

Structure of [Bis(diphenylphosphino-*P,P'*)methanide]tetrakis(phenyl isocyanide)-iron(II) Perchlorate 0.37-Pyridine Solvate

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Abstract. $[\text{Fe}(\text{C}_7\text{H}_5\text{N})_4(\text{C}_{25}\text{H}_{21}\text{P}_2)]\text{ClO}_4 \cdot 0.37\text{C}_5\text{H}_5\text{N}$, $M_r = 980.45$, monoclinic, $P2_1/n$, $a = 13.912$ (4), $b = 21.518$ (8), $c = 18.705$ (8) Å, $\beta = 107.86$ (3)°, $V = 5330$ (4) Å³, $Z = 4$, $D_m = 1.30$ (1), $D_x = 1.22$ Mg m⁻³, Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0.71069$ Å), $\mu(\text{Mo } K\alpha) = 0.436$ mm⁻¹, $F(000) = 2024$, $T = 291$ K, final $R = 0.088$, $wR = 0.083$ for 1935 observed reflections and 239 variables. The structure consists of a complex cation and a disordered perchlorate anion, solvated with a molecule of pyridine, which is highly disordered and its refined occupation factor converge to 0.37 (2). The cation exhibits a distorted octahedral coordination around the Fe atom [average distances Fe—P 2.279 (6), Fe—C 1.84 (2) Å and a dppm-H bite angle of 69.9 (2)°]. This small bite angle is the main distortion from the ideal octahedral geometry. No unusual geometric features are present in the structure.

Introduction. The title compound belongs to a series of cationic complexes $[\text{FeL}(\text{dppm-H})(\text{CNPh})_3]^{n+}$ studied by Riera & Ruiz (1986). In the present work the ligand L is phenyl isocyanide.

Experimental. The density of the yellow prismatic crystals was determined by flotation in hexane/carbon tetrachloride. A crystal, $0.1 \times 0.2 \times 0.3$ mm, was mounted on a Enraf-Nonius CAD-4 four-circle diffractometer. The unit-cell parameters were determined from 24 reflections ($7 \leq \theta \leq 10^\circ$) and refined by least squares. Intensities were collected using the ω - 2θ scan technique, up to $\theta = 27^\circ$ in the hkl range -15 – 15 , 0 – 24 , 0 – 21 . Two reflections, 107 and $\bar{1}07$, were measured every two hours as orientation and intensity control; no significant intensity decay was observed. 9046 reflections were measured, corresponding to 8317 unique reflections ($R_{\text{int}} =$

0.0148), 1935 of which were assumed as observed applying the condition $I \geq 3\sigma(I)$. Lorentz and polarization corrections were applied. The structure was solved by locating the Fe atom in the Patterson map; the other atoms were found by Fourier synthesis; in these first stages XRAY76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) was used. The structure was refined by least squares, using SHELX (Sheldrick, 1976); full-matrix refinement on F was used. The function minimized was $\sum[w(|F_o| - |F_c|)^2]$, $w = [\sigma^2(F_o) + 0.0008|F_o|^2]^{-1}$.

In the complex cation the H atoms were geometrically placed and their overall isotropic temperature factor refined [final value $U = 0.18$ (2) Å²]. The methanide hydrogen [H(10)] was geometrically placed and its isotropic temperature factor refined [final value $U = 0.09$ (6) Å²]. The remaining atoms were refined with anisotropic temperature factors, except those of the phenyl rings, which were isotropically refined in geometrically idealized rigid groups.

One non-bonded pyridine ring was found. Because of disorder the pyridine was refined as a rigid group with ideal geometry and its occupation factor was also refined to $U = 0.37$ (2). We could not identify the N atom in the pyridine, so all were treated as C atoms and their isotropic temperature factor fixed at $U = 0.12$ Å². The temperature factor of H atoms of pyridine was fixed at $U = 0.2$ Å². The perchlorate group was refined anisotropically although, as usual, it was disordered.

After the isotropic refinement, an empirical absorption correction was applied (Walker & Stuart, 1983), correction factors were in the range 0.803–1.186. Anisotropic thermal parameters were comparable after refinement with and without absorption correction.

The final R was 0.088 and wR was 0.083. Maximum shift/e.s.d. was 0.049. The final difference Fou-

rier map showed a residual electron density between -0.41 and $0.41 \text{ e } \text{Å}^{-3}$. The values of f , f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 149–150).

Final positional and thermal parameters, for non-H atoms, are given in Table 1.* A selection of the molecular geometry data is collected in Table 2. The geometry and the crystallographic numbering scheme of the complex cation are given in Fig. 1. Values for selected torsion angles and angles between least-squares planes and lines have been deposited. No unusual geometric features are present in the molecule. The geometric calculations were performed with *PARST* (Nardelli, 1983), and Figs. 1 and 2 were drawn with *PLUTO* (Motherwell & Clegg, 1976).

