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Platinum(II) Complexes of Piperazine (and Derivatives): *cis*-Diiodo(*N*-methylpiperazine-*N*,*N*′)platinum(II)

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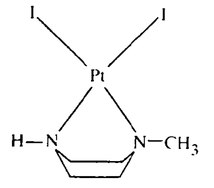
Abstract

The neutral chelate title complex, *cis*-[$PtI_2(C_5H_{12}N_2)$], has a distorted square-planar geometry around the Pt atom. The N and I atoms lie almost perfectly in a plane but the N—Pt—N angle is reduced to 70.1 (7)° while the I—Pt—I angle is 93.40 (5)°. The molecular structure, which resembles roughly that of the more symmetric *cis*-dichloro(*N*,*N*′-dimethylpiperazine-*N*,*N*′)platinum(II), shows some asymmetric distortions, for example, the two Pt—N distances of 2.05 (2) and 2.13 (1) Å. These distortions are mainly caused by steric hindrance between the bulky I atom and the methyl group of the *N*-methylpiperazine ligand.

Comment

Piperazine (H_2ppz), *N*-methylpiperazine (HMeppz) and *N*,*N*′-dimethylpiperazine (Me_2ppz) are extensively used by us as ligands towards metal ions, especially platinum(II) (Marzotto *et al.*, 1997, 1998; Ciccarese *et al.*, 1998*a*,*b*) and cobalt(II) (Visona', 1998). Moreover, piperazine and its derivatives possess pharmacological activity including antitumor properties (Hempel *et al.*, 1982). The literature reports metal complexes in which piperazine or its derivatives act as monodentate, bidentate or bidentate-chelate ligands. The chair conformation of the six-membered ring is always observed when monodentate coordination occurs, whereas the rare boat conformation is observed only when there is bidentate-chelate coordination.

We have recently synthesized and characterized, also through X-ray analysis, two platinum(II) complexes possessing the boat conformation, *i.e.* *cis*-dichloro(*N*,*N*′-dimethylpiperazine-*N*,*N*′)platinum(II), *cis*-[$PtCl_2(Me_2ppz)$] (Ciccarese *et al.*, 1998*a*), and *trans*-bis(*N*-methylpiperazine-*N*,*N*′)platinum(II) dichloride tetrahydrate, *trans*-[$Pt(HMeppz)_2]Cl_2\cdot 4H_2O$ (Marzotto *et al.*, 1997). In addition, piperazine is forced to assume the boat conformation when it is incorporated into a macrocyclic ring for bonding to a metal atom in a bidentate fashion (Wade *et al.*, 1990; Kowallick *et al.*, 1997). This behaviour may be explained by the fact that the chair conformation of the hexa-atomic ring is 17.2 kJ mol^{-1} more stable than the boat one (Niemeyer, 1979). Since during the above-mentioned studies we have noticed strong steric hindrance between *N*-methylpiperazine and the groups bonded to platinum(II), we have synthesized the neutral complex *cis*-diiodo(*N*-methylpiperazine-*N*,*N*′)platinum(II), *cis*-[PtI_2(HMeppz)], in order to study the effect of the bulky I atoms on the Pt—N bond lengths.



cis-[PtI_2(HMeppz)]

The molecular structure of the title complex shows remarkable distortions due to unbalanced steric interactions, in fact, I2···CH_3 causes greater hindrance than I1···H1. For example, Pt—N2 [2.13 (1) Å] is longer than Pt—N1 [2.05 (2) Å], which is, on the contrary, close to the Pt—N distances [2.061 (10) and 2.065 (9) Å] found in *cis*-[$PtCl_2(Me_2ppz)$]. Furthermore, the I1···N1 distance, 3.45 (2) Å, could be explained by the presence of an intramolecular hydrogen bond which restricts the N1—Pt—I1 angle to 95.7 (5)°, while the N2—Pt—I2 angle is enlarged to 100.9 (4)° as a consequence of the requested planarity of platinum(II) coordination and steric hindrance between the I atom and the methyl group. This is confirmed by the average of the N—Pt—I angles, 98.3 (6)°, which is close to the N—Pt—Cl angle values, 98.5 (3) and 98.3 (3)°, found for the symmetrical *cis*-[$PtCl_2(Me_2ppz)$].

