

Table 3. *Comparison of results*

	Taga & Osaki (1976)	This determination
Calcium coordination	2.458 (63) Å	2.445 (57) Å
Bond lengths:		
C—C	1.540 (26)	1.543 (17)
Hydroxyl C—O	1.443 (20)	1.427 (8)
Carboxyl C—O	1.257 (24)	1.239 (11)
Bond angles:		
Tetrahedral C	112.0 (3.5)°	111.6 (3.9)°
Trigonal C	127.1 (1.5)	126.1 (0.9)

These eight O atoms involve two carboxyl O atoms O(11) and O(12) (of different molecules), three hydroxyl O atoms O(2), O(3) and O(4) and those of three of the water molecules. The O atoms of the second carboxyl group, O(61) and O(62), are not directly involved in calcium coordination, but they are hydrogen-bonded to O(W1) *via* H(W12) and H(W11) respectively, and through this to the Ca<sup>2+</sup> ion. Similarly, hydroxyl O(5) is not coordinated, but is hydrogen-bonded to O(W4) *via* H(W41). This is the only water not involved in calcium coordination, but is itself hydrogen-bonded *via* H(W42) to water molecule O(W2). O(5) is also hydrogen-bonded to O(W3), which is involved in calcium coordination. Therefore, the overall calcium coordination combines with the hydrogen bonding to ensure that each O atom is directly or indirectly bound to the cation.

The hydrogen-bonding scheme is shown in Fig. 2. There are no intramolecular hydrogen bonds, but intermolecular hydrogen bonds including the water molecules stabilize the arrangement. This study has enabled a comparison to be made between the results presented

here and those of Taga & Osaki (1976). Comparison of atom coordinates of the non-H atoms shows very little difference though the errors in those given in this paper are, on average, halved compared with the original study. Thus, calcium-coordination distances, bond lengths and bond angles show slight differences only. These are shown in Table 3, figures in parentheses being the variance of the samples. This shows the overall improvement of the data, and verification of Taga & Osaki's (1976) results. The determination of H-atom positions has enabled a clear specification of the hydrogen-bonding scheme to be made.

We thank the University of Leeds Computing Service for the provision of computing facilities.

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*Acta Cryst.* (1985). **C41**, 695–697

### Structure of *trans*-Dichlorobis[3,4,5,6-tetrafluoro-*o*-phenylenebis(dimethylphosphine)]iron(III) Tetrafluoroborate, [FeCl<sub>2</sub>(C<sub>10</sub>H<sub>12</sub>F<sub>4</sub>P<sub>2</sub>)<sub>2</sub>]BF<sub>4</sub>

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(Received 29 October 1984; accepted 1 January 1985)

**Abstract.**  $M_r = 753.8$ , monoclinic,  $C2/c$ ,  $a = 19.194$  (4),  $b = 11.748$  (5),  $c = 13.416$  (3) Å,  $\beta = 100.50$  (2)°,  $U = 2974.5$  (25) Å<sup>3</sup>,  $Z = 4$ ,  $D_m$  (floatation) = 1.70 (2),  $D_x = 1.683$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.7107$  Å,  $\mu = 0.93$  mm<sup>-1</sup>,  $F(000) = 1508$ , room tem-

perature,  $R = 0.049$  for 1687 observed reflections. The iron atom is *trans* octahedrally coordinated and is located on a crystallographic centre of symmetry, with bond lengths Fe—P 2.292 (1), 2.295 (1), Fe—Cl 2.234 (1) Å and the BF<sub>4</sub><sup>-</sup> anions are disordered. The cation structure is very similar to those of  $[M\{o-C_6H_4(PMe_2)_2\}_2Cl_2]^{n+}$  ( $M = Mn, Co$ ).

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**Introduction.** *o*-Phenylenebis(dimethylphosphine), *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>, is a particularly effective ligand in stabilizing high oxidation states of the transition metals (Warren & Bennett, 1976). We have recently prepared the tetrafluoro analogue *o*-C<sub>6</sub>F<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub> and cyclic voltammetry data suggest that oxidation of its complexes with Ni<sup>II</sup> and Fe<sup>II</sup> (to M<sup>III</sup> and M<sup>IV</sup>, M = Ni and Fe) is considerably harder than for the analogous complexes of *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub> (Higgins & Levason, 1985). Whilst the electron-withdrawing effect of the fluorine atoms (an electronic effect) is the most likely explanation, it is also necessary to consider steric effects. Several complexes of *o*-C<sub>6</sub>H<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub> have been structurally characterized (Warren & Bennett, 1976; Gray, Higgins, Levason & Webster, 1984) and we have carried out an X-ray study of the title compound to establish any significant differences in ligand geometry.

