

# The Crystal Structure of Racemic Tetracarbonyl(fumaric acid)iron

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The crystal structure of racemic tetracarbonyl(fumaric acid)iron,  $\text{Fe}(\text{CO})_4(\text{CH}_2\text{COOH})_2$ , has been determined by single-crystal three-dimensional X-ray analysis. The unit cell, of space group  $Pccn$ , has the dimensions  $a = 6.02$ ,  $b = 13.42$ ,  $c = 12.65 \text{ \AA}$ . 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  $11^\circ$  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:

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

Three-dimensional intensity data ( $h0l \dots h5l, 0kl \dots 2kl$ ) 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  $3 \text{ \AA}$  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 ( $\sum |AF| / \sum |F_o|$ ) for the observed reflexions of 0.35.

A three-dimensional electron density function was then 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 ( $2.5 \text{ \AA}^2$ ) 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 then made for the real contribution of the anomalous scattering of the iron atom and a value of  $-1.4 \text{ e}$  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  $0.5\sigma$  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 ( $1.42 \pm 0.04$  Å)

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

	$b_{11}$	$b_{22}$	$b_{33}$
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 ( $\times 10$ )

$h$	$k$	$F_o$	$F_c$																						
1	0	196	211	1	5	603	434	5	5	330	350	0	0	1493	1671	2	12	320	319	5	4	73	55		
4	0	168	248	2	5	243	229	1	6	182	154	1	0	311	366	0	13	127	132	0	5	337	296		
6	0	214	299	3	5	209	121	2	6	193	251	2	0	433	398	-3	5	1	5	166	142	0	1	448	508
1	1	1188	259	4	5	139	86	3	6	107	260	3	0	206	181	1	1	151	175	2	5	567	470		
3	1	561	525	1	6	121	49	4	6	444	405	4	0	549	534	3	1	179	160	3	5	268	235		
5	1	499	524	2	6	216	197	5	6	94	109	0	1	803	743	1	2	159	135	4	5	458	466		
0	2	923	1015	3	6	127	83	7	7	763	745	1	1	902	916	2	2	155	169	5	5	102	154		
2	2	499	566	4	6	241	220	1	7	609	685	2	1	539	490	3	2	273	206	0	6	513	558		
4	2	193	170	5	6	56	58	2	7	609	55	3	1	239	237	4	2	200	108	1	6	496	537		
6	2	151	224	2	7	320	310	0	8	137	151	4	1	412	374	1	3	188	188	2	6	68	52		
1	3	822	697	2	8	116	103	1	8	149	136	5	1	280	348	2	3	199	140	3	6	330	275		
3	3	296	348	1	9	315	316	2	8	931	649	0	2	148	130	4	3	218	124	4	6	65	70		
5	3	104	78	2	10	55	43	3	9	381	271	1	2	326	342	2	4	214	138	0	7	631	622		
0	4	339	311	1	11	127	125	1	9	593	518	2	2	551	530	3	4	310	245	1	7	272	311		
2	4	721	750	2	11	98	67	0	10	487	475	3	2	607	478	5	4	81	64	2	7	216	232		
4	4	795	736	1	12	157	132	1	10	373	303	4	2	296	267	1	5	242	197	0	8	424	429		
1	5	1540	1375	2	12	259	207	2	10	234	229	5	2	193	202	2	5	296	255	1	8	267	247		
3	5	619	549	1	2	110	116	2	11	110	116	0	3	482	533	5	5	72	78	2	8	322	323		
5	5	241	208	0	0	479	681	0	12	254	215	1	3	158	153	1	6	281	236	0	9	514	523		
0	6	1125	1020	1	0	786	868	1	12	169	160	2	3	644	602	3	6	127	124	1	9	373	367		
2	6	792	819	2	0	328	320	2	12	271	279	3	3	404	416	1	7	149	126	2	9	66	77		
4	6	500	459	3	0	108	79	1	13	241	260	4	3	209	196	1	8	224	272	0	10	301	254		
1	7	703	631	4	0	599	631	1	2	152	153	5	3	163	151	9	13	171	161	0	5	326	316		
0	8	577	529	5	0	82	73	1	1	876	835	0	4	195	203	1	10	184	199	0	11	264	252		
2	8	524	509	6	0	90	179	2	1	145	106	1	4	107	36	2	10	134	128	1	11	144	154		
1	9	487	386	0	1	442	431	3	1	231	190	2	4	455	423	1	11	43	32	2	11	172	206		
0	10	678	648	1	1	723	684	4	1	104	90	3	4	491	465	1	12	82	98	0	12	57	59		
2	10	326	349	2	1	535	460	2	2	943	979	4	4	491	428	2	6	12	130	1	12	178	178		
1	11	558	465	3	1	152	386	2	2	226	160	5	4	326	341	0	0	437	443	2	7	342	335		
0	12	121	97	5	1	292	310	3	2	265	197	0	5	489	510	0	5	551	570	3	1	89	89		
2	12	444	449	6	1	32	69	5	2	170	144	1	5	529	549	2	6	161	159	3	1	73	53		
1	13	91	99	0	2	917	896	3	3	772	765	3	5	524	544	1	2	194	184	8	3	60	59		
2	1	1	561	539	4	3	148	65	3	5	744	674	3	6	459	463	1	2	145	145	5	1	91	97	
1	1	450	367	2	2	1112	995	5	3	188	143	5	5	535	509	1	2	274	230	1	3	593	591		
2	2	459	410	4	2	513	478	1	4	486	416	0	6	886	970	0	1	1041	1153	3	2	322	320		
3	1	382	307	5	2	162	270	2	4	151	174	1	6	119	97	1	1	573	580	3	2	140	140		
4	1	138	83	0	3	116	127	3	4	320	249	2	6	451	418	2	1	450	504	5	2	276	276		
6	1	58	82	1	3	809	730	4	4	187	94	3	6	220	235	5	1	66	53	3	3	123	124		
1	2	124	101	2	3	275	289	5	4	176	156	4	6	327	306	2	3	148	143	5	5	321	314		
2	2	145	131	3	3	888	865	1	5	120	64	5	6	161	194	1	2	351	340	5	4	435	435		
3	2	235	168	4	3	48	48	3	5	247	223	0	7	116	136	2	2	637	621	2	4	91	91		
6	2	79	75	5	3	438	520	4	5	196	160	1	7	272	260	3	2	334	338	4	4	70	93		
1	3	94	83	0	4	986	973	5	5	75	74	2	7	246	188	4	2	151	103	1	5	144	144		
2	3	379	356	1	4	302	242	1	6	224	185	0	8	285	271	5	2	106	109	3	5	154	154		
3	3	138	76	2	4	572	558	2	6	192	162	1	8	479	410	0	3	301	337	1	6	106	106		
4	3	86	18	3	4	335	291	3	6	124	141	2	8	326	306	1	3	554	521	2	6	142	141		
5	3	77	49	4	4	466	450	5	6	172	169	0	9	238	250	2	3	506	464	3	6	178	170		
6	3	73	149	5	4	81	31	1	7	162	105	1	9	263	304	3	3	436	389	4	6	40	40		
1	4	1016	902	0	5	636	694	2	8	116	130	2	9	196	180	4	3	299	276	1	7	136	119		
2	4	230	169	1	5	201	190	1	10	214	208	0	10	402	309	5	3	70	93	2	8	81	83		
3	4	391	303	2	5	204	188	1	11	91	57	1	10	113	141	0	4	480	523	1	10	87	75		
4	4	176	82	3	5	285	328	2	11	264	199	2	10	259	230	1	4	544	521	2	10	48	52		
5																									

