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Structure of Bis(dimethylphenylphosphine)(*meso*-5,10,15,20-tetraphenylporphinato)-iron(III) Perchlorate

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Abstract. [Fe(C₄₄H₂₈N₄)(C₈H₁₁P)₂]ClO₄, *M_r* = 985.4, monoclinic, *C2/c*, *a* = 25.127 (9), *b* = 15.174 (5), *c* = 15.239 (5) Å, β = 110.22 (3)°, *V* = 5452 (1) Å³, *Z* = 4, *D_x* = 1.23 Mg m⁻³, λ(Mo *Kα*) = 0.71073 Å, μ = 4.04 cm⁻¹, *F*(000) = 2112, *T* = 297 K. Final *R* = 0.060 for 2766 observed reflections. This first X-ray study of a phosphine–porphinato–iron(III) complex confirms the low-spin state of the ferric atom. The metal–phosphorus bond length [2.350 (1) Å] is longer than those observed in the analogous iron(II) complex containing dimethylphosphine ligands [2.284 (1) Å].

Introduction. This investigation is part of a program to examine the structure of phosphine–iron–porphyrin complexes (Sodano, Simonneaux & Toupet, 1988). Phosphines with small alkyl groups are new structural probes of hemoproteins (Bondon, Petrinko, Sodano & Simonneaux, 1986) and are a class of ligands which can bind to both valence states of hemoglobin (Fe^{II} and Fe^{III}) (Simonneaux, Bondon & Sodano, 1987). As an essential complement of our hemoprotein studies, it is of interest to understand the effect of the phosphine on the ferric porphyrin structure because of the absence of structural studies on model phosphine complexes of iron(III).

Experimental. The sample (prism 0.25 × 0.25 × 0.30 mm) was obtained by crystallization from a 50/50 mixture of dichloromethane and hexane. Data collection on an Enraf–Nonius CAD-4 diffractometer. Unit cell and standard deviations were obtained from a least-squares fit of 25 reflections, 8 < θ < 12°. Unique data set: *h* 0–28, *k* 0–17, *l* –17–17, 2θ_{max} = 54°, scan ω/2θ = 1, Zr-filtered Mo *Kα* radiation; intensity control reflections without appreciable decay (226, 226, 12, 0, 2); 6397 reflections measured, 2766 unique (*R*_{int} = 0.013) with *I* > 3.0σ(*I*). After data reduction (Lorentz and polarization correction, no absorption correction), resolution of the structure in centrosymmetric group *C2/c* by direct methods (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982) revealed the porphinato moiety. The remaining phenyl groups, the dimethylphenylphosphine ligand and ClO₄⁻ were found with Fourier techniques. The perchlorate anion appears disordered. The porphyrin structure was anisotropically refined and the H atoms placed in fixed positions respecting stereochemistry. The best full-matrix least-squares refinement (on *F*) of the structure {*x*, *y*, *z*, β_{*ij*} for Fe, P, Cl, N and C atoms; *x*, *y*, *z*, *B* for O; 346 variables and 2766 observations; max. Δ/σ = 0.22; *w* = 1/σ(*F_o*)² = [σ²(*I*) + (0.04*F_o*²)²]^{-1/2}} gives *R* =

Table 1. Atomic coordinates and equivalent isotropic thermal parameters with *e.s.d.*'s in parentheses
$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (abc\cos\gamma)\beta_{12} + (accos\beta)\beta_{13} + (bccos\alpha)\beta_{23}]$$