The Pt—I distances, 2.579 (2) and 2.588 (2) Å, are consistent with the observed bond lengths found in other *cis*-diiodobis(*N*-donor)platinum(II) complexes (Raudaschl-Siebert *et al.*, 1986; Oksanen *et al.*, 1989). This finding is also supported by the I· · ·I intramolecular separation, 3.760 (3) Å, and the corresponding I—Pt—I angle, 93.40 (5)°, which has almost always been found to be greater than 90°, except for (bipyridyl-*N*,*N′*)diiodoplatinum(II), owing to the symmetrical steric interaction between the iodine and the H atoms of the bipyridyl moiety which is constrained to lie in the coordination plane (Connick & Gray, 1994). The molecules are held together by a hydrogen bond between N1 and I2 translated along **a** (Table 2).

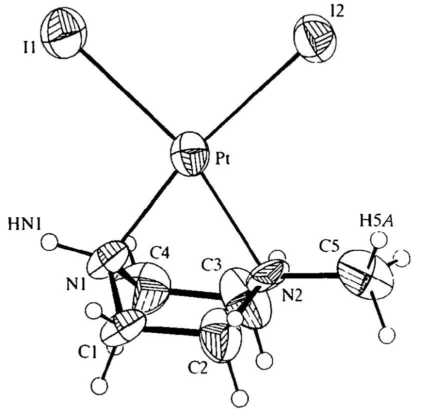


Fig. 1. Displacement ellipsoid plot (50% probability) of the molecular structure of *cis*-$[PtI_2(C_5H_{12}N_2)]$ showing the labelling of the non-H atoms. H atoms are drawn as small circles of arbitrary radii.

Experimental

The title complex was prepared according to Dhara's (1970) procedure. The final product was obtained as a yellow–orange powder in 90% yield based on platinum. Orange X-ray-quality single crystals were obtained by slow recrystallization from an acetone/diethyl ether solution. Found: C 10.88, H 2.23, N 5.06, I 46.12, Pt 35.48%; calculated for $C_5H_{12}I_2N_2Pt$: C 10.94, H 2.20, N 5.10, I 46.23, Pt 35.53%.

Crystal data

$[PtI_2(C_5H_{12}N_2)]$
M_r = 549.06
Monoclinic
$P2_1/n$
a = 7.446 (2) Å
b = 12.179 (3) Å
c = 12.279 (3) Å
β = 102.60 (5)°
V = 1086.7 (5) Å^3
Z = 4
D_x = 3.356 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71070 Å
Cell parameters from 25 reflections
θ = 13–19°
μ = 18.538 mm^{-1}
T = 292 (2) K
Block
0.12 × 0.11 × 0.10 mm
Orange

Data collection

Philips PW1100/20 diffractometer
ω–2θ scans
Absorption correction: semi-empirical *via* ψ scan (North *et al.*, 1968)
T_{min} = 0.10, T_{max} = 0.15
2728 measured reflections
2620 independent reflections

1561 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 28°
$h = -9 \rightarrow 9$
$k = 0 \rightarrow 16$
$l = 0 \rightarrow 16$
3 standard reflections every 60 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.205
S = 1.060
2620 reflections
91 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1142P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = −0.048
$\Delta\rho_{max}$ = 2.73 e Å^{-3}
$\Delta\rho_{min}$ = −3.28 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pt—N1	2.05 (2)	Pt—I1	2.579 (2)
Pt—N2	2.13 (1)	Pt—I2	2.588 (2)
N1—Pt—N2	70.1 (7)	N2—Pt—I2	100.9 (4)
N1—Pt—I1	95.7 (5)	I1—Pt—I2	93.40 (5)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H· · ·*A*	*D*—H	H· · ·*A*	*D*· · ·*A*	*D*—H· · ·*A*
N1—H1· · ·I2^i	0.91	2.90	3.74 (2)	155

Symmetry code: (i) $x - 1, y, z$.