**Experimental.** Air-stable deep-red crystals of the complex were obtained by addition of excess 25% HBF<sub>4</sub> to a saturated acetone solution of [Fe{*o*-C<sub>6</sub>F<sub>4</sub>(PMe<sub>2</sub>)<sub>2</sub>}<sub>2</sub>Cl<sub>2</sub>][FeCl<sub>4</sub>] and cooling overnight to 273 K (Higgins & Levason, 1985). Crystal 0.4 × 0.1<sub>5</sub> × 0.1<sub>5</sub> mm mounted in Lindemann capillary. Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Cell dimensions from 25 reflections. Data collected: 1.5 ≤  $\theta$  ≤ 25° for *h* 0–22, *k* 0–13, *l* –15–+15, systematic absences *hkl*, *h*+*k* ≠ 2*n*; *h*0*l*, *l* ≠ 2*n* (*h* ≠ 2*n*); 0*k*0, *k* ≠ 2*n*. No

Table 2. Selected bond lengths (Å) and angles (°) and non-bonded distances

Fe–Cl	2.234 (1)	P(1)–C(1)	1.815 (7)
Fe–P(1)	2.292 (1)	P(1)–C(2)	1.820 (6)
Fe–P(2)	2.295 (1)	P(1)–C(3)	1.819 (7)
		P(2)–C(8)	1.828 (6)
F(1)–C(4)	1.34 (1)	P(2)–C(9)	1.807 (7)
F(2)–C(5)	1.35 (1)	P(2)–C(10)	1.816 (6)
F(3)–C(6)	1.34 (1)		
F(4)–C(7)	1.35 (1)		
C–C(max.)	1.41 (1)	B–F(max.)	1.46 (3)
(min.)	1.34 (1)	(min.)	1.28 (2)
(mean)	1.38	(mean)	1.37
P(1)···P(2)	3.098 (2)	P(2)···Cl	3.277 (2)
P(1)···P(2) <sup>†</sup>	3.382 (3)	P(1) <sup>†</sup> ···Cl	3.108 (2)
P(1)···Cl	3.290 (2)	P(2) <sup>†</sup> ···Cl	3.126 (2)
Cl–Fe–P(1)	93.3 (1)	Fe–P(1)–C(1)	116.1 (2)
Cl–Fe–P(2)	92.7 (1)	Fe–P(1)–C(2)	118.5 (3)
Cl–Fe–P(1) <sup>†</sup>	86.8 (1)	Fe–P(1)–C(3)	107.9 (2)
Cl–Fe–P(2) <sup>†</sup>	87.3 (1)	Fe–P(2)–C(8)	107.4 (2)
P(1)–Fe–P(2)	85.0 (1)	Fe–P(2)–C(9)	115.6 (2)
P(1)–Fe–P(2) <sup>†</sup>	95.0 (1)	Fe–P(2)–C(10)	117.9 (3)
P(1)–C(3)–C(4)	123.8 (6)	C–C–C(max.)	122.5 (1)
P(1)–C(3)–C(8)	117.3 (4)	(min.)	118.5 (1)
P(2)–C(8)–C(3)	118.5 (4)	F–C–C(max.)	122.7 (1)
P(2)–C(8)–C(7)	122.6 (6)	(min.)	116.1 (1)

Symmetry code: (i)  $\frac{1}{2} - x, \frac{1}{2} - y, -z$ .