	x	y	z	$B_{eq}/B_{iso}(\text{\AA}^2)$
Fe	0.250	0.250	0.000	2.69 (2)
Cl	0.4107 (2)	0.3544 (3)	0.7156 (2)	7.1 (1)
P	0.22861 (6)	0.1209 (1)	0.0663 (2)	3.89 (3)
C(1)	0.4190 (6)	0.431 (1)	0.6597 (9)	6.5 (3)*
C(1)'	0.4236 (9)	0.379 (1)	0.805 (1)	5.3 (5)*
O(2)	0.3903 (5)	0.3810 (9)	0.7871 (9)	5.3 (3)*
O(2)'	0.3881 (8)	0.419 (1)	0.768 (1)	5.2 (5)*
O(3)	0.4009 (9)	0.282 (1)	0.665 (1)	10.5 (6)*
O(3)'	0.413 (1)	0.401 (2)	0.619 (2)	6.9 (6)*
O(4)	0.3554 (9)	0.304 (2)	0.700 (1)	12.0 (6)*
O(4)'	0.4393 (9)	0.281 (2)	0.702 (1)	5.9 (5)*
N(1)	0.2516 (2)	0.3173 (3)	0.1131 (2)	3.20 (9)
N(2)	0.1677 (2)	0.2755 (3)	-0.0602 (2)	2.90 (9)
C(1)	0.1330 (2)	0.2509 (4)	-0.1471 (3)	3.4 (1)
C(2)	0.0773 (2)	0.2826 (5)	-0.1639 (4)	4.8 (2)
C(3)	0.0778 (2)	0.3260 (4)	-0.0867 (4)	4.9 (1)
C(4)	0.1334 (2)	0.3204 (4)	-0.0215 (3)	3.5 (1)
C(5)	0.1498 (2)	0.3563 (4)	0.0661 (3)	3.9 (1)
C(6)	0.2061 (2)	0.3553 (4)	0.1287 (3)	3.8 (1)
C(7)	0.2240 (3)	0.3921 (4)	0.2208 (4)	5.4 (2)
C(8)	0.2792 (3)	0.3786 (4)	0.2593 (4)	5.4 (2)
C(9)	0.2974 (2)	0.3306 (4)	0.1934 (3)	3.7 (1)
C(10)	0.1481 (2)	0.2004 (4)	-0.2111 (3)	3.5 (1)
C(11)	0.1027 (2)	0.1782 (4)	-0.3022 (4)	4.5 (1)
C(12)	0.0967 (3)	0.2225 (7)	-0.3813 (5)	10.4 (3)
C(13)	0.0552 (5)	0.202 (1)	-0.4635 (5)	14.8 (4)
C(14)	0.0192 (4)	0.1365 (7)	-0.4684 (5)	10.6 (3)
C(15)	0.0222 (4)	0.0941 (6)	-0.3919 (7)	11.3 (3)
C(16)	0.0630 (4)	0.1149 (6)	-0.3081 (6)	10.1 (3)
C(17)	0.1057 (2)	0.4001 (4)	0.0975 (4)	5.1 (1)
C(18)	0.1027 (3)	0.4896 (5)	0.1024 (4)	6.8 (2)
C(19)	0.0596 (3)	0.5279 (5)	0.1282 (5)	8.7 (2)
C(20)	0.0221 (3)	0.4798 (6)	0.1488 (4)	9.9 (2)
C(21)	0.0257 (3)	0.3916 (7)	0.1462 (5)	10.4 (2)
C(22)	0.0669 (3)	0.3511 (5)	0.1195 (4)	7.6 (2)
C(23)	0.2659 (2)	0.0240 (4)	0.0510 (4)	4.4 (1)
C(24)	0.3205 (3)	0.0076 (4)	0.1103 (4)	5.5 (2)
C(25)	0.3480 (3)	-0.0692 (6)	0.1002 (5)	8.5 (2)
C(26)	0.3214 (4)	-0.1270 (5)	0.0323 (6)	10.8 (3)
C(27)	0.2690 (5)	-0.1130 (5)	-0.0266 (6)	10.0 (3)
C(28)	0.2398 (3)	-0.0361 (5)	-0.0202 (5)	7.4 (2)
C(29)	0.1540 (3)	0.0907 (5)	0.0214 (5)	6.8 (2)
C(30)	0.2447 (3)	0.1280 (4)	0.1909 (4)	5.6 (2)

* Starred atoms were refined isotropically with multiplicity = 0.5.

