

[Phthalocyaninato(2-)]antimony(III)  
chloride

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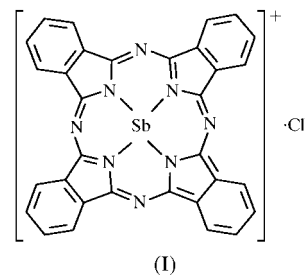
The title antimony(III) complex,  $[\text{Sb}(\text{C}_{32}\text{H}_{16}\text{N}_8)]\text{Cl}$  or  $[\text{SbPc}]\text{Cl}$  (where  $\text{Pc} = \text{C}_{32}\text{H}_{16}\text{N}_8^{2-}$ ), has been obtained from the reaction of pure powdered antimony with 1,2-dicyanobenzene under a stream of  $\text{ICl}$  vapour. The asymmetric unit of this complex consists of an  $[\text{SbPc}]^+$  cation and a  $\text{Cl}^-$  anion. The phthalocyaninate residue  $[\text{SbPc}]^+$  is not planar. The Sb atom lies 1.057 (3) Å from the plane defined by the four isoindole N atoms. A combination of ionic and donor-acceptor interactions links the  $[\text{SbPc}]\text{Cl}$  molecules to form centrosymmetric  $[(\text{SbPc})\text{Cl}]_2$  pseudo-dimers in the crystal. The Sb—Cl distances in the pseudo-dimer are not equivalent [3.043 (2) and 3.201 (2) Å]. The pseudo-dimers are weakly linked through  $\text{Cl}\cdots\text{H}-\text{C}_{\text{benzo}}$  interactions to form a three-dimensional network. As a result of these interactions, the four  $\text{Sn}-\text{N}_{\text{isoindole}}$  bond lengths in the  $[\text{SbPc}]^+$  residue are not equivalent and the symmetry of the Sb—N core is only close to  $C_s$ .

## Comment

As a continuation of our studies on the synthesis and characterization of the halogenide-doped metallophthalocyanines (especially iodine doped), we have obtained several phthalocyaninate complexes (Kubiak & Janczak, 1997; Janczak *et al.*, 1998; Janczak, Kubiak & Jezierski, 1999; Janczak, Kubiak & Hahn, 1999; Janczak *et al.*, 2000; Janczak & Kubiak, 1999a,b,c,d). Previously, only two kinds of antimony phthalocyanines had been prepared, which were characterized by elemental analyses only (Barrett *et al.*, 1936). Next, the syntheses and spectral investigations of  $[\text{Sb}^{\text{III}}\text{Pc}]\text{F}$  and  $[\text{Sb}^{\text{V}}\text{Pc}(\text{OH})_2]\text{F}$ , and the electrochemical studies of  $[\text{Sb}^{\text{V}}\text{Pc}-\text{Cl}_2]\text{SbCl}_6\cdot\text{CH}_2\text{Cl}_2$  were reported (Knör, 1996; Kagaya & Isagi, 1994). Recently, the syntheses and structural investigations of iodide antimony(III) phthalocyanine  $[\text{SbPc}]\text{I}$ , and triiodide antimony(III) phthalocyanine,  $[\text{SbPc}]\text{I}_3$ , have been reported (Kubiak & Razik, 1998; Kubiak *et al.*, 1999). To our knowledge, the present paper reports the third X-ray single-crystal structure determination of antimony phthalocyanine.

The crystal of the title compound, (I), is built up from a saucer-shaped macrocyclic  $[\text{SbPc}]^+$  residue and a  $\text{Cl}^-$  anion

(Fig. 1). The tetradentate phthalocyaninate(2-) ligand is not strictly planar. All atoms of the  $\text{Pc}^{2-}$  ring are displaced from the plane defined by the four isoindole N atoms. The largest deviations (besides the H atoms) from the  $\text{N}_4$ -isoindole plane



are for C4 [0.893 (3) Å] and C28 [0.878 (3) Å]. The Sb atom lies 1.056 (3) Å from the  $\text{N}_4$ -isoindole plane. A similar deviation of the central metal can be found in  $[\text{BiPc}]\text{I}$  (Kubiak & Ejsmont, 1999), in  $[\text{SbPc}]\text{I}$  (Kubiak & Razik, 1998) and in the non-planar metal(II) phthalocyanines, *e.g.*  $\text{Sn}^{\text{II}}\text{Pc}$  (Friedel *et al.*, 1970; Kubiak & Janczak, 1992) and  $\text{Pb}^{\text{II}}\text{Pc}$  (Ukei, 1973; Iyechika *et al.*, 1982).

