Cl(1)—Zr—Cl(2)	98.76 (1)	97.3 (1)
Cp(1)—Zr—Cp(2)	127.8	126.4 (2)
C(1)—Si—C(2)	111.2 (1)	110.8 (2)
C(11)—Si—C(21)	94.57 (6)	94.3 (2)

* Herrmann *et al.* (1989).

† Average.

‡ Zr η^5-bonded C distances, minimum–maximum.

§ Cp C—C bond distance, minimum–maximum.

The structure was solved by direct methods and refined by full-matrix least-squares techniques. C(27) and C(28) in Cp(2) show large displacement parameters indicating a slight disorder in the structure. H atoms were placed with idealized geometries (C—H = 0.96 Å) riding on their respective C atoms with fixed $U = 0.08$ Å^2.

Data collection: *P*3 *Data Collection Software* (Siemens, 1990). Cell refinement: *P*3 *Data Collection Software*. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Structure solution: *SHELXTL-Plus*. Structure refinement: *SHELXTL-Plus*. Molecular graphics: *SHELXTL-Plus*. Preparation of material for publication: *SHELXTL-Plus*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1236). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Molecular Stereochemistry of $[Fe^{III}(TPP)(OCOCF_3)]$

Shirley A. Moy, Jorge A. González and Lon J. Wilson*

Department of Chemistry and Laboratory for Biochemical and Genetic Engineering, Rice University, PO Box 1892, Houston, Texas 77251, USA

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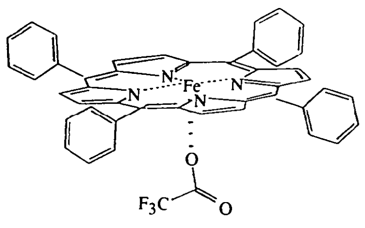
Abstract

(*meso*-Tetraphenylporphinato)(trifluoroacetato)iron(III), $[Fe(C_2F_3O_2)(C_{44}H_{28}N_4)]$, consists of a central Fe atom equatorially coordinated to four pyrrole N atoms and axially coordinated to an O atom of the trifluoroacetate group. The average Fe—N bond distance is 2.054 (5) Å and the Fe atom is displaced 0.483 (1) Å from the porphinato plane. The Fe—O distance is 1.921 (4) Å. The out-of-plane displacement and the Fe—N bond lengths indicate that the Fe atom is in a high-spin state.

Comment

The structures of five mononuclear high-spin pentacoordinate oxygen-ligated iron complexes of the type $[Fe^{III}(Por)(X)]$ (where Por = tetraphenylporphinato, TPP, or tetrakis(*p*-methoxyphenyl)porphinato, t_p-MePP, and $X = OCH_3$, $OCOCH_3$, $OSOC_6H_5$, OSO_3H or OSO_2CH_3) have been determined previously (Lecomte, Chadwick, Coppens & Stevens, 1983; Oumous, Lecomte, Protas, Cocolios & Guilard, 1984; Cocolios, Lagrange, Guilard, Oumous & Lecomte, 1984; Scheidt, Lee & Finnegan, 1988; Li *et al.*, 1987). We report here the molecular stereochemistry of $[Fe^{III}(TPP)(OCOCF_3)]$, (I), along with a structural comparison with related complexes.



(I)

Fig. 1 presents an *ORTEP* (Johnson, 1965) view of the molecule along with the numbering scheme employed for the non-H atoms. The packing diagram given in Fig. 2 shows that the molecules of the compound interact in pairs in the lattice. The coordination-group parameters for $[Fe^{III}(TPP)(OCOCF_3)]$ are presented in Table 3 and are typical of those for a pentacoordinate (porphinato)iron(III) compound in the high-spin state (Scheidt & Reed, 1981). The trifluoroacetate group was found to be disordered over two positions with site occupancies of 0.57 and 0.43. The CF_3 group was treated as a rigid group and fractional C, O and F atoms were allowed to occupy two possible positions during all refinement cycles.

