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Dibromo[5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinato-κ^4N]platinum(IV) chloroform acetonitrile solvate

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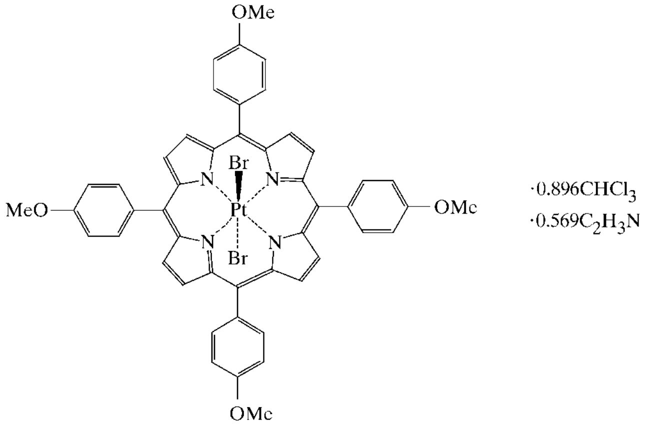
In the title compound, $[\mathrm{PtBr_2(C_{48}H_{36}N_4O_4)}]\cdot0.896\mathrm{CHCl_3}\cdot0.569\mathrm{CH_3CN}$, the centrosymmetric metal complex is octahedral, with the porphyrin ring essentially planar and the Br atoms occupying axial positions. The two independent methoxyphenyl substituents are tilted at angles of 89.0 and 67.0° with respect to the porphyrin plane. The Pt—N distances are 2.035 (4) and 2.036 (4) Å and the Pt—Br distance is 2.4666 (6) Å. Chloroform and acetonitrile solvent molecules, exhibiting substantial disorder, occupy positions between the porphyrin molecules. This is the first crystal and molecular structure of a Pt$^{\mathrm{IV}}$–porphyrin complex to be reported.

Comment

Metalloporphyrin reactivity is found to be dependent upon the central metal, the substituents on the porphyrin ring and the axially coordinated ligands (Dolphin, 1978). Platinum porphyrins have been investigated as oxygen-sensing probes (Gouin & Gouterman, 2000), phosphorescent probes in bioanalytical applications (Papkovsky *et al.*, 2000), photosensitizers (Kunkely & Vogler, 1997), potential antitumour agents (Brunner *et al.*, 1997) and molecular conductors (Hiroyuki *et al.*, 2000). Most of the recent studies have focused on Pt$^{\mathrm{II}}$–porphyrins, with relatively few studies pertaining to Pt$^{\mathrm{IV}}$–porphyrin systems. Here, we report the first crystal structure of a Pt$^{\mathrm{IV}}$–porphyrin compound, *viz.* the title compound, (I).

Complex (I) (Fig. 1) crystallizes in the centrosymmetric space group $P2/n$, with the Pt atom located at a centre of inversion. The structure of the molecule is typical of many porphyrin complexes. The porphyrin moiety is essentially planar, while the bond lengths and angles within the macrocycle are unremarkable. The p-methoxyphenyl groups are rotated at angles of 89 and 67° with respect to the porphyrin mean plane, due to steric hindrance with the pyrrole-H atoms of the macrocycle. Strict coplanarity of the Pt atom and the four pyrrole N atoms is imposed by the inversion center. The Pt—N bond lengths (Table 1) are longer than those found in the Pt$^{\mathrm{II}}$ analogues. For example, the Pt$^{\mathrm{II}}$—N distances in tetraphenylporphinatoplatinum(II) (Hazell, 1984) and analogous 2,3,7,8,12,13,17,18-octaethylporphinatoplatinum(II) (Milgrom *et al.*, 1988) are found to be 2.008 and 2.012 (3) Å, respectively. Pt$^{\mathrm{II}}$—N$_{\mathrm{porphyrin}}$ bonds are considered to be shorter than typical Pt$^{\mathrm{II}}$—N complex bonds due to extensive metal-$d(\pi)$–porphyrin-π^* overlap (Milgrom *et al.*, 1988). The longer Pt$^{\mathrm{IV}}$—N bonds observed in (I) are attributed to a decrease in metal-$d(\pi)$–porphyrin-π^* bonding upon oxidation



(I)

