

Structure of (η^5 -Cyclopentadienyl) (dicarbonyl) (*O, O'*-diisopropyl dithiophosphato)-iron(II)

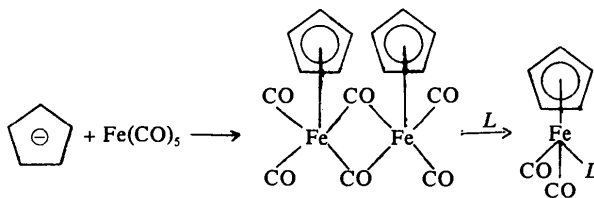
BY J. SANZ-APARICIO, S. MARTÍNEZ-CARRERA AND S. GARCÍA-BLANCO

Departamento de Rayos X, Inst. de Química-Física 'Rocasolano', Serrano 116, 28006 Madrid, Spain

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Abstract. $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_6\text{H}_{14}\text{O}_2\text{PS}_2)(\text{CO})_2]$, $M_r = 390.23$, monoclinic, $P2_1/c$, $a = 13.189(4)$, $b = 8.636(2)$, $c = 16.113(4)$ Å, $\beta = 94.190(4)^\circ$, $V = 1830.4(8)$ Å³, $Z = 4$, $D_x = 1.416$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 1.137$ mm⁻¹, $F(000) = 808$, room temperature, final $R = 0.048$ for 2216 [$I > 3\sigma(I)$] observed reflections. The compound consists of discrete molecules of the familiar 'three-legged piano stool' geometry. The dithiophosphate ester ligand is, unusually, monodentate.

Introduction. We are currently studying a series of cyclopentadienyl-iron(II) derivatives, resulting by partial substitution from the dimer of tricarbonyl(cyclopentadienyl)iron(II), by the following reaction:



There has been significant interest in compounds containing metal- π -bonded aromatic ligands over recent years; Fe complexes are currently being studied in particular (Mitschler, Rees & Lehmann, 1978; Berndt & Barnett, 1980; Teller & Williams, 1980; Korp & Bernal, 1981; Jens & Weiss, 1985).

In this paper we report the structure of $\{(\text{C}_5\text{H}_5)\text{[SP}(=\text{S})(\text{OPr}^i)_2](\text{CO})_2\text{Fe}\}$ as determined by single-crystal X-ray diffractometry.

Experimental. Red needles were prepared by Morán & Cuadrado (1985) and provided by Professor J. G. Rodríguez, Facultad de Ciencias, Dep. de Química Orgánica, Univ. Autónoma de Madrid. Crystal $0.18 \times 0.12 \times 0.45$ mm used to collect 5218 hkl intensities (range of hkl : $0 \leq h \leq 17$, $0 \leq k \leq 11$, $-21 \leq l \leq 21$) with 2216 observed reflections [$I > 3\sigma(I)$]. CAD-4 diffractometer, graphite-monochromated Mo K α radiation. Systematic absences consistent with $P2_1/c$, unit-cell parameters refined from 25 reflections, with $2 < \theta < 28^\circ$; scan mode $\omega/2\theta$. 500 and 500 measured

every 90 minutes, intensities showed no decay throughout data collection; R_{int} from merging 178 equivalent reflections, 0.007. Corrected for Lorentz and polarization factors, but no absorption correction.

Fe atom position found from Patterson function, the other atoms by direct methods in two sets: non-C atoms (*MULTAN80*, Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and C atoms (*DIRDIF*, Beurskens, Bosman, Doesburg, Gould, Van der Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). Atom parameters refined by full-matrix least squares, anisotropic thermal parameters for all the non-H atoms. Five H atoms located from geometric calculation, the remaining ones from successive difference maps and included fixed with isotropic thermal parameters of the atom to which they were attached. Empirical weighting scheme (*PESOS*, Martínez-Ripoll & Cano, 1975) so as to give no trends in $\langle w\Delta^2F \rangle$ vs $\langle F_o \rangle$ and $\langle \sin\theta/\theta \rangle$; final refinement gave $R = 0.048$ ($wR = 0.043$), $(\Delta/\sigma)_{\text{max}} = 0.016$ and $(\Delta/\sigma)_{\text{av}} = 0.003$; $S = 0.92$. Residual electron density in final difference map within -0.75 (near Fe atom) and 0.47 e Å⁻³; atomic scattering factors and anomalous-dispersion corrections for all non-H atoms from *International Tables for X-ray Crystallography* (1974). Calculations performed with the *XRAY* system (Stewart, Kundell & Baldwin, 1976) and *PARST* (Nardelli, 1983) on a VAX 11/750 computer.

