960). No correction for absorption was applied.

Structure determination

On the basis of previous X-ray studies on iron carbonyl compounds (Luxmoore & Truter, 1962) and iron pentacarbonyl itself (Hanson, 1962), it seemed reasonable to assume also for this molecule a trigonal bipyramidal coordination around the iron atom. The presence of only four molecules in a unit cell of *Pccn* symmetry suggested that the twofold symmetry axis of the molecule was retained in the crystal. Accordingly, an attempt was made to solve the structure by means of a three-dimensional Patterson synthesis. The positions of the iron atoms were easily identified and it was possible to explain the presence of peaks about 3 Å from the origin, along the *b* axis, as due to Fe–O vectors of apical carbonyl groups. This information was sufficient to build up a preliminary model of the crystal structure. The structure factor calculation with the preliminary atomic coordinates thus obtained yielded an *R* index ($\Sigma |\Delta F|/\Sigma |F_o|$) for the observed reflexions of 0.35.

A three-dimensional electron density function was than calculated and the resulting image confirmed the over-all correctness of the model.

Refinement of the structure

After two cycles of Fourier synthesis calculations the *R* value was 0.19, using the same isotropic temperature factor (2.5 Å²) for all the atoms. At this stage the refinement was carried out by the differential synthesis method.

After two cycles of isotropic refinement with different temperature factors for each atom, *R* decreased to 0.16. At this stage the temperature factor of the iron atom was higher than those of the carbon and oxygen atoms. This was interpreted as due to the anomalous scattering of the iron atom. A correction was than made for the real contribution of the anomalous scattering of the iron atom and a value of -1.4 e agreed well with differential synthesis data.

Anisotropic temperature factors were subsequently introduced for all atoms. At the final stage the *R* value was 0.127 and the mean shift in the coordinates was about 0.5σ for the light atoms. The final atomic coordinates together with the corresponding standard deviations are reported in Table 1. A comparison between observed and calculated structure factors is listed in Table 2.

Molecular structure

Fig. 1 shows a molecular model of tetracarbonyl(fumaric acid)iron. A list of molecular parameters is given in Table 3. As expected, a trigonal bipyramidal

configuration of the ligands around the iron atom has been found, with the –CH = CH– group of the fumaric acid in an equatorial position. Similar features were observed by Hanson (1962) for iron pentacarbonyl and by Luxmoore & Truter (1962) for tetracarbonyl(acrylo-nitrile)iron. On the basis of the calculated standard deviations no particularly significant differences can be found between the Fe–CO bond lengths [1·81 Å, $\sigma = 0.02$ for Fe–C(2) and 1·88 Å, $\sigma = 0.02$ for Fe–C(1)]. The value of the –CH = CH– bond length (1.42 ± 0.04Å)

Table 1. Final atomic parameters

	x/a	$\sigma(x)$ (Å)	y/b	$\sigma(y)$ (Å)	z/c	$\sigma(z)$ (Å)
Fe	0·2500		0·7500		0·2253	0·003
C(1)	0·3975	0·014	0·8736	0·023	0·2275	0·020
C(2)	0·0297	0·021	0·8057	0·017	0·3039	0·020
C(3)	0·1377	0·031	0·7665	0·020	0·0741	0·024
C(4)	0·0764	0·029	0·8743	0·017	0·0426	0·018
O(1)	0·4881	0·015	0·9433	0·015	0·2379	0·019
O(2)	−0·1065	0·015	0·8414	0·021	0·3501	0·015
O(3)	0·2217	0·021	0·9320	0·016	0·0228	0·018
O(4)	−0·1373	0·015	0·8854	0·013	0·0426	0·018

Thermal parameters $\times 10^4$

T.F. $= \exp\left[-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2)\right]$

	b_{11}	b_{22}	b_{33}
Fe	142	27	34
C(1)	155	18	44
C(2)	114	32	41
C(3)	220	32	41
C(4)	184	31	48
O(1)	344	39	86
O(2)	300	47	63
O(3)	280	36	74
O(4)	260	38	71