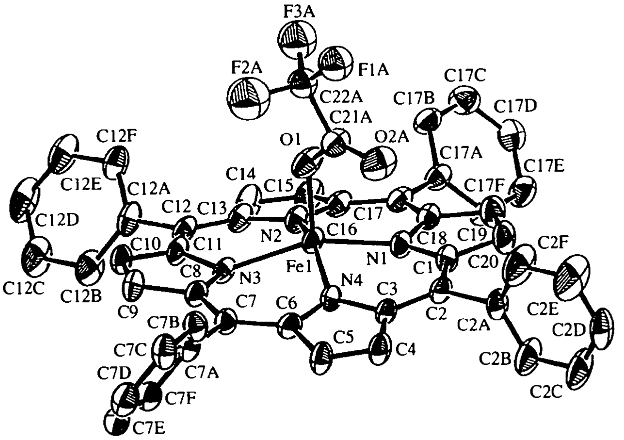


Fig. 1. An *ORTEP* (Johnson, 1965) drawing of [Fe^{III}(TPP)($OCOCF_3$)] with displacement ellipsoids at the 50% probability level. (Atoms C22A, F1A, F2A and F3A were refined isotropically.)

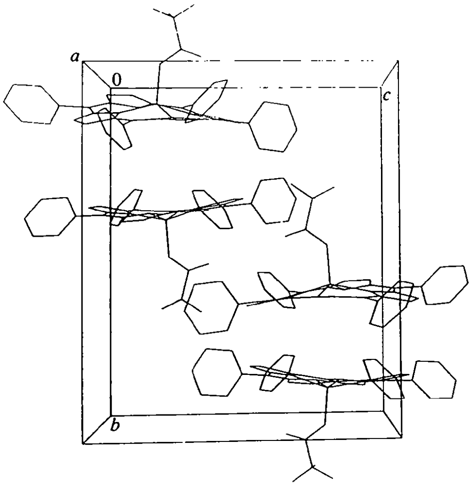


Fig. 2. A packing diagram for [Fe^{III}(TPP)($OCOCF_3$)].

The structural parameters of [Fe^{III}(TPP)($OCOCF_3$)] are compared to those of other high-spin and intermediate-spin pentacoordinate oxygen-ligated (Por)iron(III) compounds in Table 3. This table shows that there is an obvious trend in these compounds between the increasing distances from the Fe atom to the O atom (Fe—O), the decreasing out-of-plane distances of the Fe atom to the mean plane of the 24-atom core ($Fe\cdots C_{t'}$) and the decreasing average distances between the Fe atom and the porphinato core N atoms ($Fe—N_p$). Shorter Fe—O distances and longer $Fe\cdots C_{t'}$ and $Fe—N_p$ distances are indicative of iron(III) complexes in the high-spin state. For such cases, typical $Fe\cdots C_{t'}$ and $Fe—N_p$ distances are greater than 2.045 and 0.42 Å, respectively. These long distances indicate that the iron $d_{x^2-y^2}$ and d_{z^2} orbitals are both occupied and that the spin state S is $\frac{5}{2}$ (Scheidt & Reed, 1981; Scheidt & Lee, 1987). On the other hand, values previously reported for five-coordinate admixed-spin iron(III)–porphyrin compounds are in the range 1.961–2.038 Å for $Fe—N_p$ and 0.10–0.38 Å for the out-of-plane displacement of the Fe atom, varying according to the amount of $S = \frac{3}{2}$ or $\frac{5}{2}$ character present in the system. These shorter distances are indicative of an unoccupied or partially occupied $d_{x^2-y^2}$ antibonding orbital raised in energy relative to the d_{z^2}, d_{xy}, d_{yz} and d_{xz} orbitals because of the proximity of (and subsequent repulsion between) the $d_{x^2-y^2}$ electron and the sp^2 lone-pair electrons of the equatorial porphyrin N atoms (Scheidt & Reed, 1981; Scheidt & Lee, 1987; Reed *et al.*, 1979, Gupta *et al.*, 1987; Masuda *et al.*, 1980).

