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(Phthalocyaninato)antimony Iodide

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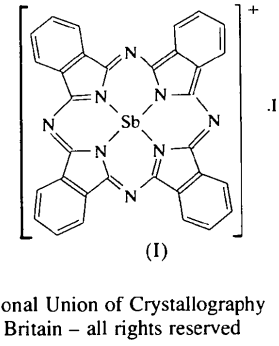
Abstract

The asymmetric unit of the title complex, [SbPc]I (Pc = $C_{32}H_{16}N_8$), consists of an [SbPc]$^+$ cation and an I$^-$ anion. A combination of ionic and acceptor–donor interactions links the [SbPc]I moieties to form pseudo-dimers in the unit cell. The pseudo-dimers are linked through I$\cdots$H—C$_{\rm benzole}$ hydrogen-bond interactions to form a two-dimensional network. As a result of these interactions, the four Sb—N$_{\rm isoindole}$ bonds in the [SbPc]$^+$ moiety are not equivalent and the symmetry of the Sb–N core is only close to C_s.

Comment

Previously, two kinds of antimony phthalocyanines have been prepared, which were characterized only by elemental analyses (Barrett *et al.*, 1938). Recently, the synthesis and spectral data of [SbPc]F and [SbPc(OH)$_2$]F have been reported (Knör, 1996). To our knowledge, this paper reports the first X-ray single-crystal structure determination of an antimony phthalocyanine, (I).



(I)

The asymmetric unit of the title compound consists of a saucer-shaped macrocyclic [SbPc]$^+$ cation and an I$^-$ anion (Fig. 1). A combination of ionic and acceptor–donor interactions, *e.g.* Sb1$\cdots$I1 [3.438 (1) Å], I1$\cdots$Sb1$^{\rm i}$ [3.474 (1) Å], I1$\cdots$N7 [3.591 (4) Å] and I1$\cdots$N1$^{\rm i}$ [3.568 (4) Å] [symmetry code: (i) $-x$, $-y+1$, $-z+1$], link the [SbPc]I moieties to form pseudo-dimers in the unit cell. These pseudo-dimers are linked through I$\cdots$H—C$_{\rm benzole}$ interactions, *e.g.* I1$\cdots$H14$^{\rm ii}$ [3.06 (5) Å] and I1$^{\rm i}\cdots$H20$^{\rm ii}$ [3.22 (5) Å] [symmetry code: (ii) $-x+1$, $-y+1$, $-z+1$], which could be considered as weak hydrogen-bond interactions, to form a two-dimensional network (Fig. 2).

The influence of these interactions is clearly manifested in the Sb—N$_{\rm isoindole}$ coordination. The four Sb—N$_{\rm isoindole}$ distances fall into two groups, *i.e.* the Sb1—N1 [2.203 (4) Å] and Sb1—N7 [2.202 (4) Å] distances are shorter than Sb1—N3 [2.236 (4) Å] and Sb1—N5 [2.211 (4) Å] (Fig. 1). As a consequence, the molecular symmetry of the Sb–N core is close to C_s and not to C_{4v}, which is possible for saucer-shaped $M^{\rm II}$Pc macrocycles (Friedel *et al.*, 1970; Ukei, 1973; Iyechika *et al.*, 1982).

The average interatomic distances in the phthalocyanine ring are similar to those observed for other phthalocyanine structures. In contrast to fluorides of antimony(III) phthalocyanine and dihydroxoantimony(V) phthalocyanine complexes (Knör, 1996), the (phthalocyaninato)antimony iodide complex is not readily soluble, in particular in alcohols, acetone or acetonitrile.

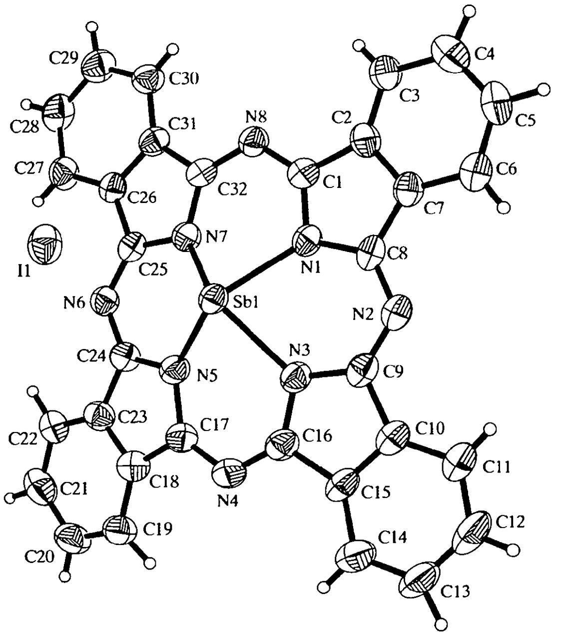


Fig. 1. The molecular structure of [SbPc]I with 50% probability ellipsoids.