0.060, $wR = 0.065$ and $S = 1.80$ (residual $\Delta\rho \leq 0.3 \text{ e \AA}^{-3}$). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All the calculations were performed on a Digital PDP 11/60 computer with *SDP-Plus* (Frenz, 1985).

Discussion. Table 1 lists final coordinates and equivalent isotropic thermal factors.* Table 2 gives selected bond lengths and angles. The crystal structure consists of monomeric molecules of bis(dimethylphosphine)(*meso*-5,10,15,20-tetraphenylporphinato)-iron(III) perchlorate as illustrated in Fig. 1. The geometry of the porphyrin moiety is very similar to that found in ferrous porphyrins (Sodano, Simonneaux & Toupet, 1988). The averaged bond

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52814 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and bond angles ($^\circ$) with *e.s.d.*'s in parentheses

Fe—P	2.350 (1)	C(5)—C(17)	1.504 (4)
Fe—N(1)	1.992 (2)	C(6)—C(7)	1.430 (4)
Fe—N(2)	1.988 (2)	C(7)—C(8)	1.323 (5)
Cl—O(1)	1.493 (10)	C(8)—C(9)	1.436 (4)
Cl—O(1)'	1.339 (14)	C(10)—C(11)	1.498 (4)
Cl—O(2)	1.416 (10)	C(11)—C(12)	1.342 (6)
Cl—O(2)'	1.494 (14)	C(11)—C(16)	1.366 (6)
Cl—O(3)	1.315 (14)	C(12)—C(13)	1.361 (7)
Cl—O(3)'	1.65 (2)	C(13)—C(14)	1.325 (10)
Cl—O(4)	1.53 (2)	C(14)—C(15)	1.311 (9)
Cl—O(4)'	1.378 (15)	C(15)—C(16)	1.371 (8)
P—C(23)	1.801 (4)	C(17)—C(18)	1.362 (6)
P—C(29)	1.817 (4)	C(17)—C(22)	1.357 (6)
P—C(30)	1.804 (4)	C(18)—C(19)	1.401 (6)
N(1)—C(6)	1.372 (4)	C(19)—C(20)	1.313 (9)
N(1)—C(9)	1.374 (4)	C(20)—C(21)	1.343 (9)
N(2)—C(1)	1.362 (4)	C(21)—C(22)	1.380 (6)
N(2)—C(4)	1.382 (4)	C(23)—C(24)	1.381 (5)
C(1)—C(2)	1.417 (4)	C(23)—C(28)	1.395 (5)
C(1)—C(10)	1.391 (4)	C(24)—C(25)	1.390 (6)
C(2)—C(3)	1.345 (5)	C(25)—C(26)	1.345 (8)
C(3)—C(4)	1.409 (4)	C(26)—C(27)	1.329 (9)
C(4)—C(5)	1.367 (4)	C(27)—C(28)	1.401 (7)
C(5)—C(6)	1.407 (4)		
P—Fe—N(1)	89.73 (6)	Fe—N(2)—C(4)	127.1 (2)
P—Fe—N(2)	90.28 (6)	C(1)—N(2)—C(4)	105.4 (2)
N(1)—Fe—N(2)	90.35 (9)	N(2)—C(1)—C(2)	110.0 (3)