The formal diagram of the porphinato core of [Fe^{III}(TPP)($OCOCF_3$)] is presented in Fig. 3. The conformation of the core is that of a rather pronounced S_4 ('Sad') ruffling. The dihedral angles formed by the peripheral phenyl rings and the 24-atom core are 85.29, 55.39, 52.60 and 49.33°. These values are somewhat smaller than usual for typical metallotetraarylporphyrins, which often possess phenyl ring dihedral angles in the 60 to 90° range (Scheidt & Lee, 1987).

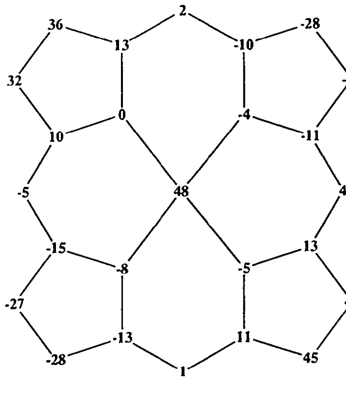


Fig. 3. A formal diagram of the porphinato core of [Fe^{III}(TPP)($OCOCF_3$)] displaying the perpendicular displacements, in units of 0.01 Å, of each atom from the mean plane of the 24-atom core. The atom labels have been replaced by the value of the displacement.

Experimental

meso-Tetraphenylporphyrin (H_2TPP) and [Fe^{III}(TPP)Cl] were synthesized by previously reported methods (Adler *et al.*, 1967; Kim, Adler & Longo, 1978; Fleischer, Palmer, Srivastava & Chaterjee, 1971). [Fe^{III}(TPP)($OCOCF_3$)] was synthesized by the general method of Reed *et al.* (1979). Single crystals suitable for the X-ray structure determination were grown over a period of 2 to 3 days at 273 K under an Ar atmosphere from a 1:3 thf/heptane solvent mixture.

Crystal data

$[Fe(C_2F_3O_2)(C_{44}H_{28}N_4)]$
$M_r = 781.6$
Monoclinic
$P2_1/a$
$a = 14.212\,(3)$ Å
$b = 17.390\,(4)$ Å
$c = 14.840\,(1)$ Å
$\beta = 96.10\,(1)°$
$V = 3647\,(1)$ Å^3
$Z = 4$
$D_x = 1.423$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.52–17.66°$
$\mu = 0.4707$ mm^{-1}
$T = 193$ K
Rectangular
0.40 × 0.25 × 0.25 mm
Purple

Data collection

Rigaku AFC-5*S* diffractometer
$2\theta–\omega$ scans
Absorption correction: ψ scans
$T_{\min} = 0.967$, $T_{\max} = 1.000$
9006 measured reflections
8669 independent reflections
4167 observed reflections $[I > 3\sigma(I)]$

$R_{\rm int} = 0.037$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 22$
$l = -19 \rightarrow 19$
3 standard reflections monitored every 150 reflections intensity decay: 0.24%

Refinement

Refinement on F
$R = 0.064$
$wR = 0.083$
$S = 1.95$
4167 reflections
508 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters* (Å^2)