Discussion. In the literature there are no other complexes of iron with dppm-H ligand, but there are known complexes of Ni, Pd and Pt with this ligand. The only one of those complexes whose structure has been studied by X-ray diffraction is $\text{Pt}[(\text{CH}_2)_2\text{P}(\text{CH}_3)_2][(\text{PPh}_2)_2\text{CH}]$ (Bassett, Mandl & Schmidbaur, 1980); however, as it corresponds to a

* Lists of structure factors, anisotropic thermal parameters, complete bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53547 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

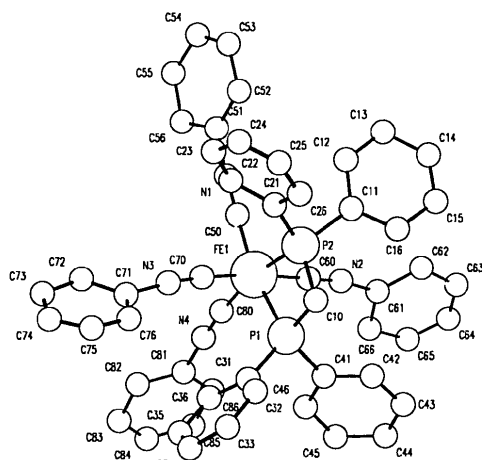


Fig. 1. *PLUTO* drawing of complex cation.

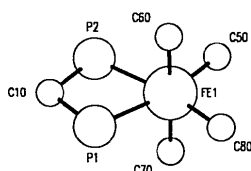


Fig. 2. Coordination sphere of Fe atom.