Table 1. Atomic coordinates and isotropic temperature factors (Å<sup>2</sup> × 10<sup>3</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Fe	0.2500	0.2500	0.0000	39.4 (5)*
Cl	0.2147 (1)	0.1150 (1)	–0.1154 (1)	54.9 (8)*
P(1)	0.2989 (1)	0.3594 (1)	–0.1108 (1)	52.3 (8)*
P(2)	0.3613 (1)	0.1732 (1)	0.0434 (1)	52.4 (8)*
C(1)	0.2758 (4)	0.5094 (5)	–0.1155 (6)	75.3 (41)*
C(2)	0.2860 (5)	0.3163 (7)	–0.2432 (5)	80.8 (44)*
C(3)	0.3947 (3)	0.3542 (6)	–0.0719 (5)	60.6 (36)*
C(4)	0.4419 (5)	0.4239 (8)	–0.1133 (6)	87.1 (52)*
C(5)	0.5148 (5)	0.4051 (11)	–0.0862 (8)	103.9 (66)*
C(6)	0.5406 (4)	0.3190 (10)	–0.0241 (8)	96.4 (63)*
C(7)	0.4959 (4)	0.2535 (8)	0.0167 (6)	84.1 (48)*
C(8)	0.4226 (3)	0.2678 (6)	–0.0059 (5)	61.5 (34)*
C(9)	0.3959 (4)	0.1644 (8)	0.1778 (5)	81.7 (45)*
C(10)	0.3777 (4)	0.0363 (6)	–0.0108 (7)	78.7 (43)*
F(1)	0.4165 (3)	0.5077 (5)	–0.1775 (4)	114.6 (37)*
F(2)	0.5569 (3)	0.4753 (6)	–0.1290 (5)	150.5 (48)*
F(3)	0.6109 (2)	0.3045 (6)	–0.0013 (5)	150.2 (49)*
F(4)	0.5243 (2)	0.1692 (5)	0.0789 (4)	111.2 (37)*
B	0.0000	0.3616 (12)	0.2500	83.3 (36)
F(5) <sup>†</sup>	–0.0137 (4)	0.4271 (7)	0.3256 (6)	150.8 (26)
F(6)	0.0458 (7)	0.2694 (12)	0.2658 (10)	59.5 (32)
F(7)	0.0000	0.2530 (14)	0.2500	108.5 (45)
F(8)	0.0761 (15)	0.3511 (23)	0.2872 (21)	135.1 (83)
F(9)	–0.0211 (13)	0.3992 (19)	0.1501 (17)	95.6 (62)

\* Equivalent isotropic temperature factor for anisotropic atom:  $U_{eq} = \frac{1}{3}$  trace *U*.

<sup>†</sup> F(5) to F(9) are associated with the disordered BF<sub>4</sub><sup>–</sup> anion; site populations 1, 0.25, 0.5, 0.25 and 0.25 respectively.

significant variation of 3 check reflections.  $\psi$  scan, empirical absorption correction applied [transmission (%): 99.9(max.)–97.4(min.)]. 2827 data merged ( $R_{int} = 0.013$ ) to 2616 unique reflections of which 1687 with  $F > 4\sigma(F)$  used in refinement. Structure solved by Patterson and structure factor/electron density synthesis. H atoms introduced in calculated positions [ $d(C-H) = 1.0 \text{ \AA}$ ] with common refined temperature factor. Extensive disorder of F atoms in BF<sub>4</sub><sup>–</sup> anion. Least-squares refinement on *F* converged to  $R 0.049$  ( $wR 0.072$ ), 217 parameters,  $w = 1/[\sigma^2(F) + 0.004F^2]$ , max.  $\Delta/\sigma 0.39$ . Final difference electron density synthesis showed residual electron density  $-0.77$  to  $+0.71 \text{ e \AA}^{-3}$ . Scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). All calculations performed on ICL 2970 computer using *SHELX76* (Sheldrick, 1976), *ORTEP* (Johnson, 1965) and *XANADU* (Roberts & Sheldrick, 1979).

**Discussion.** Tables 1\* and 2 show the final atomic coordinates and selected bond lengths and angles and Fig. 1 the cation geometry and numbering scheme.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42002 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The structure determination reveals the presence of *trans* pseudo-octahedral  $[\text{Fe}\{o\text{-C}_6\text{F}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]^+$  cations with Fe located on a crystallographic centre of symmetry. The C atoms of the benzene ring and the attached F atoms are coplanar (max. deviation from plane 0.02 Å), with the P atoms out of the plane through the C atoms by 0.20 (1) and 0.07 (1) Å. The cation forms a slightly 'stepped' structure with a dihedral angle of 13 (1)° between the FeP(1)P(2) plane and the plane of the benzene ring. The  $\text{BF}_4^-$  anion is extensively disordered, as is frequently found (see for example van den Heuvel, Franke, Verschoor & Zuur, 1983), with a mean B–F distance of 1.37 Å.

A comparison of the bond lengths (C–C, C–P) within the  $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$  ligand in  $[\text{Ni}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{I}_{10}]$  (Gray *et al.*, 1984) with those in the title compound reveals no significant differences and the C–F bond lengths in the latter are comparable with those in tetrafluorophenyl derivatives such as  $[(2,3,5,6\text{-F}_4\text{HC}_6)_2\text{Tl}(\text{OPPh}_3)\text{Cl}]_2$  (Henrick, McPartlin, Matthews, Deacon & Phillips, 1980) and  $[(\mu\text{-C}_6\text{F}_4)\text{Fe}_2(\text{CO})_8]$  (Bennett, Graham, Stewart & Tuggle, 1973).

