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μ-Carbonyl-μ-(hydroxooxophosphido)-bis(carbonyl-η-cyclopentadienyliron) (*Fe–Fe*), $C_{13}H_{11}Fe_2O_5P$

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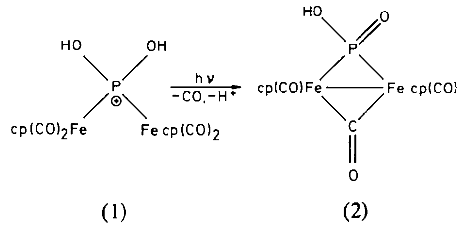
Abstract. $M_r = 389{\cdot}9$, monoclinic, $P2_1/c$, $a = 9{\cdot}112\,(5)$, $b = 23{\cdot}52\,(1)$, $c = 9{\cdot}244\,(5)$ Å, $\beta = 132{\cdot}02\,(4)°$, $V = 1472\,(1)$ Å^3, $Z = 4$, $D_x = 1{\cdot}759\,(1)$, $D_m = 1{\cdot}78\,(3)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 2{\cdot}09$ mm^{-1}, $F(000) = 784$, $T = 295$ K. Final $R = 0{\cdot}054$ for 1555 observed reflections. Hydrogen bridges between the molecules form dimers. The cyclopentadienyl ligands coordinate in *cis* positions. The distance between the Fe atoms within the molecule is 2·615 (4) Å and the mean Fe—P bond length is 2·189 (7) Å.

Introduction. Upon UV irradiation of aqueous solutions containing the cation (1) CO is evolved and red crystals of the title compound (2) are precipitated (Schäfer, 1981), which were directly used for the structure determination.



(1) (2)

(2) is the first complex containing a P(O)OH group as a ligand and can be described as a cyclic diferriophosphinic acid derivative. The IR spectra of the crystals of (2) indicated associated P(O)OH groups. The structure determination was undertaken to find out the configuration of the molecule and the scheme of the suspected hydrogen bonds.

Experimental. As it was not possible to find a single crystal, a crystal which consisted of several needle-like thin plates (0·05 × 0·15 × 0·25 mm) which grew together nearly parallel was chosen for data collection; resulting reflection profiles broadened but not essentially split; space group $P2_1/c$ (systematic absences $h0l$: $l = 2n + 1$; $0k0$: $k = 2n + 1$); lattice parameters from angle settings of 20 reflections; Syntex $R3$ diffractometer, 6673 reflections collected, graphite-monochromatized Mo $K\alpha$, 2θ–θ scan, $2\theta \leq 50°$; data scaled according to variation in intensities of three standard reflections measured periodically after observation of 100 normal reflections, their mean intensity decreased about 12% during time of data collection; after averaging ($R_{\text{int}} = 0{\cdot}053$), 1563 symmetrically independent reflections considered observed [$I > 3\sigma(I)$]; intensities corrected for absorption effects by empirical method of *SHELXTL* (Sheldrick, 1981) using 351 ψ-scan data of 11 reflections (merging R value before correction $R_m = 0{\cdot}076$, after correction $R_m = 0{\cdot}025$, minimum transmission 0·129, maximum transmission 0·223); structure solved by direct methods using *SHELXTL* (Sheldrick, 1981); refinement based on $|F|$ values carried out with block-cascade algorithm of same program system, non-H atoms included with anisotropic thermal parameters and H atoms of cyclopentadienyl rings on calculated positions with fixed isotropic thermal parameters; refinement finished when average ratio of shift-to-error less than 0·02 with maximum ratio 0·05; maximum and minimum heights in final difference Fourier synthesis 1·37 and −1·1 e Å^{-3}; final $R = R_w = 0{\cdot}054$ for 1555 observed reflections with weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}00001F^2$; all calculations performed with *SHELXTL* on a Nova 3 computer; scattering factors and appropriate dispersion corrections taken from *International Tables for X-ray Crystallography* (1974).

Discussion. The final atomic coordinates with the equivalent isotropic temperature factors U_{eq} of the non-H atoms are listed in Table 1 according to the labelling of the atoms in Fig. 1.* The bond lengths are given in Table 2.

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* Lists of bond angles and anisotropic temperature factors of the non-H atoms, the coordinates and the isotropic temperature factors of the H atoms of the cyclopentadienyl groups as well as a list of observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38438 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic temperature factors* (Å^2 × 10^3) *of the non*-H *atoms with e.s.d.'s in parentheses*

	x	*y*	*z*	U_{eq}*
Fe(1)	3660 (2)	6398 (1)	7508 (2)	39 (1)
Fe(2)	1980 (2)	6305 (1)	8936 (2)	50 (1)
P	1537 (4)	5745 (1)	6790 (4)	40 (2)
O(1)	−583 (9)	5768 (3)	4660 (8)	55 (5)
O(2)	2185 (9)	5129 (3)	7274 (8)	45 (5)
O(3)	567 (12)	7021 (4)	3992 (11)	94 (7)
O(4)	3946 (12)	7375 (3)	9565 (11)	75 (8)
O(5)	−1677 (11)	6913 (3)	5973 (10)	81 (6)
C(1)	1765 (18)	6772 (5)	5369 (18)	62 (10)
C(2)	3349 (16)	6897 (5)	8836 (16)	57 (9)
C(3)	−288 (17)	6667 (5)	7094 (15)	59 (9)
C(10)	6097 (15)	5846 (5)	9200 (17)	56 (9)
C(11)	5224 (17)	5838 (6)	7309 (16)	62 (10)
C(12)	5357 (16)	6368 (5)	6851 (14)	73 (9)
C(13)	6251 (17)	6733 (5)	8357 (18)	69 (12)
C(14)	6715 (15)	6401 (5)	9888 (15)	66 (9)
C(20)	3955 (15)	5822 (6)	11449 (14)	100 (10)
C(21)	2042 (18)	5620 (5)	10424 (15)	76 (12)
C(22)	950 (21)	5997 (6)	10063 (30)	180 (19)
C(23)	1905 (26)	6423 (9)	11138 (21)	150 (21)
C(24)	3887 (27)	6384 (6)	11917 (17)	166 (19)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *involving the non*-H *atoms*