$B_{\rm iso}$ for C22A, F1A, F2A and F3A, $B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$B_{\rm eq}/B_{\rm iso}$
Fe1	0.71112 (6)	0.09414 (5)	0.21536 (5)	3.03 (3)
N1	0.5850 (3)	0.1253 (3)	0.2599 (3)	3.2 (2)
N2	0.6479 (3)	0.1134 (2)	0.0858 (3)	3.1 (2)
N3	0.8386 (3)	0.1112 (2)	0.1650 (3)	3.0 (2)
N4	0.7767 (3)	0.1275 (3)	0.3392 (3)	3.1 (2)
C1	0.5693 (4)	0.1284 (3)	0.3508 (4)	3.5 (3)
C2	0.6377 (4)	0.1355 (3)	0.4245 (3)	3.3 (2)
C3	0.7348 (4)	0.1393 (3)	0.4180 (3)	3.3 (2)
C4	0.8042 (4)	0.1538 (4)	0.4914 (3)	3.9 (3)
C5	0.8886 (4)	0.1503 (4)	0.4591 (4)	3.9 (3)
C6	0.8727 (4)	0.1319 (3)	0.3640 (4)	3.6 (3)
C7	0.9430 (4)	0.1190 (3)	0.3075 (4)	3.2 (2)
C8	0.9262 (4)	0.1068 (3)	0.2147 (3)	3.2 (2)
C9	0.9967 (4)	0.0896 (4)	0.1555 (4)	3.7 (3)
C10	0.9543 (4)	0.0854 (3)	0.0707 (4)	3.7 (3)
C11	0.8559 (4)	0.1005 (3)	0.0753 (3)	3.2 (2)
C12	0.7877 (4)	0.1075 (3)	−0.0001 (3)	3.5 (3)
C13	0.6911 (4)	0.1174 (3)	0.0067 (3)	3.4 (3)
C14	0.6223 (5)	0.1336 (4)	−0.0683 (4)	4.4 (3)
C15	0.5379 (5)	0.1398 (4)	−0.0366 (4)	4.3 (3)
C16	0.5516 (4)	0.1253 (3)	0.0593 (3)	3.3 (2)
C17	0.4796 (4)	0.1264 (3)	0.1166 (4)	3.4 (2)
C18	0.4964 (4)	0.1234 (3)	0.2112 (4)	3.4 (3)
C19	0.4249 (4)	0.1219 (4)	0.2722 (4)	4.3 (3)
C20	0.4690 (4)	0.1255 (4)	0.3575 (4)	4.5 (3)
C2*A*	0.6034 (4)	0.1431 (4)	0.5156 (3)	3.6 (3)
C2*B*	0.5855 (5)	0.2130 (4)	0.5507 (5)	5.8 (4)
C2*C*	0.5514 (6)	0.2204 (5)	0.6333 (5)	6.8 (4)
C2*D*	0.5342 (5)	0.1582 (5)	0.6825 (4)	5.5 (4)
C2*E*	0.5556 (8)	0.0885 (6)	0.6520 (6)	9.3 (6)
C2*F*	0.5908 (7)	0.0808 (5)	0.5681 (5)	7.9 (5)
C7*A*	1.0437 (4)	0.1174 (3)	0.3506 (4)	3.3 (3)
C7*B*	1.0717 (4)	0.0637 (4)	0.4175 (4)	3.8 (3)
C7*C*	1.1628 (5)	0.0625 (4)	0.4607 (4)	4.5 (3)
C7*D*	1.2272 (5)	0.1156 (4)	0.4363 (4)	4.9 (3)
C7*E*	1.2021 (5)	0.1681 (4)	0.3702 (5)	4.8 (3)
C7*F*	1.1114 (5)	0.1698 (3)	0.3271 (4)	4.1 (3)
C12*A*	0.8213 (4)	0.1051 (4)	−0.0918 (4)	4.0 (3)
C12*B*	0.8891 (5)	0.1585 (4)	−0.1137 (4)	5.5 (4)
C12*C*	0.9220 (6)	0.1537 (5)	−0.1984 (5)	6.8 (4)
C12*D*	0.8883 (6)	0.0985 (5)	−0.2604 (4)	6.4 (4)
C12*E*	0.8234 (6)	0.0482 (4)	−0.2389 (4)	5.7 (4)
C12*F*	0.7891 (4)	0.0511 (4)	−0.1559 (4)	4.4 (3)
C17*A*	0.3792 (4)	0.1335 (3)	0.0755 (3)	3.4 (3)
C17*B*	0.3410 (4)	0.0814 (3)	0.0116 (4)	3.9 (3)
C17*C*	0.2473 (5)	0.0886 (4)	−0.0253 (4)	4.8 (3)
C17*D*	0.1917 (4)	0.1465 (4)	0.0025 (4)	4.6 (3)
C17*E*	0.2292 (5)	0.1980 (4)	0.0670 (5)	4.7 (3)
C17*F*	0.3229 (5)	0.1919 (4)	0.1026 (4)	4.4 (3)
O1	0.7089 (3)	−0.0159 (2)	0.2257 (3)	4.4 (2)
C21*A*	0.7001 (9)	−0.0567 (7)	0.2938 (8)	4.2 (6)
O2*A*	0.6768 (6)	−0.0376 (5)	0.3661 (5)	6.0 (5)
C21*B*	0.765 (2)	−0.061 (1)	0.262 (1)	7 (1)
O2*B*	0.849 (1)	−0.056 (1)	0.294 (1)	9.2 (9)
C22*A*	0.7281 (7)	−0.1421 (6)	0.2707 (6)	4.5 (7)
F1*A*	0.7133 (8)	−0.1821 (9)	0.3427 (6)	6.0 (4)
F2*A*	0.6790 (9)	−0.172 (1)	0.1993 (6)	7.6 (5)
F3*A*	0.8183 (7)	−0.144 (1)	0.2596 (8)	9.3 (4)