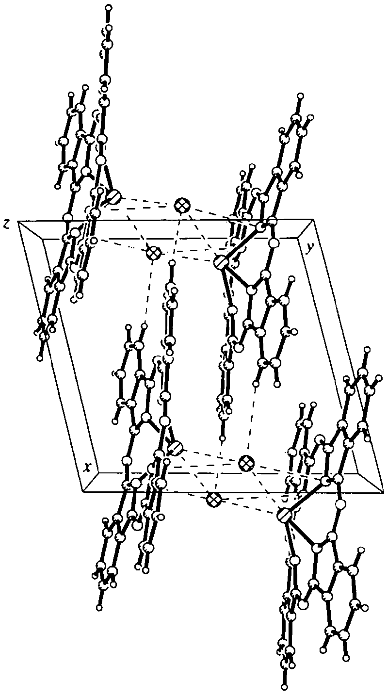


Fig. 2. The molecular packing in the unit cell.

Experimental

Crystals of [SbPc]I were obtained in the reaction of antimony with 1,2-dicyanobenzene (Kubiak & Janczak, 1993) under I$_2$ vapour.

Crystal data

[Sb(C$_{32}$H$_{16}$N$_8$)]I
M_r = 761.18
Triclinic
$P\bar{1}$
a = 10.458 (2) Å
b = 10.925 (2) Å
c = 12.097 (2) Å
α = 86.17 (3)°
β = 81.83 (3)°
γ = 76.31 (3)°
V = 1328.4 (4) Å^3
Z = 2
D_x = 1.903 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 30 reflections
θ = 7–13°
μ = 2.241 mm^{-1}
T = 293 (2) K
Plate
0.319 × 0.192 × 0.040 mm
Black–violet

Data collection

Kuma KM-4 diffractometer
ω–2θ scans
Absorption correction: ψ scan (Sheldrick, 1990)
$T_{\min}$ = 0.707, $T_{\max}$ = 0.914
12 122 measured reflections
6960 independent reflections
4411 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.034
$\theta_{\max}$ = 30.06°
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -16 \rightarrow 16$
2 standard reflections every 50 reflections intensity decay: 1.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.100
S = 0.985
6960 reflections
443 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0463P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.806 e Å^{-3}
$\Delta\rho_{\min}$ = −0.865 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Sb1—N7	2.202 (4)	N4—C16	1.319 (6)
Sb1—N1	2.203 (4)	N4—C17	1.321 (6)
Sb1—N5	2.211 (4)	N5—C24	1.380 (6)
Sb1—N3	2.236 (4)	N5—C17	1.392 (6)
N1—C1	1.387 (6)	N6—C25	1.314 (6)
N1—C8	1.390 (6)	N6—C24	1.324 (6)
N2—C9	1.319 (6)	N7—C32	1.377 (6)
N2—C8	1.319 (6)	N7—C25	1.384 (6)
N3—C16	1.366 (6)	N8—C32	1.323 (6)
N3—C9	1.387 (6)	N8—C1	1.324 (6)
N7—Sb1—N1	77.01 (14)	C24—N5—Sb1	124.9 (3)
N7—Sb1—N5	77.37 (14)	C17—N5—Sb1	124.4 (3)
N1—Sb1—N5	122.80 (15)	C25—N6—C24	123.1 (4)
N7—Sb1—N3	123.52 (14)	C32—N7—C25	107.9 (4)
N1—Sb1—N3	76.57 (14)	C32—N7—Sb1	121.5 (3)
N5—Sb1—N3	76.70 (14)	C25—N7—Sb1	123.7 (3)
C1—N1—C8	107.1 (4)	C32—N8—C1	122.2 (4)
C1—N1—Sb1	120.9 (3)	N8—C1—N1	127.7 (4)
C8—N1—Sb1	123.4 (3)	N2—C8—N1	127.4 (5)
C9—N2—C8	122.6 (4)	N2—C9- -N3	127.9 (4)
C16—N3—C9	108.7 (4)	N4—C16—N3	129.1 (4)
C16—N3—Sb1	123.2 (3)	N4—C17—N5	127.7 (5)
C9—N3—Sb1	123.4 (3)	N6—C24—N5	127.7 (4)
C16—N4—C17	121.9 (4)	N6—C25—N7	127.3 (4)
C24—N5—C17	107.5 (4)	N8—C32—N7	127.7 (4)

Data collection: *Kuma KM-4 Users Guide* (Kuma, 1995). Cell refinement: *Kuma KM-4 Users Guide*. Data reduction: *Kuma KM-4 Users Guide*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1152). Services for accessing these data are described at the back of the journal.