In the crystal, as a consequence of the contribution of the ionic and donor-acceptor interactions, *e.g.*  $\text{Sb}\cdots\text{Cl}$  [3.043 (2) Å] and  $\text{Sb}\cdots\text{Cl}^{\text{I}}$  [3.201 (2) Å] [symmetry code: (i)  $1-x, 2-y, -z$ ], the  $[\text{SbPc}]\text{Cl}$  molecules form pseudo-dimers. A similar interaction in the crystal can be found in antimony(III) phthalocyanine iodide (Kubiak & Razik, 1998). The difference in the radius of the  $\text{Cl}^-$  and  $\text{I}^-$  ions (about 0.21 Å) implicated the difference in the distances between Sb and the halogenide ( $\text{Cl}^-$  and  $\text{I}^-$ ) ions. The equivalent  $\text{Sb}\cdots\text{I}$  distances in the crystal of  $[\text{SbPc}]\text{I}$  are 3.438 (2) and 3.474 (2) Å, respectively. The pseudo-dimers are linked through  $\text{Cl}\cdots\text{H}-$

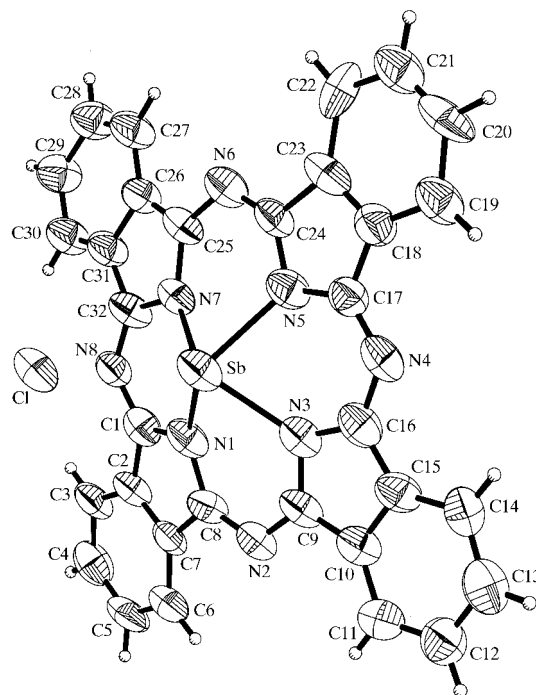


Figure 1

The molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

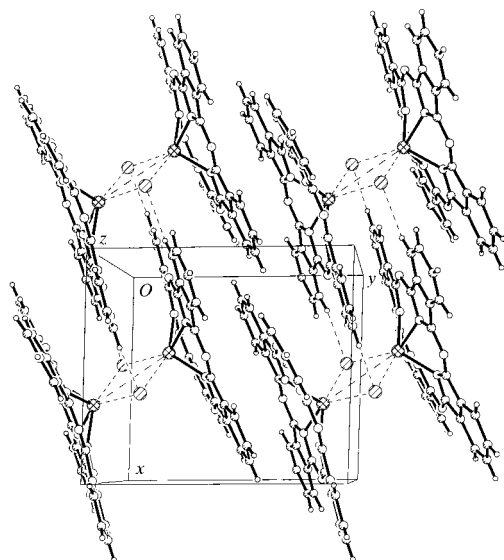
$C_{\text{benzo}}$  interactions, e.g.  $\text{Cl}\cdots\text{H5}^{\text{ii}}$  (2.83 Å) and  $\text{Cl}\cdots\text{H11}^{\text{iii}}$  (2.72 Å) [symmetry codes: (ii)  $x - 1, y, z$ ; (iii)  $2 - x, 2 - y, -z$ ], which could be considered as weak hydrogen-bond interactions, to form a three-dimensional network in the crystal (Fig. 2).

The interatomic distance between the Sb atoms in this dinuclear pseudo-dimer is 4.334 (1) Å and between the Cl atoms is 4.498 (2) Å, and the angles  $\text{Sb}-\text{Cl}-\text{Sb}^{\text{i}}$  and  $\text{Cl}-\text{Sb}-\text{Cl}^{\text{i}}$  are 87.87 (3) and 92.13 (3)°, respectively. The equivalent interatomic distances in the antimony(III) and bismuth(III) phthalocyaninato iodide analogues are 5.036 (2) (Sb $\cdots$ Sb) and 4.733 (2) Å (I $\cdots$ I), and 4.904 (2) (Bi $\cdots$ Bi) and 4.571 (2) Å (I $\cdots$ I), and the angles are 86.0 (1) and 94.0 (1)°, and 85.98 (3) and 94.02 (3)°, respectively.