Table 2. *Selected geometric parameters* (Å, °)

Fe1—N1	2.048 (5)	C17—C18	1.400 (8)
Fe1—N2	2.061 (4)	C17—C17*A*	1.496 (8)
Fe1—N3	2.054 (5)	C18—C19	1.432 (9)
Fe1—N4	2.054 (4)	C19—C20	1.353 (8)
Fe1—O1	1.921 (4)	C2*A*—C2*B*	1.36 (1)
N1—C1	1.392 (7)	C2*A*—C2*F*	1.36 (1)
N1—C18	1.383 (7)	C2*B*—C2*C*	1.37 (1)
N2—C13	1.383 (7)	C2*C*—C2*D*	1.34 (1)
N2—C16	1.399 (7)	C2*D*—C2*E*	1.34 (1)
N3—C8	1.379 (7)	C2*E*—C2*F*	1.40 (1)
N3—C11	1.393 (7)	C7*A*—C7*B*	1.390 (8)
N4—C3	1.382 (7)	C7*A*—C7*F*	1.396 (9)
N4—C6	1.378 (7)	C7*B*—C7*C*	1.383 (8)
C1—C2	1.389 (7)	C7*C*—C7*D*	1.37 (1)
C1—C20	1.441 (9)	C7*D*—C7*E*	1.36 (1)
C2—C3	1.396 (8)	C7*E*—C7*F*	1.376 (9)
C2—C2*A*	1.491 (8)	C12*A*—C12*B*	1.40 (1)
C3—C4	1.412 (7)	C12*A*—C12*F*	1.379 (8)
C4—C5	1.340 (8)	C12*B*—C12*C*	1.39 (1)
C5—C6	1.441 (8)	C12*C*—C12*D*	1.38 (1)
C6—C7	1.389 (8)	C12*D*—C12*E*	1.33 (1)
C7—C8	1.389 (7)	C12*E*—C12*F*	1.373 (9)
C7—C7*A*	1.505 (8)	C17*A*—C17*B*	1.381 (8)
C8—C9	1.432 (8)	C17*A*—C17*F*	1.378 (9)
C9—C10	1.339 (7)	C17*B*—C17*C*	1.391 (9)
C10—C11	1.431 (8)	C17*C*—C17*D*	1.37 (1)
C11—C12	1.405 (7)	C17*D*—C17*E*	1.376 (9)
C12—C13	1.398 (9)	C17*E*—C17*F*	1.384 (9)
C12—C12*A*	1.490 (8)	O1—C21*A*	1.25 (1)
C13—C14	1.429 (8)	O1—C21*B*	1.21 (2)
C14—C15	1.339 (9)	C21*A*—O2*A*	1.20 (2)
C15—C16	1.439 (8)	C21*B*—O2*B*	1.23 (3)
C16—C17	1.398 (8)		