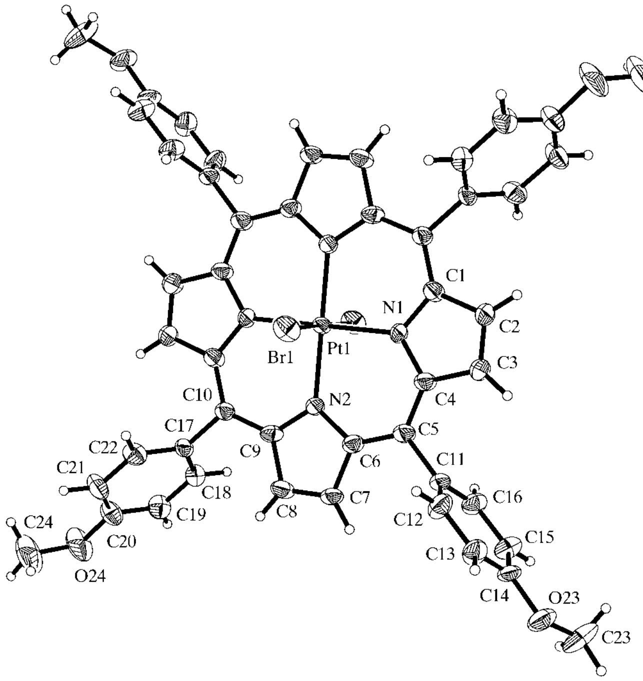


Figure 1
A view of the molecule of (I). Displacement ellipsoids are drawn at the 50% probability level, H atoms are shown as small spheres of arbitrary radii and the solvent molecules have been omitted for clarity.

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of Pt^{II} to Pt^{IV}, as evident in the electronic spectrum of the compound (Mink *et al.*, 1997, 2000).

The molecules of (I) pack with the porphyrin moieties forming face-centered parallel layers along the *ac* face of the unit cell. Within each layer, the porphyrin moieties at the corners of the unit cell lie parallel to each other, each making angles of 29.6 and 19.5° with the *b* and *c* edges, respectively (measured in the *ac* and *bc* planes). The moiety at the centre of the face makes the same angles with the *b* and *c* edges but in the opposite direction. The overall effect is to produce a layer with a herring-bone pattern when viewed from the side (Fig. 2).

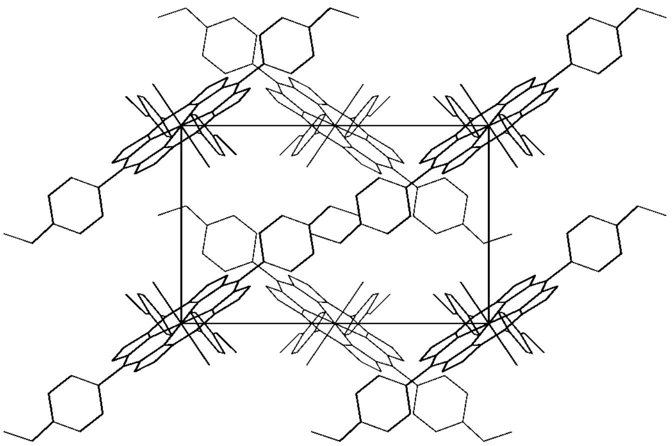

Figure 2

A view of (I) down the (001) face, showing the herring-bone packing arrangement of the porphyrin moieties. H atoms and solvent molecules have been omitted for clarity.

Solvent molecules are packed between the porphyrin layers in (I). A chloroform molecule is found on a twofold axis, while another solvent site is shared between the chloroform and acetonitrile molecules. The solvent molecules appear to be within van der Waals contact distances of the porphyrins, suggesting that it is the solvent that holds the crystal together. This is borne out by the rapid deterioration of the crystals when they are removed from the solvent and allowed to desolvate; the crystals become very brittle and crumble easily.

Experimental

Compound (I) was synthesized by direct oxidation of the Pt^{II} analogue with bromine, according to methods reported previously by Mink *et al.* (2000).

Crystal data

$[PtBr_2(C_{48}H_{36}N_4O_4)]\cdot 0.896CHCl_3\cdot 0.569C_2H_3N$
$M_r = 1348.32$
Monoclinic, *P*2/*n*
$a = 14.8727\ (7)$ Å
$b = 9.4421\ (5)$ Å
$c = 18.5973\ (9)$ Å
$\beta = 99.3480\ (10)°$
$V = 2576.9\ (2)$ Å^3
$Z = 2$
$D_x = 1.728$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6264 reflections
$\theta = 9.5–28.3°$
$\mu = 4.60$ mm^{-1}
$T = 294\ (2)$ K
Elongated prism, purple
0.30 × 0.15 × 0.10 mm

Data collection

Siemens SMART *P*3/512 CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.517$, $T_{max} = 0.629$
25 609 measured reflections
5931 independent reflections
4440 reflections with $I > 2\sigma(I)$
$R_{int} = 0.058$
$\theta_{max} = 28.3°$
$h = -19 \rightarrow 19$
$k = -11 \rightarrow 12$
$l = -23 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.120$
$S = 0.82$
5931 reflections
371 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.033$
$\Delta\rho_{max} = 0.61$ e Å^{-3}
$\Delta\rho_{min} = -0.80$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0019 (3)

Table 1

Selected geometric parameters (Å, °) for (I).

Pt1—N2	2.035 (4)	Pt1—Br1	2.4668 (6)
Pt1—N1	2.036 (4)		
N2—Pt1—N1	90.07 (16)	C4—N1—Pt1	125.9 (3)
N2—Pt1—Br1	89.70 (13)	C9—N2—Pt1	126.6 (3)
N1—Pt1—Br1	88.87 (12)	C6—N2—Pt1	126.1 (3)
C1—N1—Pt1	126.6 (3)		

H atoms were treated as riding, with C—H distances in the range 0.93–0.98 Å.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1222). Services for accessing these data are described at the back of the journal.

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