Table 1. *Fractional positional and thermal parameters with e.s.d.'s*

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{\text{eq}} (\text{Å}^2 \times 10^3)$
Fe(1)	0-1165 (2)	0-0593 (1)	0-7716 (1)	4.4 (2)
P(1)	-0-0180 (3)	0-0581 (3)	0-8166 (3)	6.9 (4)
P(2)	0-1706 (3)	0-0513 (3)	0-8994 (3)	4.7 (4)
Cl(1)	-0-1888 (6)	-0-1808 (3)	0-4465 (4)	7.7 (6)
O(1)	-0-234 (2)	-0-153 (1)	0-377 (2)	18 (3)
O(2)	-0-252 (2)	-0-225 (1)	0-461 (2)	24 (3)
O(3)	-0-154 (2)	-0-1357 (9)	0-502 (1)	13 (2)
O(4)	-0-102 (2)	-0-214 (1)	0-444 (2)	28 (3)
N(1)	0-325 (1)	0-0599 (8)	0-7589 (7)	4 (1)
N(2)	0-096 (1)	-0-0793 (9)	0-7554 (9)	5 (1)
N(3)	0-106 (1)	0-1978 (9)	0-775 (1)	8 (1)
N(4)	-0-009 (1)	0-0655 (8)	0-6104 (8)	6 (1)
C(10)	0-054 (1)	0-053 (1)	0-910 (1)	10 (2)
C(16)	0-1948 (7)	-0-0708 (6)	0-9544 (7)	4.8 (5)
C(15)	0-2484 (7)	-0-1259 (6)	0-9768 (7)	7.5 (7)
C(14)	0-3510 (7)	-0-1286 (6)	0-9837 (7)	6.4 (6)
C(13)	0-4000 (7)	-0-0762 (6)	0-9681 (7)	6.9 (7)
C(12)	0-3464 (7)	-0-0211 (6)	0-9456 (7)	5.2 (6)
C(11)	0-2438 (7)	-0-0184 (6)	0-9388 (7)	4.7 (5)
C(26)	0-273 (1)	0-1114 (6)	1-0326 (8)	8.4 (7)
C(25)	0-340 (1)	0-1540 (6)	1-0780 (8)	8.5 (8)
C(24)	0-392 (1)	0-1953 (6)	1-0461 (8)	7.9 (7)
C(23)	0-378 (1)	0-1940 (6)	0-9690 (8)	5.8 (6)
C(22)	0-311 (1)	0-1513 (6)	0-9236 (8)	4.6 (5)
C(21)	0-258 (1)	0-1100 (6)	0-9555 (8)	5.8 (6)
C(36)	-0-144 (1)	0-1499 (7)	0-7275 (7)	6.7 (6)
C(35)	-0-214 (1)	0-1981 (7)	0-7150 (7)	8.3 (7)
C(34)	-0-245 (1)	0-2213 (7)	0-7743 (7)	8.9 (8)
C(33)	-0-205 (1)	0-1963 (7)	0-8462 (7)	9.3 (8)
C(32)	-0-134 (1)	0-1481 (7)	0-8587 (7)	7.1 (7)
C(31)	-0-104 (1)	0-1249 (7)	0-7994 (7)	4.0 (5)
C(46)	-0-168 (1)	-0-0078 (7)	0-7056 (8)	8.1 (7)
C(45)	-0-232 (1)	-0-0585 (7)	0-6794 (8)	9.3 (7)
C(44)	-0-235 (1)	-0-1070 (7)	0-7281 (8)	9.8 (8)
C(43)	-0-174 (1)	-0-1049 (7)	0-8029 (8)	11 (1)
C(42)	-0-111 (1)	-0-0542 (7)	0-8291 (8)	7.5 (6)
C(41)	-0-107 (1)	-0-0057 (7)	0-7804 (8)	5.0 (6)
C(50)	0-243 (1)	0-058 (1)	0-7636 (9)	3.9 (4)
C(56)	0-451 (1)	0-0701 (8)	0-6955 (6)	8.4 (7)
C(55)	0-552 (1)	0-0707 (8)	0-6976 (6)	10.4 (9)
C(54)	0-628 (1)	0-0593 (8)	0-7649 (6)	8.7 (7)
C(53)	0-603 (1)	0-0472 (8)	0-8302 (6)	6.7 (6)
C(52)	0-502 (1)	0-0466 (8)	0-8282 (6)	5.7 (6)
C(51)	0-426 (1)	0-0580 (8)	0-7608 (6)	5.1 (5)
C(60)	0-105 (1)	-0-026 (1)	0-762 (1)	3.7 (5)
C(66)	-0-007 (1)	-0-1554 (6)	0-6721 (8)	6.4 (6)
C(65)	-0-037 (1)	-0-2169 (6)	0-6545 (8)	7.0 (7)
C(64)	0-008 (1)	-0-2645 (6)	0-7041 (8)	9.6 (9)
C(63)	0-083 (1)	-0-2507 (6)	0-7713 (8)	13 (1)
C(62)	0-113 (1)	-0-1892 (6)	0-7888 (8)	11 (1)
C(61)	0-068 (1)	-0-1416 (6)	0-7392 (8)	4.9 (5)
C(70)	0-113 (1)	0-145 (1)	0-776 (1)	3.8 (5)
C(76)	0-032 (1)	0-2869 (8)	0-8107 (8)	9.1 (8)
C(75)	0-011 (1)	0-3504 (8)	0-8058 (8)	9.8 (9)
C(74)	0-045 (1)	0-3879 (8)	0-7581 (8)	9.5 (8)
C(73)	0-102 (1)	0-3619 (8)	0-7154 (8)	12. (1)
C(72)	0-123 (1)	0-2984 (8)	0-7203 (8)	11 (1)
C(71)	0-088 (1)	0-2609 (8)	0-7680 (8)	6.1 (7)
C(80)	0-043 (1)	0-064 (1)	0-670 (1)	4.1 (5)
C(86)	-0-121 (1)	0-0107 (6)	0-5070 (8)	6.3 (6)
C(85)	-0-189 (1)	0-0099 (6)	0-4346 (8)	6.7 (6)
C(84)	-0-213 (1)	0-0649 (6)	0-3936 (8)	7.8 (6)
C(83)	-0-169 (1)	0-1208 (6)	0-4250 (8)	8.6 (8)
C(82)	-0-100 (1)	0-1216 (6)	0-4974 (8)	5.9 (6)
C(81)	-0-076 (1)	0-0665 (6)	0-5384 (8)	4.9 (5)
C(1)	-0-016 (4)	0-340 (2)	0-024 (3)	12
C(2)	0-074 (4)	0-361 (2)	0-014 (3)	12
C(3)	0-147 (4)	0-318 (2)	0-010 (3)	12
C(4)	0-130 (4)	0-254 (2)	0-016 (3)	12
C(5)	0-041 (4)	0-234 (2)	0-026 (3)	12
C(6)	-0-033 (4)	0-276 (2)	0-031 (3)	12

nearly square-planar coordination of the Pt, the comparison with our case is not too useful.