N1—Fe1—N2	87.0 (2)	N2—C13—C14	110.0 (5)
N1—Fe1—N3	156.3 (2)	C12—C13—C14	124.3 (5)
N1—Fe1—N4	88.1 (2)	C13—C14—C15	107.9 (5)
N1—Fe1—O1	102.4 (2)	C14—C15—C16	107.4 (5)
N2—Fe1—N3	87.2 (2)	N2—C16—C15	109.3 (5)
N2—Fe1—N4	154.2 (2)	N2—C16—C17	126.1 (5)
N2—Fe1—O1	103.2 (2)	C15—C16—C17	124.6 (5)
N3—Fe1—N4	87.2 (2)	C16—C17—C18	123.4 (5)
N3—Fe1—O1	101.3 (2)	C16—C17—C17*A*	118.8 (5)
N4—Fe1—O1	102.7 (2)	C18—C17—C17*A*	117.7 (5)
Fe1—N1—C1	124.0 (3)	N1—C18—C17	124.9 (5)
Fe1—N1—C18	127.2 (4)	N1—C18—C19	109.8 (5)
C1—N1—C18	106.1 (5)	C17—C18—C19	125.3 (5)
Fe1—N2—C13	127.7 (4)	C18—C19—C20	107.5 (5)
Fe1—N2—C16	127.1 (3)	C1—C20—C19	107.5 (5)
C13—N2—C16	105.3 (4)	C2—C2*A*—C2*B*	121.3 (6)
Fe1—N3—C8	125.3 (3)	C2—C2*A*—C2*F*	121.7 (6)
Fe1—N3—C11	125.5 (3)	C2*B*—C2*A*—C2*F*	117.0 (6)
C8—N3—C11	105.2 (4)	C2*A*—C2*B*—C2*C*	121.6 (7)
Fe1—N4—C3	127.2 (4)	C2*B*—C2*C*—C2*D*	120.9 (8)
Fe1—N4—C6	126.7 (4)	C2*C*—C2*D*—C2*E*	119.0 (7)
C3—N4—C6	105.6 (4)	C2*D*—C2*E*—C2*F*	120.2 (8)
N1—C1—C2	126.6 (5)	C2*A*—C2*F*—C2*E*	121.1 (8)
N1—C1—C20	109.1 (4)	C7—C7*A*—C7*B*	120.2 (5)
C2—C1—C20	124.3 (5)	C7—C7*A*—C7*F*	122.1 (5)
C1—C2—C3	124.4 (5)	C7*B*—C7*A*—C7*F*	117.7 (5)
C1—C2—C2*A*	116.9 (5)	C7*B*—C7*C*—C7*D*	119.0 (6)
C3—C2—C2*A*	118.6 (5)	C7*C*—C7*D*—C7*E*	120.6 (6)
N4—C3—C2	124.7 (5)	C7*D*—C7*E*—C7*F*	120.7 (6)
N4—C3—C4	110.5 (5)	C7*A*—C7*F*—C7*E*	120.4 (6)
C2—C3—C4	124.8 (5)	C12—C12*A*—C12*B*	119.2 (5)
C3—C4—C5	107.2 (5)	C12—C12*A*—C12*F*	122.3 (6)
C4—C5—C6	107.9 (5)	C12*B*—C12*A*—C12*F*	118.5 (6)
N4—C6—C5	108.8 (5)	C12*A*—C12*B*—C12*C*	118.3 (6)
N4—C6—C7	125.8 (5)	C12*B*—C12*C*—C12*D*	121.3 (8)
C5—C6—C7	125.4 (5)	C12*C*—C12*D*—C12*E*	119.7 (7)
C6—C7—C8	124.4 (5)	C12*D*—C12*E*—C12*F*	120.7 (7)
C6—C7—C7*A*	117.3 (5)	C12*A*—C12*F*—C12*E*	121.4 (6)
C8—C7—C7*A*	118.3 (5)	C17—C17*A*—C17*B*	120.9 (5)
N3—C8—C7	124.9 (5)	C17—C17*A*—C17*F*	120.0 (5)
N3—C8—C9	109.5 (4)	C17*B*—C17*A*—C17*F*	119.1 (5)
C7—C8—C9	125.6 (5)	C17*A*—C17*B*—C17*C*	120.1 (6)
C8—C9—C10	108.3 (5)	C17*B*—C17*C*—C17*D*	120.4 (6)
C9—C10—C11	106.8 (5)	C17*C*—C17*D*—C17*E*	119.6 (6)
N3—C11—C10	110.0 (4)	C17*D*—C17*E*—C17*F*	120.1 (6)
N3—C11—C12	124.9 (5)	C17*A*—C17*F*—C17*E*	120.7 (6)
C10—C11—C12	125.0 (5)	Fe1—O1—C21*A*	129.3 (6)
C11—C12—C13	123.6 (5)	Fe1—O1—C21*B*	132 (1)
C11—C12—C12*A*	117.6 (5)	O1—C21*B*—O2*B*	134 (2)
C13—C12—C12*A*	118.8 (5)	O1—C21*A*—O2*A*	129 (1)
N2—C13—C12	125.6 (5)	C7*A*—C7*B*—C7*C*	121.6 (6)