Discussion. Final atomic coordinates, with the equivalent isotropic temperature factors of the non-H atoms, are listed in Table 1 and derived structural parameters in Table 2. Fig. 1 shows a general view of the molecule.*

The coordination around iron is that of a distorted octahedron, with three facial points occupied by the cyclopentadiene ring. The average of the three angles defined by Fe, S(1), C(1) and C(2) is 94.8° , *i.e.* not far from the expected value of 90° .

* Lists of structure factors and anisotropic thermal parameters, along with further details of the weighting scheme, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42918 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The Fe—centroid (Cp) distance is 1.724 (1) Å, while the individual Fe—C distances involving the carbocyclic ring show significant variations, possibly due to the carbon atoms experiencing differing steric interactions; thus, the longest distance, Fe—C(10) = 2.106 (9) Å, involves the C atom that lies above S(1) [C(10)—S(1) = 3.027 (8) Å]. The average Fe—C distance is 2.085 (7) Å, not significantly different from the value of 2.070 (7) Å found in the [FeCp(CO)₃]⁺ cation (Gress

& Jacobson, 1973). The cyclopentadienyl C atoms are coplanar with a maximum deviation of 0.004 (8) Å; the Fe atom lies 1.721 (1) Å out of that plane (details of this plane have been deposited).

The Fe—S distance of 2.322 (2) Å agrees well with the value reported for a single bond (English, Nassimbeni & Haines, 1978). The dithiophosphate ester ligand usually adopts a bidentate configuration forming monomeric chelates, bridged oligomers or one-dimensional polymers. This is one of the very few structures (Molloy, Hossain, Van der Helm, Zuckerman & Haiduc, 1979; Shetty & Fernando, 1970) where the ligand is monodentate. According to Pauling's scheme (Pauling, 1960) and corrected for the electronegativity difference (Schomaker & Stevenson, 1941), the lengths of P—S single and double bonds are 2.116 and 1.916 Å respectively. Thus, our observed bond

Table 1. Atomic parameters for [Fe(C₅H₅)(C₆H₁₄O₂PS₂)(CO)₂]

$$U_{eq} = [\frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \cos(a_i, a_j)] \times 10^4.$$

	x	y	z	U _{eq} (Å ²)
Fe	0.38152 (5)	0.75693 (9)	0.13266 (4)	478 (2)
P	0.24976 (10)	0.40795 (15)	0.16825 (8)	489 (4)
S(1)	0.38901 (10)	0.48924 (15)	0.14501 (8)	575 (5)
S(2)	0.25325 (13)	0.19285 (17)	0.20396 (10)	746 (6)
O(3)	0.20855 (25)	0.52636 (38)	0.23237 (19)	564 (12)
O(4)	0.17247 (23)	0.43944 (38)	0.08983 (19)	556 (12)
O(2)	0.36258 (33)	0.79854 (56)	0.31015 (23)	902 (18)
O(1)	0.16524 (31)	0.80580 (50)	0.08950 (29)	883 (18)
C(1)	0.24796 (41)	0.77849 (57)	0.10684 (32)	569 (18)
C(2)	0.36941 (37)	0.77935 (64)	0.24143 (32)	593 (19)
C(3)	0.12315 (45)	0.49514 (70)	0.28331 (34)	709 (21)
C(4)	0.17913 (45)	0.35289 (70)	0.01201 (34)	715 (21)
C(5)	0.02859 (65)	0.54514 (160)	0.23871 (63)	1739 (59)
C(6)	0.14907 (74)	0.57855 (120)	0.36359 (47)	1447 (46)
C(7)	0.07743 (67)	0.26945 (106)	-0.00463 (50)	1330 (39)
C(8)	0.20079 (59)	0.46544 (95)	-0.05484 (37)	1029 (31)
C(9)	0.42849 (61)	0.81611 (115)	0.01568 (34)	946 (31)
C(10)	0.50653 (60)	0.73595 (84)	0.05926 (58)	1001 (32)
C(11)	0.53363 (45)	0.82307 (108)	0.13165 (41)	873 (28)
C(12)	0.47221 (63)	0.95244 (86)	0.12941 (45)	890 (29)
C(13)	0.40823 (52)	0.94894 (95)	0.06040 (52)	931 (30)