The influence of the ionic and donor-acceptor interactions in the [SbPc]Cl pseudo-dimers is clearly manifested in the Sb–N<sub>isoindeole</sub> bond lengths. The four Sb–N<sub>isoindeole</sub> bond distances are not equivalent and fall into two groups, i.e. the Sb–N1 and Sb–N7 distances are shorter than Sb–N3 and Sb–N5. These differences in the Sb–N bond lengths do appear to affect the molecular symmetry of the Sb–N<sub>isoindeole</sub> core, which is close to  $C_s$  symmetry and not to  $C_{4v}$ , which is possible for saucer-shaped  $M^{\text{II}}$ Pc molecules such as Sn<sup>II</sup>Pc or Pb<sup>II</sup>Pc.

Although there is no imposed crystallographic symmetry on the phthalocyaninate(2–) ring, the bond distances and angles for chemically equivalent bonds do not differ significantly and compare well with the bond lengths and angles of other saucer-shaped metallophthalocyaninate structures. The closest non-bonded contact between back-to-back phthalocyaninate rings is  $\sim 3.3$  Å.

In contrast to fluorides of antimony(III) and dihydroxy-antimony(V) phthalocyanines and [Sb<sup>V</sup>PcCl<sub>2</sub>]SbCl<sub>6</sub>·CH<sub>2</sub>Cl<sub>2</sub> complexes, the phthalocyaninate(2–) antimony(III) chloride



**Figure 2**

The molecular packing in the unit cell showing the pseudo-dimers of [SbPc]Cl molecules.

complex is not readily soluble in polar and non-polar solvents, in particular alcohol, acetone, acetonitrile, cyclohexane *etc.*

## Experimental

Crystals of SbPcCl were obtained by the direct reaction of pure powdered antimony with 1,2-dicyanobenzene (Kubiak & Janczak, 1993) under a stream of ICl vapour at about 453 K. At this temperature, the liquid 1,2-dicyanobenzene undergoes catalytic tetramerization with simultaneous transfer of two electrons from Sb metal to the forming of the Pc ring, the third electron from Sb is transferred to the ICl to form I<sup>–</sup> and Cl<sup>–</sup> ions. The crystals of SbPcCl were grown alongside those of the iodine analogue (SbPcI).

### Crystal data

[Sb(C <sub>32</sub> H <sub>16</sub> N <sub>8</sub> )]Cl	$D_x = 1.741 \text{ Mg m}^{-3}$
$M_r = 669.73$	$D_m = 1.74 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	$D_m$ measured by flotation
$a = 9.560$ (2) Å	Mo $K\alpha$ radiation
$b = 10.806$ (2) Å	Cell parameters from 200 reflections
$c = 12.462$ (2) Å	$\theta = 3\text{--}25^\circ$
$\alpha = 91.96$ (3)°	$\mu = 1.226 \text{ mm}^{-1}$
$\beta = 96.21$ (3)°	$T = 293$ (2) K
$\gamma = 92.37$ (3)°	Plate, violet
$V = 1277.8$ (4) Å <sup>3</sup>	$0.32 \times 0.17 \times 0.15 \text{ mm}$
$Z = 2$	

### Data collection

Kuma KM-4 diffractometer	11 638 measured reflections
equipped with a two-dimension area CCD detector	6190 independent reflections
$\omega$ scans	2834 reflections with $I > 2\sigma(I)$
Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990)	$R_{\text{int}} = 0.035$
$T_{\text{min}} = 0.695, T_{\text{max}} = 0.838$	$\theta_{\text{max}} = 29.51^\circ$
	$h = -12 \rightarrow 13$
	$k = -14 \rightarrow 11$
	$l = -17 \rightarrow 17$

### Refinement

Refinement on $F^2$	H atoms constrained
$R[F^2 > 2\sigma(F^2)] = 0.050$	$w = 1/[\sigma^2(F_o^2) + (0.0110P)^2]$
$wR(F^2) = 0.061$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.026$	$(\Delta/\sigma)_{\text{max}} = 0.002$
6190 reflections	$\Delta\rho_{\text{max}} = 0.75 \text{ e \AA}^{-3}$
379 parameters	$\Delta\rho_{\text{min}} = -0.65 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

Sb–Cl	3.043 (2)	Sb–N5	2.244 (3)
Sb–N7	2.199 (3)	Sb–N3	2.257 (3)
Sb–N1	2.208 (3)		
N7–Sb–N1	77.43 (11)	N7–Sb–N3	123.47 (10)
N7–Sb–N5	77.10 (10)	N1–Sb–N3	77.66 (11)
N1–Sb–N5	123.30 (10)	N5–Sb–N3	75.85 (11)

Data collection: *Kuma-KM4 CCD Diffraction Software* (Kuma, 1998); cell refinement: *Kuma-KM4 CCD Diffraction Software*; data reduction: *Kuma-KM4 CCD Diffraction Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1489). Services for accessing these data are described at the back of the journal.

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