Table 3. *Spin states, coordination-group parameters* (Å) *and space groups for mononuclear high-spin and intermediate-spin pentacoordinate oxygen-ligated* (*Por*)*iron*(III) *compounds*

$\mathrm{Fe}\cdots C_{t'}$ is the distance from the Fe atom to the center of the mean plane of the 24-atom core and $\mathrm{Fe—N}_p$ is the average distance from the Fe atom to the porphinato-core N atoms.

	S	Fe—O	$\mathrm{Fe}\cdots C_{t'}$	$\mathrm{Fe—N}_p$	Space group
$[\mathrm{Fe(TTP)(OCH_3)}]^a$	5/2	1.816 (2)	0.562 (1)	2.082 (2)	$P2_1/n$
$[\mathrm{Fe}(\mathrm{t}_p\text{-MePP})(\mathrm{CO_2CH_3})].\text{-}1/2\mathrm{CH_3COOH}^b$	5/2	1.898 (4)	0.520 (1)	2.067 (3)	$I2/c$
$[\mathrm{Fe(TPP)(OCOCF_3)}]^c$	5/2	1.921 (4)	0.483 (1)	2.054 (5)	$P2_1/a$
$[\mathrm{Fe(TPP)(SO_2C_6H_5)}]^d$	5/2	1.92 (1)	0.45 (2)	2.05 (2)	$P1$
$[\mathrm{Fe(TPP)(OSO_3H)}].\text{-}1/2\mathrm{C_6H_6}^e$	5/2	1.926 (4)	0.42	2.042 (5)	$P2/c$
$[\mathrm{Fe(TPP)(SO_3CH_3)}].\text{-}\mathrm{CHCl_3}^f$	5/2	1.95 (1)	0.412 (2)	2.05 (2)	$Pbca$
$[\mathrm{Fe(TPP)(SO_3CF_3)}]^g$	5/2, 3/2*	1.946 (6)	0.38	2.030 (6)	$P2_1/a$
$[\mathrm{Fe(TPP)(OClO_3)}].\text{-}1/2(m\text{-xylene})^h$	5/2, 3/2†	2.029 (4)	0.30	2.001 (5)	$P2_1/n$

References: (*a*) Lemcomte, Chadwick, Coppens & Stevens (1983); (*b*) Oumous, Lecomte, Protas, Cocolios & Guilard (1984); (*c*) this work; (*d*) Cocolios, Lagrange, Guilard, Oumous & Lecomte (1984); (*e*) Scheidt, Lee & Finnegan (1988); (*f*) Li *et al.* (1987); (*g*) Gonzalez & Wilson (1994); (*h*) Reed *et al.* (1979).

* Spin state is ~75% $S = 5/2$.

† Spin state is ~45% $S = 5/2$.

The crystal used for data collection was mounted on the tip of a glass fiber with epoxy cement. Measurements were made at 193 K using a fixed-tube, low-temperature attachment designed and manufactured by Molecular Structure Corporation; temperature control during data collection was ±2 K. All independent data to $[(\sin\theta)/\lambda]_{\max} = 0.65\ \text{Å}^{-1}$ were measured. Laue symmetry and systematic absences indicated the space group $P2_1/a$. The structure was solved using the program *MITHRIL* (Gilmore, 1984) to locate the Fe atom. All remaining non-H atoms were located using the direct methods program *DIRDIF* (Beurskens, 1984) and further refined by difference Fourier syntheses using *TEXSAN* (Molecular Structure Corporation, 1988). H atoms were included in the structure-factor calculations with idealized geometries (C—H 0.95 Å) and were assigned isotropic displacement parameters which were 20% greater than the B_{eq} of the atom to which they were bonded. Full-matrix least-squares refinement minimized $\sum w(|F_o|-|F_c|)^2$ with all non H-atoms, except the trifluoromethyl group, refined anisotropically. A decay correction was not applied.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and rigid-group parameters have been deposited with the IUCr (Reference: BK0001). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis-Dichloro[*N*,*N'*-dimethyl-*N*,*N'*-bis(2-pyridylmethyl)-1,3-propanediamine]chromium(III) Hexafluorophosphate