Table 2. Bond lengths (Å) and angles (°), with e.s.d.'s in parentheses

Fe—Cp*	1.724 (1)	C(1)—Fe—Cp	121.5 (2)
Fe—S(1)	2.322 (2)	C(2)—Fe—Cp	123.5 (2)
Fe—C(1)	1.790 (5)	S(1)—Fe—Cp	120.4 (1)
Fe—C(2)	1.782 (5)	C(1)—Fe—C(2)	93.4 (2)
Fe—C(9)	2.090 (6)	S(1)—Fe—C(1)	99.1 (2)
Fe—C(10)	2.106 (9)	S(1)—Fe—C(2)	91.7 (2)
Fe—C(11)	2.087 (6)	O(3)—P—O(4)	100.3 (2)
Fe—C(12)	2.072 (8)	S(2)—P—O(4)	113.5 (1)
Fe—C(13)	2.071 (8)	S(2)—P—O(3)	115.3 (1)
P—S(1)	2.026 (2)	S(1)—P—O(4)	109.3 (1)
P—S(2)	1.944 (2)	S(1)—P—O(3)	104.9 (1)
P—O(3)	1.578 (3)	S(1)—P—S(2)	112.5 (1)
P—O(4)	1.588 (3)	Fe—S(1)—P	109.1 (1)
O(3)—C(3)	1.466 (7)	P—O(3)—C(3)	124.2 (3)
O(4)—C(4)	1.468 (6)	P—O(4)—C(4)	121.2 (3)
O(2)—C(2)	1.130 (6)	Fe—C(1)—O(1)	173.8 (5)
O(1)—C(1)	1.131 (7)	Fe—C(2)—O(2)	177.7 (5)
C(3)—C(5)	1.458 (11)	O(3)—C(3)—C(6)	105.0 (5)
C(3)—C(6)	1.498 (10)	O(3)—C(3)—C(5)	109.5 (6)
C(4)—C(7)	1.529 (11)	C(5)—C(3)—C(6)	114.6 (7)
C(4)—C(8)	1.494 (9)	O(4)—C(4)—C(8)	108.1 (5)
C(9)—C(10)	1.388 (11)	O(4)—C(4)—C(7)	106.5 (5)
C(9)—C(13)	1.391 (12)	C(7)—C(4)—C(8)	113.1 (5)
C(10)—C(11)	1.412 (11)	C(10)—C(9)—C(13)	108.2 (6)
C(11)—C(12)	1.380 (11)	C(9)—C(10)—C(11)	106.6 (7)
C(12)—C(13)	1.346 (11)	C(10)—C(11)—C(12)	107.3 (6)
		C(11)—C(12)—C(13)	109.6 (7)
		C(9)—C(13)—C(12)	108.3 (7)

* Cp is the centroid of the cyclopentadienyl ring.