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 coplanarity of the carbon atoms of the fumaric acid. In fact the internal rotation angle  $C(4)C(3)C(3') \wedge C(3)$ -

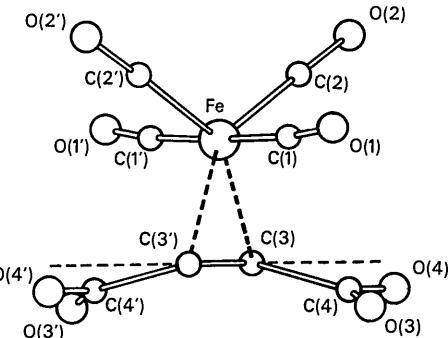


Fig. 1. Molecular model of racemic tetracarbonyl(fumaric acid)iron.

Table 3. Bond lengths and angles

	$\sigma$
Fe—C(1)	1.881 Å
Fe—C(2)	1.817
Fe—C(3)	2.040
C(1)—O(1)	1.090
C(2)—O(2)	1.115
C(3)—C(3')	1.421
C(3)—C(4)	1.545
C(4)—O(3)	1.194
C(4)—O(4)	1.294
C(1)—Fe—C(1')	178.3°
C(2)—Fe—C(2')	113.7
C(1)—Fe—C(2)	91.5
C(1)—Fe—C(2')	90.6
C(1)—Fe—C(3)	94.3
C(3)—Fe—C(3')	40.5
C(1)—Fe—C(3')	88.0
C(2)—Fe—C(3)	103.9
C(2)—Fe—C(3')	144.6
Fe—C(2)—O(2)	178.3
Fe—C(1)—O(1)	173.6
C(3')—C(3)—C(4)	121.2
C(3)—C(4)—O(3)	119.1
C(3)—C(4)—O(4)	110.2
O(3)—C(4)—O(4)	130.7

