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Structural Studies of Organometallic Compounds. II. The Crystal and Molecular Structure of 1′,1″,1‴,1⁗-Tetracarbonyl-3,4-dicyclopropyl-1-ferracyclopent-3-ene-2,5-dione

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$C_{14}H_{10}O_6Fe$ is tetragonal, $a = 11{\cdot}222\,(4)$, $c = 11{\cdot}410\,(4)$ Å, $Z = 4$, space group $P4_12_12$ (assumed, enantiomorph not determined). The structure was determined from 898 counter intensities and refined to $R = 0{\cdot}081$. The dimensions are very similar to those found for analogous LL'Fe(CO)$_4$ molecules (L,L' are *cis*-ligands with C atoms σ-bonded to Fe); the coordination about the Fe atom is octahedral. The Fe–C-(carbonyl) and Fe–C(σ) lengths are slightly but significantly longer than those in tricarbonylferracyclopentadiene rings. The chirality of the title compound derives from the disposition of the two cyclopropyl rings.

1. Introduction

The title compound was an uncharacterized minor product of a photochemical reaction between dicyclopropylacetylene and iron pentacarbonyl (Victor, Usieli & Sarel, 1977). Crystal structure analysis showed it to be a typical member of the group of octahedral *cis*-disubstituted Fe tetracarbonyls, of formula LL'Fe(CO)$_4$ where L and L' are σ-bonded ligands in two of the equatorial positions of the Fe octahedron.

2. Experimental

The crystals were orange needles elongated along [001]. Crystal data are summarized in Table 1.

Intensities were measured on a Stoe Weissenberg semi-automatic diffractometer with Mo $K\alpha$ radiation (graphite monochromator). No absorption correction was applied.

The four Fe atoms must lie at (x,x,0) and equivalent positions. The structure was solved by Patterson techniques and refined by least squares. The final R was 0·081 for 898 observed reflexions (weighted R = 0·018, goodness of fit = 6·74). The numbering of the atoms is shown in Fig. 1 and the final parameters are given in Table 2.*

The average e.s.d.'s of bond lengths and angles are: Fe–C 0·009, C–C 0·012, C–O 0·010, C–H 0·04 Å, and ∠C–Fe–C 0·4, ∠Fe–C–O 0·7, ∠C–C–O 0·7, ∠Fe–C–C 0·6, ∠C–C–C 0·7°.

Table 1. *Crystal data*

$C_{14}H_{10}O_6Fe$
Tetragonal
$a = 11{\cdot}222\,(4)$ Å
$c = 11{\cdot}410\,(4)$
$V = 1436{\cdot}9$ Å^3
$D_m = 1{\cdot}50$ g cm^{-3} (flotation)
$D_c = 1{\cdot}526$ for $Z = 4$
μ(Mo $K\alpha$) = 10·88 cm^{-1}
Crystal shape: needle cut to a cube ~0·3 mm on edge

FW 330·075
Space group $P4_12_12$*
Systematic absences
$h00: h = 2n + 1$
$00l: l \neq 4n$

* Assumed; intensities were not measured accurately enough to permit distinction between $P4_12_12$ and $P4_32_12$.

3. Results

3.1. *The crystal structure*

The crystal structure (Fig. 2) is that of a typical molecular crystal; intermolecular distances are characteristic of van der Waals interactions and are not given.

3.2. *The molecular structure*

An overall view of the molecular structure is given in Fig. 3 and dimensions in Table 3. The five atoms of the ferrole ring are essentially coplanar (Table 4) with O(1) and C(3) displaced slightly below this plane on one side of the molecule and above it on the other.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32662 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