O(1)—Cl—O(1)'	109.3 (8)	O(1)—C(1)—C(10)	126.5 (3)
O(1)—Cl—O(2)	112.1 (7)	C(2)—C(1)—C(10)	123.4 (3)
O(1)—Cl—O(2)'	87.3 (8)	O(1)—C(2)—C(3)	107.4 (3)
O(1)—Cl—O(3)	110.0 (7)	C(2)—C(3)—C(4)	107.1 (3)
O(1)—Cl—O(3)'	26.8 (6)	N(2)—C(4)—C(3)	110.0 (3)
O(1)—Cl—O(4)	126.6 (7)	C(3)—C(4)—C(5)	123.8 (3)
O(1)—Cl—O(4)'	111.1 (7)	C(4)—C(5)—C(6)	123.5 (3)
O(1)′—Cl—O(2)	33.0 (7)	C(4)—C(5)—C(17)	118.6 (3)
O(1)′—Cl—O(2)′	43.5 (8)	C(6)—C(5)—C(17)	117.9 (3)
O(1)′—Cl—O(3)	139.8 (9)	N(1)—C(6)—C(5)	126.2 (3)
O(1)′—Cl—O(3)′	136.1 (1)	N(1)—C(6)—C(7)	109.7 (3)
O(1)′—Cl—O(4)	100.7 (9)		
O(1)′—Cl—O(4)′	115.0 (9)	C(5)—C(6)—C(7)	124.1 (3)
O(2)—Cl—O(2)′	25.0 (6)	C(6)—C(7)—C(8)	107.4 (3)
O(2)—Cl—O(3)	130.4 (8)	C(7)—C(8)—C(9)	107.9 (3)
O(2)—Cl—O(3)′	134.5 (8)	N(1)—C(9)—C(8)	109.1 (3)
O(2)′—Cl—O(4)	73.2 (7)	C(1)—C(10)—C(11)	118.0 (3)
O(2)′—Cl—O(4)′	133.8 (8)	C(10)—C(11)—C(12)	122.2 (4)
O(2)′—Cl—O(3)	146. (1)	C(10)—C(11)—C(16)	121.5 (4)
O(2)′—Cl—O(3)′	109.9 (9)	C(12)—C(11)—C(16)	116.1 (4)
O(2)′—Cl—O(4)	157.2 (9)	C(11)—C(12)—C(13)	121.5 (6)
O(3)—Cl—O(3)′	83.3 (9)	C(12)—C(13)—C(14)	121.1 (7)
O(3)—Cl—O(4)	61.1 (8)	C(13)—C(14)—C(15)	119.2 (6)
O(3)—Cl—O(4)′	40.6 (7)	C(14)—C(15)—C(16)	120.7 (7)
O(3)′—Cl—O(4)	112.6 (8)	C(11)—C(16)—C(15)	121.2 (6)
O(3)′—Cl—O(4)′	91.6 (8)	C(5)—C(17)—C(18)	121.3 (4)
O(4)—Cl—O(4)′	93.6 (9)	C(5)—C(17)—C(22)	120.4 (4)
Fe—P—C(23)	114.7 (1)	C(18)—C(17)—C(22)	118.3 (4)
Fe—P—C(29)	114.1 (1)	C(17)—C(18)—C(19)	119.5 (5)
Fe—P—C(30)	113.6 (1)	C(18)—C(19)—C(20)	121.6 (6)
C(23)—P—C(29)	105.1 (2)	C(19)—C(20)—C(21)	119.0 (5)
C(23)—P—C(30)	104.4 (2)	C(20)—C(21)—C(22)	121.2 (6)
C(29)—P—C(30)	103.8 (2)	C(17)—C(22)—C(21)	120.3 (5)
C(23)—P—C(29)	105.1 (2)	P—C(23)—C(24)	120.5 (3)
C(23)—P—C(30)	104.4 (2)	P—C(23)—C(28)	120.6 (3)
C(29)—P—C(30)	103.8 (2)	C(23)—C(24)—C(25)	120.0 (4)
Fe—N(1)—C(6)	126.6 (2)	C(24)—C(25)—C(26)	119.9 (5)
Fe—N(1)—C(9)	127.4 (2)	C(25)—C(26)—C(27)	121.8 (5)
C(6)—N(1)—C(9)	105.9 (3)	C(26)—C(27)—C(28)	120.5 (6)
Fe—N(2)—C(1)	127.5 (2)	C(23)—C(28)—C(27)	118.8 (5)