Table 2. Comparison between observed and calculated structure factors ($\times 10$)

does not differ significantly from the values found in other metal–olefin complexes (Alderman, Owston & Rowe, 1960). The most interesting structural feature of the molecule appears to be the departure from co-planarity of the carbon atoms of the fumaric acid. In fact the internal rotation angle $C(4)C(3)C(3') \wedge C(3)$-
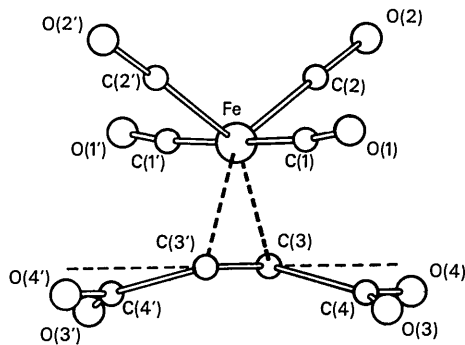

Fig. 1. Molecular model of racemic tetracarbonyl(fumaric acid)iron.

Table 3. Bond lengths and angles

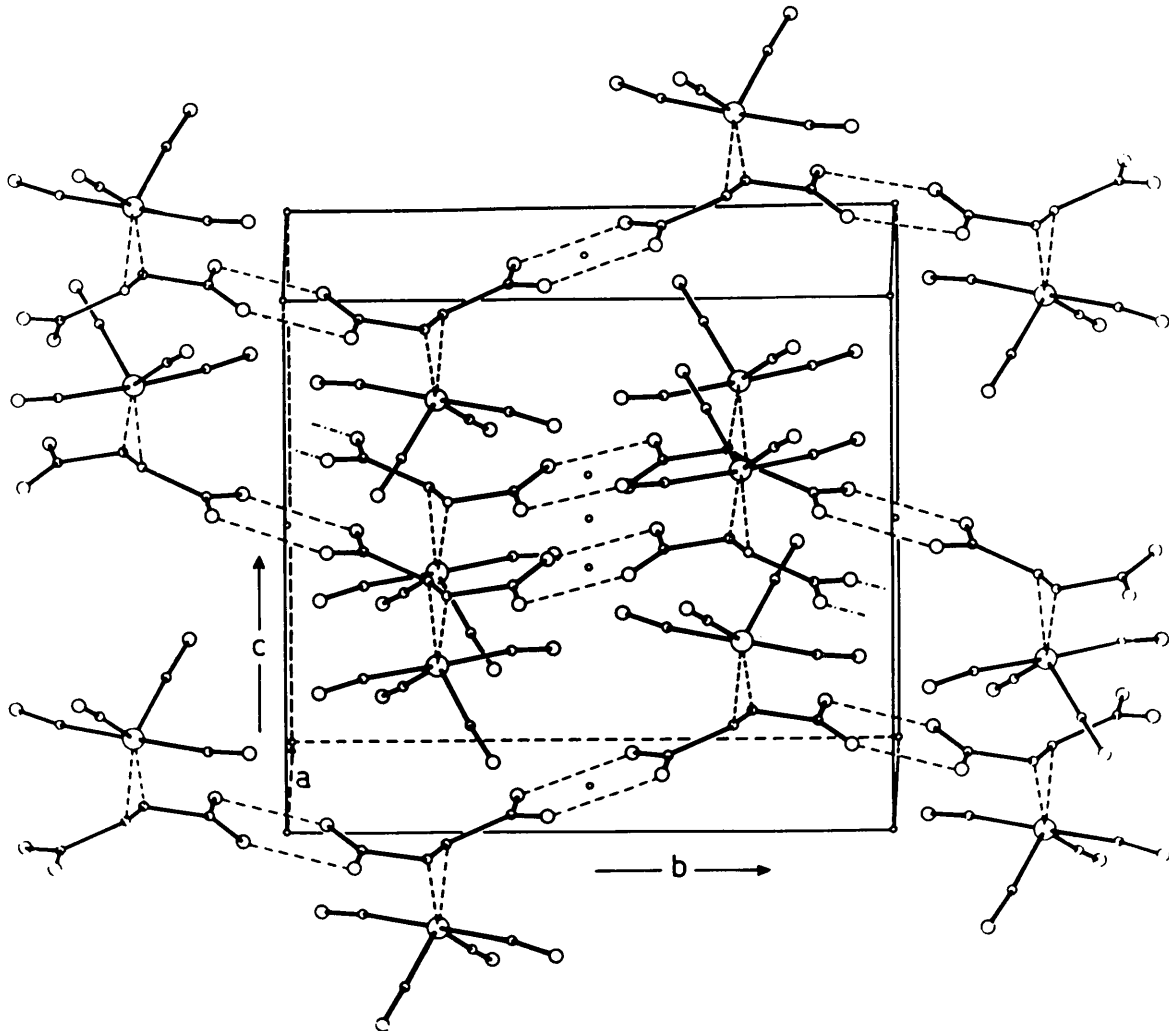|		σ
Fe —C(1)	1·881 Å	0·021 Å
Fe —C(2)	1·817	0·020
Fe —C(3)	2·040	0·025
C(1)–O(1)	1·090	0·026
C(2)–O(2)	1·115	0·026
C(3)–C(3')	1·421	0·043
C(3)–C(4)	1·545	0·028
C(4)–O(3)	1·194	0·030
C(4)–O(4)	1·294	0·031
C(1) –Fe —C(1')	178·3°	0·9°
C(2) –Fe —C(2')	113·7	0·9
C(1) –Fe —C(2)	91·5	0·8
C(1) –Fe —C(2')	90·6	0·8
C(1) –Fe —C(3)	94·3	0·9
C(3) –Fe —C(3')	40·5	0·9
C(1) –Fe —C(3')	88·0	0·9
C(2) –Fe —C(3)	103·9	0·9
C(2) –Fe —C(3')	144·6	1·0
Fe—C(2)–O(2)	178·3	1·8
Fe—C(1)–O(1)	173·6	2·0
C(3')–C(3)–C(4)	121·2	2·0
C(3) –C(4)–O(3)	119·1	2·0
C(3) –C(4)–O(4)	110·2	2·0
O(3) –C(4)–O(4)	130·7	1·9