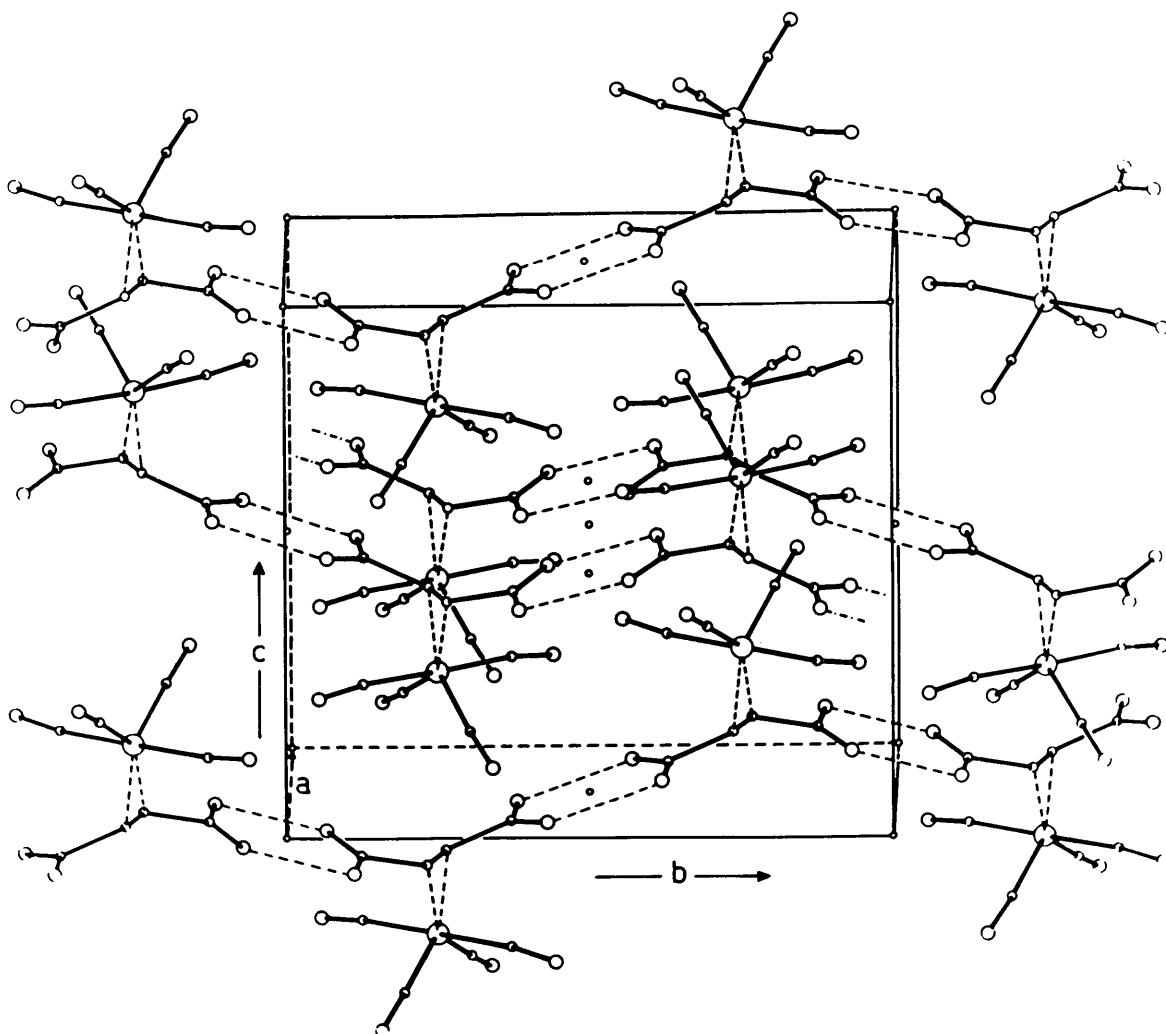


Fig. 2. Perspective view of the crystal structure of racemic tetracarbonyl(fumaric acid)iron.

$C(3')C(4')$  which was determined to be  $180^\circ$  in fumaric acid (Brown, 1966) has been found in this molecule to be  $145^\circ \pm 2^\circ$ .

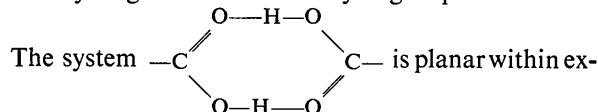
Repulsion of the carboxylic group by the apical carbonyl could be the explanation for the observed deviation. In fact the  $C(1)-C(4)$  distance, which is  $3.03\text{ \AA}$ , would be  $2.75\text{ \AA}$  if the fumaric acid molecule were planar. Moreover, interaction of the carbonyl group with the central 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  $\pm 0.03\text{ \AA}$  for  $C(2)$  and  $C(2')$  atoms). However, the deviation found for  $C(3)$  and  $C(3')$  atoms appears to be significant ( $\pm 0.13\text{ \AA}$ ). This deviation corresponds to a rotation of the fumaric acid molecule around the coordination bond of about  $11^\circ$ . 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  $6\text{ kcal.mole}^{-1}$ . 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  $2.65\text{ \AA}$  has been found between the oxygen atoms ( $O---H-O$ ) of the hydrogen bonded carboxylic groups.



perimental error; the maximum deviation from the least-squares plane ( $0.114X + 4.24Y + 12.00Z = 2.12$ ) is  $\pm 0.07\text{ \AA}$  for the C atoms. No intermolecular distance less than  $3.12\text{ \AA}$  ( $O---O$ ) has been observed.

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