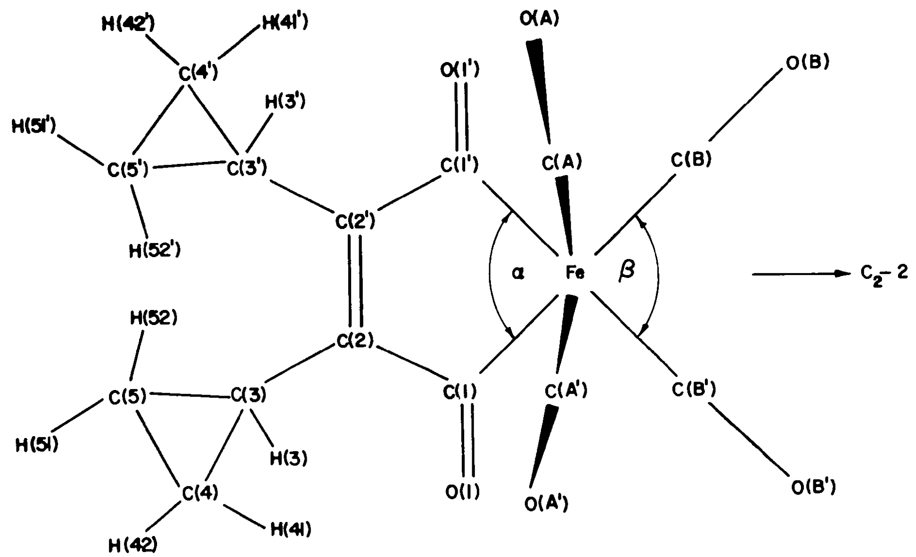

Fig. 1. Numbering of atoms.

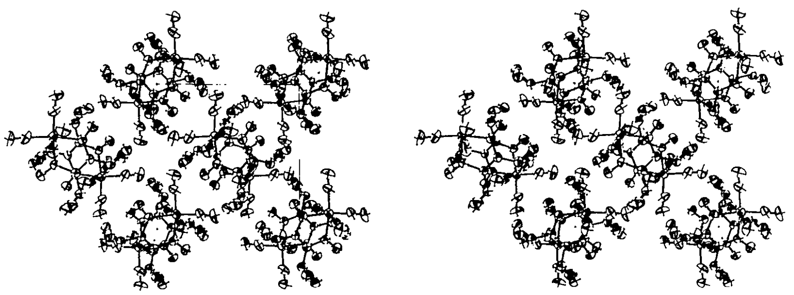

Fig. 2. *ORTEP* (Johnson, 1965) view of the molecular packing. The unit cell is viewed approximately down [001].

Table 2. *Fractional coordinates,* $\times 10^4$ *for non-hydrogen atoms, and* $\times 10^3$ *for hydrogen atoms*

For numbering of atoms see Fig. 1. Estimated standard deviations are in parentheses.

	x	*y*	*z*
Fe	1296 (1)	1296 (1)	0
O(*B*)	1141 (6)	3849 (5)	686 (6)
O(*A*)	1636 (5)	395 (6)	2403 (6)
C(*B*)	1237 (9)	2873 (7)	406 (8)
C(*A*)	1516 (6)	757 (7)	1498 (8)
C(1)	1114 (7)	−475 (6)	−372 (7)
C(2)	−122 (6)	−942 (6)	−175 (7)
C(3)	−419 (7)	−2236 (7)	−386 (8)
C(4)	54 (9)	−2917 (8)	−1416 (9)
C(5)	470 (8)	−3221 (7)	−246 (10)
O(1)	1921 (5)	−1080 (5)	−738 (6)
H(3)	−125 (7)	−239 (6)	−23 (9)
H(41)	57 (8)	−243 (8)	−187 (9)
H(42)	−53 (7)	−343 (8)	−186 (8)
H(51)	7 (7)	−405 (7)	−2 (9)
H(52)	128 (7)	−304 (7)	6 (8)

4. Discussion

4.1. *The molecular structure*

The bond lengths around the Fe atoms are remarkably similar in the six compounds whose structures have been reported (Table 5). The mean Fe—C(sp^2) length is about 2·04 Å while Fe—C(sp^3) is about 0·07 Å longer, which is nearly the difference between the radii of C in these two valence states (0·77 − 0·67 = 0·10 Å). The mean Fe—O(carbonyl) distance is 2·96 Å, slightly larger than that found for carbonyls bound to Fe in $(CO)_3Fe$–(*cis*-butadiene) moieties (2·93 Å, Herbstein & Reisner, 1977); the mean Fe—C-(carbonyl) distance is 1·825 Å, about 0·04 Å longer than that (1·788 Å) found in tricarbonylferracyclopentadiene moieties. Similarly Fe—C(sp^2) is about 0·08 Å longer than the average for analogous bond lengths in ferracyclopentadiene rings. Such effects are not