The title compound exhibits a distorted octahedral coordination around the Fe atom; four vertices are occupied by four phenyl isocyanide molecules, the remaining two are occupied by the two P atoms of

Table 2. Selected values of bond lengths (Å) and bond angles (°) with e.s.d.'s

Fe(1)—P(1)	2.276 (6)	P(2)—C(11)	1.84 (1)
Fe(1)—P(2)	2.282 (5)	P(2)—C(21)	1.84 (1)
Fe(1)—C(50)	1.81 (2)	N(1)—C(50)	1.18 (2)
Fe(1)—C(60)	1.84 (2)	N(1)—C(51)	1.39 (2)
Fe(1)—C(70)	1.84 (2)	N(2)—C(60)	1.16 (3)
Fe(1)—C(80)	1.86 (2)	N(2)—C(61)	1.40 (2)
P(1)—C(10)	1.73 (2)	N(3)—C(70)	1.15 (3)
P(1)—C(31)	1.83 (2)	N(3)—C(71)	1.38 (3)
P(1)—C(41)	1.84 (2)	N(4)—C(80)	1.13 (2)
P(2)—C(10)	1.69 (2)	N(4)—C(81)	1.38 (2)
P(1)—Fe1—P(2)	69.9 (2)	C(10)—P(1)—C(31)	111.7 (9)
P(1)—Fe1—C(50)	163.9 (6)	C(10)—P(1)—C(41)	116.5 (9)
P(1)—Fe1—C(60)	88.2 (7)	C(31)—P(1)—C(41)	100.9 (7)
P(1)—Fe1—C(70)	87.9 (7)	Fe(1)—P(2)—C(10)	95.9 (7)
P(1)—Fe1—C(80)	97.1 (6)	Fe(1)—P(2)—C(11)	116.5 (5)
P(2)—Fe1—C(50)	94.0 (6)	Fe(1)—P(2)—C(21)	119.5 (5)
P(2)—Fe1—C(60)	90.8 (7)	C(10)—P(2)—C(11)	114.0 (9)
P(2)—Fe1—C(70)	92.0 (7)	C(10)—P(2)—C(21)	113.8 (9)
P(2)—Fe1—C(80)	166.9 (6)	C(11)—P(2)—C(21)	98.3 (6)
C(50)—Fe1—C(60)	92. (1)	P(1)—C(10)—P(2)	99. (1)
C(50)—Fe1—C(70)	93.0 (9)	Fe(1)—C(50)—N(1)	178. (2)
C(50)—Fe1—C(80)	99.0 (8)	Fe(1)—C(60)—N(2)	178. (2)
C(60)—Fe1—C(70)	174.0 (9)	Fe(1)—C(70)—N(3)	176. (2)
C(60)—Fe1—C(80)	87.1 (9)	Fe(1)—C(80)—N(4)	173. (2)
C(70)—Fe1—C(80)	89.0 (9)	C(50)—N(1)—C(51)	174. (2)
Fe1—P(1)—C(10)	94.9 (7)	C(60)—N(2)—C(61)	170. (2)
Fe1—P(1)—C(31)	119.5 (5)	C(70)—N(3)—C(71)	174. (2)
Fe1—P(1)—C(41)	114.4 (5)	C(80)—N(4)—C(81)	178. (2)

the chelating dppm-H ligand. The bond lengths Fe—C and Fe—P of the first coordination sphere of the Fe, as well as the bond angles among them, are in the expected range (see Table 2), the small bite of the bidentate dppm-H ligand being the cause of the distortion of the octahedron around the Fe atom.

The bond lengths P(1)—C(10) and P(2)—C(10) are equal and show a shortening with respect to the P—C distance commonly associated with the dppm derivatives, which is in accord with the expected multiple bond character for the anionic bis(diphenylphosphino)methanide (dppm-H), present in our compound. The dihedral angle between the equatorial coordination plane of iron [defined by P(1), P(2), C(50) and C(80)] and that defined by P(1), P(2) and C(10) is 1(1)°.

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Structure of 2,2'-[5-(2-Aminoethyl)-1-hydroxy-2,5,8-triazanon-3-ene-1,9-diyl]bis-(pyridine *N*-oxide)nickel Hexafluorophosphate Monohydrate, [Ni(C₁₈H₂₆N₆O₃)]²⁺·2PF₆⁻·H₂O: a Novel Tripodal Nickel(II) Complex with Three Inequivalent Arms

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Abstract. $M_r = 741.09$, monoclinic, $P2_1/c$, $a = 13.014$ (2), $b = 15.038$ (2), $c = 14.329$ (2) Å, $\beta = 97.98$ (1)°, $V = 2777$ Å³, $Z = 4$, $D_x = 1.77$ g cm⁻³, Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å, $\mu = 9.30$ cm⁻¹, $T = 296$ K, $F(000) = 1504$, $R = 0.045$ and $wR = 0.068$

for 3621 unique observed [$I > 3.0\sigma(I)$] reflections. The nickel(II) atom is in a distorted octahedral environment of a tripodal ligand with three inequivalent arms. The compound is derived from the reaction of 2,2',2''-triaminotriethylamine with 2-pyridinecarboxaldehyde *N*-oxide in the presence of an Ni^{II} salt.

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