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Dichloro[6,7-dimethyl-2,3-bis(2-pyridyl-*N*)-quinoxaline]palladium(II) Monohydrate

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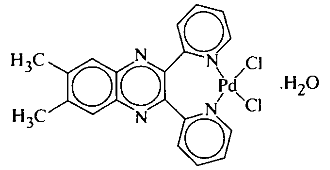
Abstract

The title compound, $[\mathrm{PdCl_2(C_{20}H_{16}N_4)}].\mathrm{H_2O}$, contains the first example of 6,7-dimethyl-2,3-bis(2-pyridyl)-quinoxaline chelating a square-planar-coordinated metal *via* its pyridine N atoms. In the solid state, pairs of centrosymmetrically-related molecules form a 'head-to-tail' arrangement, with a significant graphitic interaction between the parallel aromatic rings. The layers formed by these pairs are interconnected by Cl···H—C bonds. Molecules of water of crystallization are interposed between these layers.

Comment

We are interested in the synthesis of square-planar complexes having aromatic ligands containing N-donor atoms for study as potential DNA intercalators (Cusumano *et al.*, 1996; Cusumano & Giannetto, 1997). In this context, we have begun the synthesis of a series of platinum(II) and palladium(II) complexes of 6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline (DMeDPQ); this ligand is known to bind metal ions either through one pyrazine N and one pyridine N atom, forming a five-membered ring, or through both pyridine N atoms, disposed in a *cis* conformation to form a seven-membered ring. Several structures showing this type of coordination with DMeDPQ or related ligands have been described (Rillema *et al.*, 1987; Escuer *et al.*, 1989, 1991; Bandoli *et al.*, 1994; Goodwin *et al.*, 1990; Gordon *et al.*, 1996), however, as far as we know, no square-planar complexes of this ligand have been reported. We now describe the crystal structure of $[\mathrm{Pd(DMeDPQ)Cl_2}].\mathrm{H_2O}$, (I).



(I)

The crystal packing is characterized mainly by the presence of discrete pairs of complex molecules related by inversion centres. These two centrosymmetric molecules show a 'head-to-tail' arrangement with a parallel-ligand-plane disposition that allows overlap of the aromatic rings at a distance of 3.56 (1) Å, which indicates a significant graphitic interaction. The ring separation is slightly longer than the usual π–π (ligand–ligand) distance, probably as a result of hindrance between the two methyl substituents of one quinoxaline and the fused pyrazine ring of the paired molecule. Each pair of complex molecules is connected to neighbouring pairs by intermolecular hydrogen-bonding interactions between the coordinated $\mathrm{Cl^-}$ anions and pyridine H atoms: Cl1···HC1($1-x$, $1-y$, z) 2.802 (3) and Cl2···HC17($x-1$, y, z) 2.763 (3) Å. The hydrogen-bonded pairs form layers orthogonal to the crystallographic *b* axis; the co-crystallized water molecules (1:1 ratio with the complex) are located in cavities so as to constitute an intermediate aqueous layer between adjacent layers of the bimolecular units. The crystal packing is thus formed by alternate parallel layers of complex and water molecules.

Conjugation between the aromatic quinoxaline fragment, and the N1 and N4 pyridine rings seems slight in view of the N1—C5—C6—C13 and C6—C13—C14—N4 torsion angles [−57.1 (3) and 57.8 (3)°, respectively]. This typical butterfly arrangement, with a dihedral angle of 85.0 (1)° between the pyridine rings, allows the nitrogen lone pairs to be oriented out of the ligand plane towards the metal atom. This distortion might appear to be caused by coordination-geometry requirements, but it is also observed in the uncoordinated ligand (Wozniak, 1991). The steric requirements of the ligand bite may also be responsible for the significant deformations from planarity of the quinoxaline (Rasmussen *et al.*, 1990) and the enlargement of the pyridine substituent angles up to 130° (protonated free ligand; Wozniak *et al.*, 1994).

The pyridyl orientation causes the palladium coordination plane to be normal to the ligand mean plane, with a dihedral angle between them of 86.39 (3)°. The angles between the pyridine rings and the palladium coordination plane [63.26 (7) and 67.72 (5)°] may indicate possible interaction of the π orbitals of both rings with the