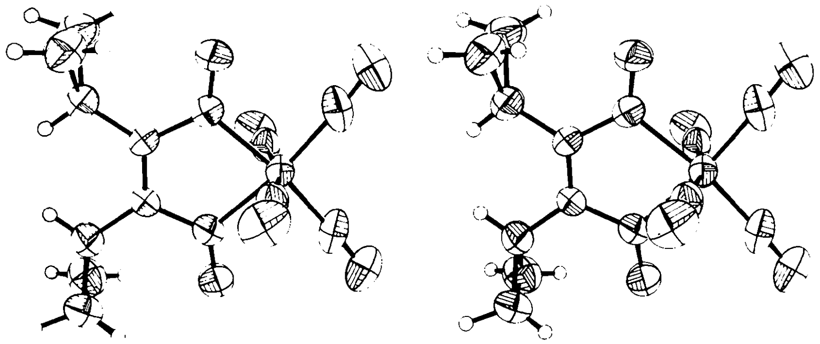

Fig. 3. *ORTEP* view of the molecule, looking approximately normal to the plane of the ferrole ring.

Table 3. *Molecular dimensions*

C–H distances are in the range 0·95–1·07 Å.

Bond lengths (Å)			
$Fe(CO)_4$ group			
Fe–C(*A*)	1·831	Fe–C(*B*)	1·831
Five-membered ring			
Fe–C(1)	2·043	C(1)–O(1)	1·206
C(1)–C(2)	1·499	C(2)–C(3)	1·510
C(2)–C(2′)	1·362		
Cyclopropyl ring			
C(3)–C(4)	1·499	C(4)–C(5)	1·454
C(3)–C(5)	1·497		
Bond angles (°)			
$Fe(CO)_4$ group			
C(*A*)–Fe–C(*B*)	95·1	C(*B*)–Fe–C(*B*′)	97·7 (*β*)
C(*A*)–Fe–C(*B*′)	95·4	C(*B*)–Fe–C(1)	171·7
C(*A*)–Fe–C(1′)	84·5	C(*B*)–Fe–C(1′)	90·5
C(*A*)–Fe–C(1)	83·4	Fe–C(*A*)–O(*A*)	177·9
C(*A*)–Fe–C(*A*′)	164·1	Fe–C(*B*)–O(*B*)	176·3
Five-membered ring			
C(1)–Fe–C(1′)	81·3 (*α*)	C(1)–C(2)–C(2′)	115·7
Fe–C(1)–C(2)	113·7	C(1)–C(2)–C(3)	123·2
Fe–C(1)–O(1)	123·0	C(2′)–C(2)–C(3)	121·1
C(2)–C(1)–O(1)	123·3		
Cyclopropyl ring			
C(2)–C(3)–C(4)	122·5	C(3)–C(4)–C(5)	60·9
C(2)–C(3)–C(5)	123·0	C(3)–C(5)–C(4)	61·0
C(4)–C(3)–C(5)	58·1		

Table 4. *Deviations from planarity* (*in units of* 10^{-3} Å)

Planes were determined by the method of Schomaker, Waser, Marsh & Bergman (1959). The unasterisked atoms and their counterparts related by the twofold axis of symmetry of the molecule have been given unit weight in calculating the best planes, the asterisked atoms have been given zero weight.

	Plane 1	Plane 2	Plane 3
Fe	0	0	0
C(1)	2	30*	–
C(2)	20	–	–
C(3)	45	–	–
O(1)	34	–	–
C(*B*)	23*	6	–
O(*B*)	52*	4	–
C(*A*)	–	–	8
O(*A*)	–	–	5

Equations of the planes [*X,Y,Z* are atomic coordinates (in Å) with respect to the crystal axes]

Plane 1: $0{\cdot}2267X - 0{\cdot}2267Y + 0{\cdot}9472Z = 0$
Plane 2: $-0{\cdot}2408X + 0{\cdot}2408Y - 0{\cdot}9402Z = 0$
Plane 3: $-0{\cdot}6658X + 0{\cdot}6658Y + 0{\cdot}3366Z = 0$

Angles between the three planes

1–2	178·7°
1–3	89·0
2–3	89·8

unexpected as there are appreciable differences between the disposition of the ligands about the Fe atoms in ferrole and ferracyclopentadiene rings. In the former the four carbonyls and two σ-bonded C atoms have an approximately octahedral arrangement, whereas in the latter, three carbonyls and two σ-bonded C atoms are in approximate octahedral positions, with the sixth octahedral position occupied remotely by another carbonyl, bonded to a second Fe atom which is also bonded (in an intermediate direction) to the Fe atom of the ferracyclopentadiene ring.