Fe(1)—Fe(2)	2·615 (4)	Fe(1)—P	2·196 (4)
Fe(1)—C(1)	1·759 (11)	Fe(1)—C(2)	1·853 (16)
Fe(1)—C(10)	2·100 (10)	Fe(1)—C(11)	2·037 (17)
Fe(1)—C(12)	2·005 (18)	Fe(1)—C(13)	2·081 (16)
Fe(1)—C(14)	2·095 (9)	Fe(2)—P	2·182 (4)
Fe(2)—C(2)	1·913 (15)	Fe(2)—C(3)	1·784 (10)
Fe(2)—C(20)	2·081 (11)	Fe(2)—C(21)	2·094 (15)
Fe(2)—C(22)	1·950 (29)	Fe(2)—C(23)	2·101 (25)
Fe(2)—C(24)	2·059 (12)	P—O(1)	1·587 (5)
P—O(2)	1·514 (7)	O(3)—C(1)	1·138 (12)
O(4)—C(2)	1·233 (14)	O(5)—C(3)	1·120 (12)
C(10)—C(11)	1·352 (20)	C(10)—C(14)	1·396 (16)
C(11)—C(12)	1·347 (19)	C(12)—C(13)	1·349 (17)
C(13)—C(14)	1·410 (21)	C(20)—C(21)	1·396 (18)
C(20)—C(24)	1·405 (22)	C(21)—C(22)	1·202 (22)
C(22)—C(23)	1·261 (23)	C(23)—C(24)	1·431 (33)

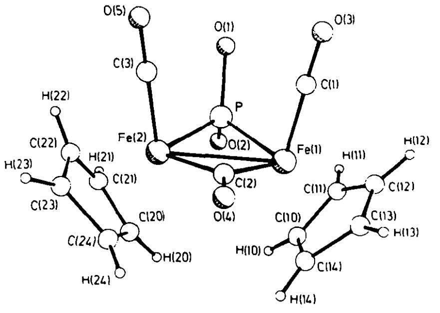

Fig. 1. Perspective drawing of the molecule with the labelling of the atoms.

The main bond angles of the Fe atoms are Fe(2)—Fe(1)—C(1) = 98·2 (7), Fe(1)—Fe(2)—C(3) = 100·0 (6), P—Fe(1)—C(2) = 98·6 (5), P—Fe(2)—C(2) = 97·2 (5)°. The P atom forms an angle of 73·4 (1)° with Fe(1) and Fe(2) and of 108·0 (3)° with O(1) and O(2). The angle Fe(1)—C(2)—Fe(2) is 88·0 (5)°.

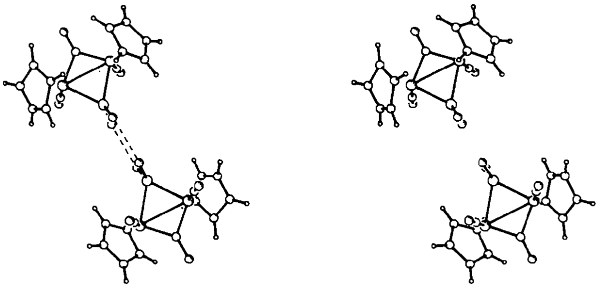

Fig. 2. Stereoscopic view of two molecules with the intermolecular hydrogen bridges.

The bond distances and angles within the four-membered ring Fe(1)—P—Fe(2)—C(2) are very similar to those found in a comparable complex containing a PMe_2 group as a bridging unit (Vahrenkamp, 1973) and also to an analogous compound in which the P atom is part of a cyclophosphazene ring system (Allcock, Greigger, Wagner & Bernheim, 1981). The four-membered ring also adopts a slight envelope conformation with the P atom sticking 0·043 (3) Å out of the plane formed by Fe(1), Fe(2), C(2) and O(4). This shows that the bonding situation within the Fe_2PC framework is quite similar in these three complexes and depends only to a minor extent upon the groups attached to phosphorus.

The cyclopentadienyl ligands are exclusively coordinated in *cis* positions. One cyclopentadienyl ring, C(20) to C(24), seems to be disordered as shown especially by the large and strongly anisotropic temperature factors of C(22), C(23) and C(24) and the nonplanarity of the ring (Fig. 2). Fig. 2 shows the arrangement of two molecules to a dimer related by a centre of symmetry and the intermolecular hydrogen bridges between the P(O)OH groups. It was not possible to find the H atoms forming these bridges definitely in a difference Fourier synthesis. The different P—O bond lengths led us to assume that the bridging H atoms are attached to O(1) forming two asymmetric hydrogen bonds with a rather short intermolecular O···O distance of 2·51 (1) Å. In accordance with the poor quality of the available crystals the e.s.d.'s for bond lengths and angles are rather high. Therefore it is doubtful whether the deviations from symmetry concerning the bonding values within the four-membered ring are significant.

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