distances for the two crystallographically non-equivalent pyrrole rings lie within the range found for other low-spin iron(III) porphyrin structures (Scheidt & Reed, 1981). The two Fe—N distances average 1.990 (2) \AA in agreement with other low-spin iron(III) porphyrin structures, *i.e.* with imidazole ligands [1.989 (5) \AA] (Collins, Countryman & Hoard, 1972) and a cyano ligand [1.970 (14) \AA] (Scheidt,

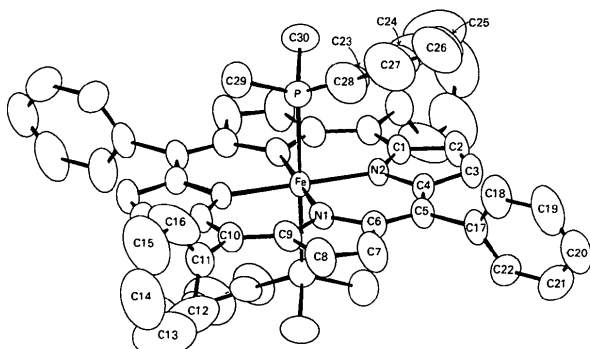


Fig. 1. Perspective view of the molecule with atom numbering.

Lee, Luangdilok, Haller, Anzai & Hatano, 1983). These distances are slightly shorter than in similar ferrous derivatives [2.001 (3) Å]. As a consequence of the increased charge, there is a small decrease in radii for iron(III) compared with iron(II). This leads to decreased bond lengths in the coordination group. The P—C distances in P(CH₃)₂C₆H₅ [average 1.807 (4) Å] are in good agreement with other metal phosphine complexes (Oumous, Lecomte, Protas, Poncet, Barbe & Guillard, 1984). The axial Fe—P(CH₃)₂C₆H₅ [2.350 (1) Å] is longer than in the iron(III) complex containing the same ligand

[2.284 (1) Å]: this is consistent with an increase in the oxidation state and a decrease in π back bonding from iron to the axial ligand.

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Diethoxybis(4,4,4-trifluoro-1-phenyl-1,3-butanedionato)titanium(IV)

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Abstract. [Ti(C₁₀H₆F₃O₂)₂(C₂H₅O)₂], *M*_r = 568.32, monoclinic, *C*2/*c*, *a* = 8.951 (2), *b* = 17.182 (2), *c* = 17.072 (2) Å, β = 99.95 (8)°, *V* = 2586 Å³, *Z* = 4, *D*_x = 1.460 g cm⁻³, λ (Mo *K* α) = 0.7107 Å, μ = 4.02 cm⁻¹, *F*(000) = 1160, room temperature, *R* = 0.088 for 978 observed reflections with *I* > 3 σ . The molecule has a crystallographic twofold axis which passes through Ti. The Ti atom is octahedrally coordinated by four O atoms from two β -diketone ligands, and by two ethoxy O atoms in a *cis* arrangement. Ti—O distances range from 1.760 to 2.090 Å.

Introduction. The first synthesis of the title compound was described by Bharara, Dgupta & Meh-

rotra (1975), and it was later reported that compounds of this type have antineoplastic action (Keller, Keppler, Krüger & Linder, 1981). We have undertaken a structural study of this compound, which was synthesized by a new method.

Experimental. Crystals suitable for X-ray analysis were obtained by slow evaporation from ethanol at room temperature. The crystal used for data collection measured 0.2 × 0.3 × 0.4 mm and was mounted with its longest dimension nearly coincident with the φ axis of an Enraf-Nonius CAD-4 diffractometer. With graphite-monochromated Mo *K* α radiation the cell parameters were obtained from a least-squares refinement of diffractometer settings for 25 reflec-