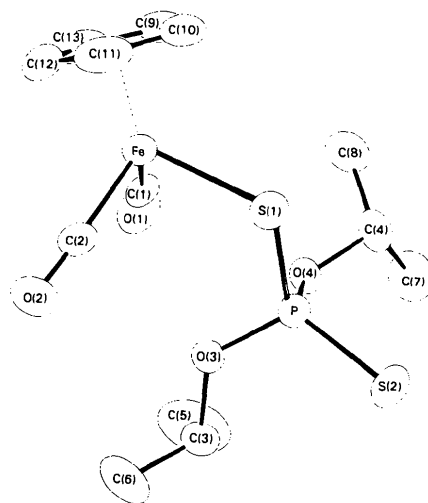


Fig. 1. General view of the molecule showing the atomic numbering. Hydrogens omitted for clarity.

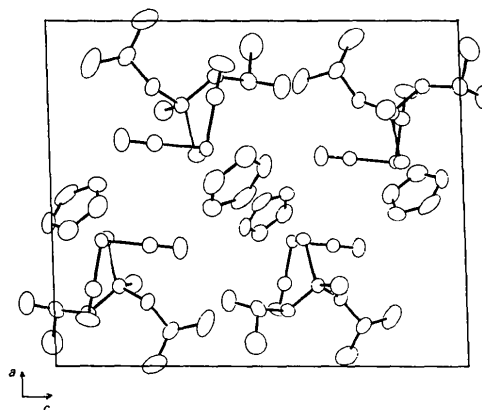


Fig. 2. Packing in the unit cell. (010) projection.

lengths, 2.026 (2) and 1.944 (2) Å, indicate the probable presence of multiple bonding in both cases. Other distances of this moiety are as expected (Lawton, 1970).

The crystal contains no significantly short intermolecular distances and it is built only by van der Waals forces. The packing in the unit cell, (010) projection, is shown in Fig. 2.

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Structure of Sodium Succinate Hexahydrate

BY I. FONSECA, S. MARTÍNEZ-CARRERA AND S. GARCÍA-BLANCO

Departamento de Rayos X, Instituto de Química-Física 'Rocasolano', Serrano 119, 28006 Madrid, Spain

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Abstract. $\text{Na}_2[\text{C}_4\text{H}_4\text{O}_4] \cdot 6\text{H}_2\text{O}$ $M_r = 270.14$, triclinic, $P\bar{1}$, $a = 5.545$ (1), $b = 6.588$ (4), $c = 9.020$ (4) Å, $\alpha = 96.87$ (4), $\beta = 102.19$ (3), $\gamma = 109.61$ (3)°, $V = 296.8$ (3) Å³, $Z = 1$, $D_x = 1.511$ Mg m⁻³, D_m not measured, $\text{Mo } K\alpha$, $\lambda = 0.7108$ Å, $\mu = 0.196$ mm⁻¹, room temperature, $F(000) = 142$, $R = 0.054$ for 1376 reflections [$I > 3\sigma(I)$] of 2611 total unique data. The succinate ion lies on a centre of symmetry. The Na^+ is coordinated to six O atoms with distances ranging from 2.346 (4) to 2.563 (4) Å. The succinate ions are linked through the oxygens of water molecules by hydrogen bonds. The crystals are highly hygroscopic and very unstable when exposed to air.

Introduction. We have performed a study of some alkaline succinates. Previously, we have reported the structure of potassium succinate trihydrate (Fonseca, Martínez-Carrera & García-Blanco, 1985).

Now, the crystal structure of sodium succinate hexahydrate has been solved.

Experimental. Recrystallized from water, a prismatic, colourless, transparent crystal of $0.17 \times 0.23 \times 0.33$ mm was sealed in a Lindemann capillary tube to inhibit alteration, since the compound is highly hygroscopic. CAD-4 diffractometer; room temperature, $\text{Mo } K\alpha$ radiation, graphite monochromator; unit-cell dimensions from a least-squares fit of 24 reflections with $2 < \theta < 35^\circ$, 1376 observed with $I > 3\sigma(I)$; maximum value of 2θ 70° ; no significant intensity variation observed for two standard reflections ($3\bar{2}\bar{1}$, $\bar{3}21$). Corrections for Lorentz and polarization, absorption ignored. The succinate ion lies on a centre of symmetry. The structure was solved by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); an *E* map