The H atoms were fixed at ideal geometrical positions riding with N—H = 0.91, methylene C—H = 0.97 and methyl C—H = 0.96 Å, with U fixed at $1.2U_{eq}$ of the N or C atom to which they are bonded, and at $1.5U_{eq}$ for the C5 methyl H atoms. The N2 and C5 atoms are affected by some disorder, as indicated by the exceptionally high ratios of the maximum and minimum principal axes of their displacement ellipsoids. The maximum (2.73 e Å^{-3}) and minimum (−3.28 e Å^{-3}) peaks of the final difference map are at distances of 0.81 and 1.00 Å from the Pt^{II} atom, respectively.

Data collection: Philips PW1100/20 software. Cell refinement: Philips–Pavia University software. Data reduction: *RIFLUP*80 (Biagini Cingi *et al.*, 1980). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1376). Services for accessing these data are described at the back of the journal.

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Vanadyl Tetrakis(pentafluorophenyl)porphyrin Dichloromethane Solvate

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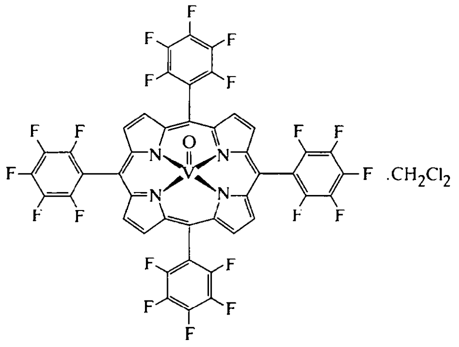
Abstract

The vanadyl complex oxo[5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato-κ^4N]vanadium(IV) dichloromethane solvate, $[VO(C_{44}H_8F_{20}N_4)].CH_2Cl_2$, crystallizes in the monoclinic space group $P2_1/c$, with four molecules per unit cell. The V atom is found to lie 0.5237 (5) Å above the mean plane of the porphyrin core. The average V—N distance is 2.067 (5) Å and the V═O bond length is 1.585 (2) Å. The doming of the porphyrin core is characteristic of five-coordinate metalloporphyrins. Moreover, the macrocycle is slightly saddle-shaped and ruffled. Van der Waals contacts between the phenyl rings and the solvent molecules lead to dihedral angles between these phenyl rings and the porphyrin core mean plane ranging from 58.23 (5) to 89.38 (6)°. These contacts could explain the deviation of the porphyrin geometry relative to the fourfold symmetry.

Comment

The vanadyl complex of the title *meso*-pentafluorophenylporphyrin, VO(TPFPP), was synthesized quantitatively by reacting an excess of $VO(acac)_2$ (acac = acetylacetonate) with the porphyrin free base at 573 K. Single crystals of $[VO(TPFPP)].CH_2Cl_2$, (I), were obtained by slow diffusion of *n*-hexane into a solution of VO(TPFPP) in CH_2Cl_2 at room temperature. The complex (Fig. 1) crystallizes in the $P2_1/c$ space group with four molecules per unit cell.



(I)

The V^{IV} atom is five-coordinate, being bonded to the four pyrrole N atoms, N_p, of the porphyrin, and to one terminal oxo group. The metal geometry is close to square pyramidal. The V atom is displaced 0.5237 (5) Å from the mean plane of the porphyrin core towards the axially bonded O atom. This out-of-plane displacement lies in the range of 0.48–0.72 Å predicted by extended Huckël molecular-orbital calculations (Zerner & Gouterman, 1966). The V═O bond length of 1.585 (2) Å and the average V—N distance of 2.067 (5) Å are similar to those found in other vanadyl porphyrins (Molinaro & Ibers, 1976; Miller *et al.*, 1984; Drew *et al.*, 1984), *e.g.* 1.620 (2) and 2.102 (6) Å, respectively, in VO(OEP) (OEP = octaethylporphyrinato; Molinaro & Ibers, 1976). The V═O bond is tilted by 3.3 (1)° with respect to the normal to the porphyrin mean plane.