Fig. 2. Perspective view of the crystal structure of racemic tetracarbonyl(fumaric acid)iron.

C(3')C(4') which was determined to be 180° in fumaric acid (Brown, 1966) has been found in this molecule to be 145°±2°.
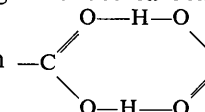
Repulsion of the carboxylic group by the apical carbonyl could be the explanation for the observed deviation. In fact the C(1)–C(4) distance, which is 3·03 Å, would be 2·75 Å if the fumaric acid molecule were planar. Moreover, interaction of the carbonyl group with the central atom might play an important role as suggested by Chatt & Duncanson (1953) for hydrogen and platinum atoms of the square planar platinum-ethylene complexes. This situation is also consistent with a hybridization of the carbon atoms of the –CH=CH– group with a larger proportion of p character.

The equation of the least-squares plane calculated for the C(3)C(3')FeC(2)C(2')O(2)O(2') atoms of the equatorial plane is: $2·92X + 11·7Y = 9·53$.

No significant deviation from the plane has been observed for C(2) and O(2) atoms (maximum deviation ±0·03 Å for C(2) and C(2') atoms). However, the deviation found for C(3) and C(3') atoms appears to be significant (±0·13 Å). This deviation corresponds to a rotation of the fumaric acid molecule around the coordination bond of about 11°. As far as we know, no other example of a similar phenomenon has been described for solid metal–olefin complexes. However, the presence of a single proton absorption signal in the nuclear magnetic resonance spectra of some square metal–ethylene complexes with unsymmetrically disposed protons has lead Cramer (1964), to postulate the possibility of a rotation of the olefin around the coordination axis. The barrier to rotation for $C_5H_5Rh(C_2H_4)_2$ was estimated by Cramer to be of the order of 6 kcal.mole^{-1}. A low-energy barrier to rotation could similarly explain the rotation of fumaric acid observed in our case. The hydrogen bonding between carboxylic groups should be sufficient to compensate for the energy involved in this distortion.

Crystal structure

A perspective view of the crystal structure is shown in Fig. 2. The structure consists of rows of enantiomeric hydrogen-bonded molecules directed along the $a+b$ and $a-b$ crystallographic axes. A distance of 2·65 Å has been found between the oxygen atoms (O---H–O) of the hydrogen bonded carboxylic groups.

$$\text{The system} \quad -C \overset{\displaystyle O----H-O}{\underset{\displaystyle O-H----O}{\Big\backslash\Big/}} C- \quad \text{is planar within ex-}$$

perimental error; the maximum deviation from the least-squares plane ($0·114X + 4·24Y + 12·00Z = 2·12$) is ±0·07 Å for the C atoms. No intermolecular distance less than 3·12 Å (O---O) has been observed.

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