Wing-Tak Wong

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

Wah-Hung Leung

Department of Chemistry, The University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

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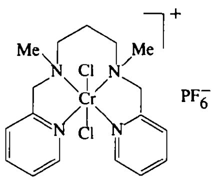
Abstract

In the title compound, $[CrCl_2(C_{17}H_{24}N_4)]PF_6$, the coordination sphere of the Cr^{3+} ion is a distorted octahedron defined by the four N atoms of the tetradentate ligand and two *cis* Cl^- ions.

Comment

The coordination chemistry of the tetradentate ligand *N*,*N'*-dimethyl-*N*,*N'*-bis(2-pyridylmethyl)-1,3-propanediamine (L_1) has been investigated extensively (Che, Tang & Li, 1990; Che, Tang, Lee, Wong & Lau, 1992), but its structural chemistry is less well established. We therefore prepared a chromium complex, (I), of this ligand and determined its structure by X-ray analysis.



(I)

An *ORTEP*II (Johnson, 1976) plot of the complex cation with the atomic numbering scheme is shown in Fig. 1. The Cr—N_{amine} distances [average 2.146 (9) Å] are slightly longer than the Cr—$N_{pyridine}$ distances [average 2.093 (9) Å]. The two Cl^- ligands coordinate to Cr in a *cis* configuration. The six-membered ring defined by atoms Cr, N1, C1, C2, C3 and N2 has a chair conformation. Some disorder of the atoms of the PF_6^- anion is indicated by their large anisotropic displacement parameters.

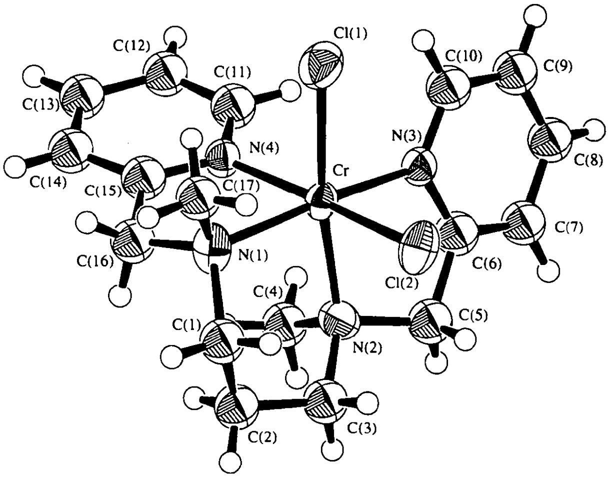


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of the complex cation showing the atom-numbering scheme and 50% probability displacement ellipsoids. H atoms are represented as spheres of arbitrary radii.

Experimental

The title complex containing the *N*,*N'*-dimethyl-*N*,*N'*-bis(2-pyridylmethyl)-1,3-propanediamine (L_1) ligand was prepared by the interaction of anhydrous $CrCl_3$ and L_1 in dimethylformamide. The dark yellow reaction mixture was heated under reflux overnight. The solvent was then evaporated off *in vacuo* and the dark yellow residue washed with diethyl ether and redissolved in a minimum amount of water. To the green filtrate was added excess $NaPF_6$. The resulting grey precipitate was collected, washed with water and dried in air. Recrystallization from acetonitrile/diethyl ether solution afforded green crystals suitable for X-ray analysis.

Crystal data

$[CrCl_2(C_{17}H_{24}N_4)]PF_6$
$M_r = 552.29$

Mo *Kα* radiation
$\lambda = 0.71073$ Å