X-ray studies on  $[\text{Mn}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]^{n+}$  ( $n = 0, 1, 2$ ) and  $[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]^+$  have been carried out but only  $M\text{--}P$  and  $M\text{--}Cl$  bond lengths are available (Table 3). The  $\text{Mn}^{\text{II}}$  complex is high spin, whilst  $[\text{Fe}\{o\text{-C}_6\text{F}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]^+$  is low spin, and this accounts for the large differences between the two  $d^5$  ions. Comparison between the  $\text{Mn}^{\text{III}}$  ( $t_{2g}^4$ ),  $\text{Co}^{\text{III}}$  ( $t_{2g}^6$ ) complexes of  $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$  and the  $\text{Fe}^{\text{III}}$  ( $t_{2g}^5$ ) title complex reveals a decrease in  $M\text{--}P$  bond lengths  $\text{Mn} > \text{Fe} > \text{Co}$ , whilst the  $M\text{--}Cl$  bonds vary  $\text{Mn} > \text{Fe} < \text{Co}$ . Since the metal covalent radii are expected to decrease  $\text{Mn} > \text{Fe} > \text{Co}$ , the trends in  $d(M\text{--}P)$  are much as expected, but the  $\text{Co}\text{--}Cl$  bond appears to be unusually long. It is interesting to extend comparison to the  $t_{2g}^6$   $\text{Fe}^{\text{II}}$  complex *trans*- $[\text{Fe}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2]$  (Di Vaira, Midollini & Sacconi, 1981) in which the  $\text{Fe}\text{--}P$  and  $\text{Fe}\text{--}Cl$  bond lengths are respectively significantly shorter and longer than in  $[\text{Fe}\{o\text{-}$

Table 3. Comparison of  $M\text{--}Cl$  and  $M\text{--}P$  bond lengths (Å) in  $[\text{M}(\text{diphosphine})_2\text{Cl}_2]^{n+}$

	$M\text{--}Cl$	$M\text{--}P$	Reference
$[\text{Mn}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]$	2.502 (1)	2.625 (av.)	(a)
$[\text{Mn}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]\text{ClO}_4$	2.239 (2)	2.344 (av.)	(a)
$[\text{Mn}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{Cl}_2][\text{H}(\text{NO}_3)_2]$	2.195 (1)	2.428 (av.)	(a)
$[\text{Co}\{o\text{-C}_6\text{H}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]\text{ClO}_4$	2.253 (av.)	2.251 (av.)	(a)
$[\text{Fe}\{o\text{-C}_6\text{F}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]\text{BF}_4$	2.234 (1)	2.292 (1)	(b)
		2.295 (1)	
$[\text{Fe}(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2\text{Cl}_2]$	2.352 (1)	2.241 (1)	(c)
		2.230 (1)	

References: (a) Unpublished work quoted by Warren & Bennett (1976); (b) this work; (c) Di Vaira, Midollini & Sacconi (1981).

$\text{C}_6\text{F}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]^+$ . This suggests that the  $t_{2g}^6$  ions have a decreased affinity for chloride ligands on the  $z$  axis, which may be due to destabilizing interactions between the filled  $p\pi$  orbitals on Cl and the filled  $d\pi$  ( $t_{2g}^6$ ) set on the metal. The latter will clearly be reduced when the  $t_{2g}$  set is only partially occupied as in  $\text{Fe}^{\text{III}}$  ( $t_{2g}^5$ ) or  $\text{Mn}^{\text{III}}$  ( $t_{2g}^4$ ).

Despite the significant differences between complexes of  $o\text{-C}_6\text{H}_4(\text{PMe}_2)_2$  and  $o\text{-C}_6\text{F}_4(\text{PMe}_2)_2$  detected electrochemically, this difference does not appear to be reflected in the structural data, and to a good approximation these two ligands can be regarded as having identical steric properties.

We thank Dr M. B. Hursthouse for the data collection by the QMC/SERC X-ray service, and the SERC and Southampton University for support (SJH and H CJ respectively).

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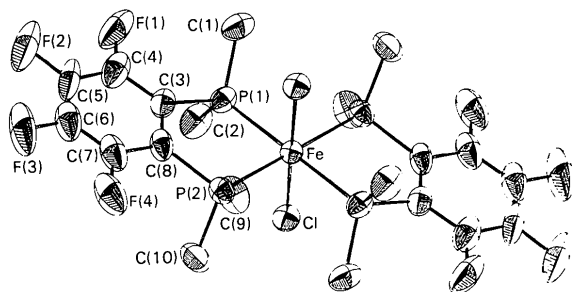


Fig. 1. The cation in  $[\text{Fe}\{o\text{-C}_6\text{F}_4(\text{PMe}_2)_2\}_2\text{Cl}_2]\text{BF}_4$  showing the atom numbering scheme. The atoms have been drawn with 40% probability thermal ellipsoids and H atoms excluded for clarity.