The bond angle *α* (Fig. 1, Table 5) is reduced below 90° when the σ-bonded C atoms are in a ring, with a larger reduction for a four-membered ring than for a five-membered ring. The opposite angle, *β*, increases above 90° but there does not seem to be a simple relation between these changes.

The four- and five-membered Fe-containing rings of the molecules of Table 5 are all essentially planar (to within 0·02–0·03 Å). In this regard they differ from the ferracyclopentadiene rings of the binuclear tricarbonyliron (tricarbonylferracyclopentadiene) compounds discussed by Herbstein & Reisner (1977) in which the Fe atom deviates by ~0·2 Å from the plane of the four C atoms.

Table 5. *Selected bond lengths* (Å) *and angles* (°) *about the iron atoms in a series of octahedral* $LL'\mathrm{Fe(CO)_4}$ *molecules*

The values have been averaged in terms of assumed molecular twofold axes. Only ligands which form Fe—C bonds have been included in this table. The distances in parentheses are for Fe—C(sp^3), those not in parentheses are for Fe—C(sp^2). The bond angles α and β are defined in Fig. 1.

	Bond lengths						
	equatorial		axial				
	Fe—C (σ)	Fe—C (carbonyl)	Fe—C (carbonyl)	Bond angles α	β	Remarks	Reference
Tetracarbonylbis(1,1,2,2-tetrafluorethyl)-iron	(2·068)	1·852	1·837	92·9°	90·0°	No ring	(*a*)
Tetracarbonyl(perfluorobutadiene)iron	2·00	1·825	1·82	–	–	Five-membered ring	(*b*)
Tetracarbonyl(2-methyl-3-prop-1-ynylmaleoyl)iron	2·023	1·843	1·821	81·5	97·5	Five-membered ring	(*c*)
Title compound	2·043	1·831	1·831	81·3	97·7	Five-membered ring	(*d*)
Dimethyl *trans*-1,1,1,1-tetracarbonyl-ferracyclopentane-2,5-dicarboxylate	(2·152)	1·831	1·824	84·7	95·1	Five-membered ring	(*e*)
$(C_{12}H_8O)Fe(CO)_4$	2·035 (2·112)	1·837	1·819	83·4	95·7	Unsymmetrical five-membered ring	(*f*)
Dibenzosemibullvalenetetracarbonyliron	(2·139)	1·086	1·811	68·9	93·7	Five-membered ring	(*g*)

References: (*a*) Churchill (1967). (*b*) Hitchcock & Mason (1967). (*c*) Pettersen & Levenson (1976). (*d*) Present paper. (*e*) Kruger & Tsay (1976). (*f*) Cotton, Troup, Billups, Lin & Smith (1975). (*g*) Flippen (1974).

The dimensions of the title compound are very close to those of tetracarbonyl(2-methyl-3-prop-1-ynylmaleoyl)iron (Pettersen & Levenson, 1976), and this resemblance even extends to the similar tilts of the axial carbonyl groups towards the five-membered ring [8° in the present molecule compared with 7° (Pettersen & Levenson, 1976)]. A similar tilt of ~8° is found in di-μ-bis(cyclopentadienyl)-stannylbis(tetracarbonyliron) (Harrison, King & Richards, 1975) while the tilts in dibenzosemibullvalenetetracarbonyliron (Flippen, 1974) are rather smaller (4°).

The title compound owes its chirality to the different dispositions of the two cyclopropyl rings with respect to the (almost) planar ferrole ring. Another example where spontaneous resolution occurs on crystallization despite only minor deviations from $m(C_s)$ molecular symmetry is the isomer of tris(cyclopentadienylcarbonylrhodium) (Paulus, 1969; space group $P2_12_12$, $Z = 4$). The molecules undoubtedly racemize immediately on solution and the spontaneous resolution that occurs on crystallization is probably due to rather subtle packing effects. None of the other molecules listed in Table 5 are chiral.

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