

Tetrakis[phthalocyaninato(2-)-antimony(III)] docsaiohexa-antimony(III)

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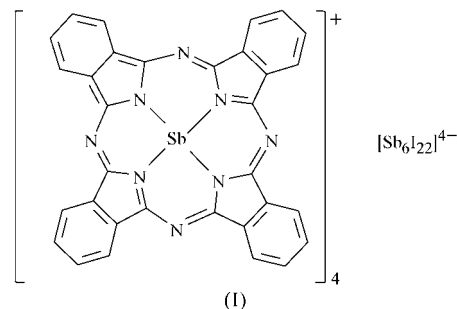
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Crystals of a novel antimony(III)–phthalocyanine complex, $[\text{Sb}(\text{C}_{32}\text{H}_{16}\text{N}_8)_4][\text{Sb}_6\text{I}_{22}]$ or $[\text{SbPc}]_4[\text{Sb}_6\text{I}_{22}]$, where Pc is the phthalocyaninato(2-) macrocycle, have been obtained from the reaction of pure powdered antimony with phthalonitrile under oxidation conditions of iodine vapour at 533 K. The crystal structure is built up from separate but interacting $[\text{SbPc}]^+$ cations and $[\text{Sb}_6\text{I}_{22}]^{4-}$ anions. Each Sb atom of the two independent $[\text{SbPc}]^+$ cations is bonded to the four isoindole N atoms of the Pc macrocycle and lies 0.986 (1) Å out of the plane defined by these N atoms. The anion consists of six distorted SbI_6 octahedra linked *via* bridging I atoms into a centrosymmetric $[\text{Sb}_6\text{I}_{22}]^{4-}$ anion. The arrangement of the oppositely charged species, *viz.* $[\text{SbPc}]^+$ and $[\text{Sb}_6\text{I}_{22}]^{4-}$, in the crystal structure is determined mainly by the ionic attractions between the ions, forming a centrosymmetric $[(\text{SbPc})_4(\text{Sb}_6\text{I}_{22})]$ unit. Neighbouring $[(\text{SbPc})_4(\text{Sb}_6\text{I}_{22})]$ units related by translation interact *via* π – π interactions between the aromatic macrocycles in a back-to-back fashion.

Comment

The present study is a continuation of our investigations of the synthesis, characterization and stereochemistry of metallo-phthalocyaninate complexes that have been obtained under oxidation conditions of iodine vapour (Janczak, 2003, and references therein). Although metallo-phthalocyaninate complexes have been known for a long time, metallo-phthalocyaninate complexes with the metals of group 15 have rarely been investigated. The title Sb^{III} –phthalocyanine–iodine complex, (I), is an example of a complex containing the same metal ion in both the cation and the anion, *i.e.* in $[\text{SbPc}]^+$ as well as in the $[\text{Sb}_6\text{I}_{22}]^{4-}$ counter-ion. A search of the Cambridge Structural Database (Version 5.24; Allen, 2002) for phthalocyaninate (Pc) structures containing the same metal in both the cation and the anion yields only two isostructural

complexes, *viz.* $[(\text{SbPc})_4(\text{Sb}_4\text{I}_{16})]$ (Janczak & Idemori, 2002) and $[(\text{BiPc})_4(\text{Bi}_4\text{I}_{16})]$ (Kubiak & Ejsmont, 1999), two non-isostructural complexes, *viz.* $[(\text{AsPc})_2(\text{As}_4\text{I}_{14})]$ (Janczak & Kubiak, 2003) and $[(\text{SbPc})_2(\text{Sb}_4\text{I}_{14})]$ (Perpétuo & Janczak, 2005), and $[(\text{AsPc})_2(\text{As}_2\text{I}_8)]$ (Janczak & Perpétuo, 2006), none of which contains an $[\text{M}_6\text{I}_{22}]^{4-}$ ion. Thus, the present $[(\text{Sb}_4\text{Pc})-(\text{Sb}_6\text{I}_{22})]$ structure is the first example of this type of phthalocyanine system to be structurally characterized.



The crystal structure of (I) is built up of separate but interacting $[\text{SbPc}]^+$ and $[\text{Sb}_6\text{I}_{22}]^{4-}$ units (Fig. 1). The two crystallographically independent $[\text{SbPc}]^+$ cations have essentially the same geometry. In both $[\text{SbPc}]^+$ cations, the phthalocyaninato(2-) macrocycle adopts a saucer-shaped form as a result of the interaction of the central Sb^{III} ion with the I atoms of the $[\text{Sb}_6\text{I}_{22}]^{4-}$ counter-ion (Fig. 2). The greatest deviations from the mean planes defined by the four isoindole N atoms of the Pc macrocycles are observed for the outermost C atoms of benzene rings C18–C23 [0.224–0.574 (1) Å] and C34–C39 [0.049–0.426 (1) Å] for the $[\text{Sb4Pc}]^+$ and $[\text{Sb5Pc}]^+$ cations, respectively. The positively charged Sb4 and Sb5 atoms of the $[\text{SbPc}]^+$ cations are each significantly displaced [by 0.984 (1) and 0.989 (1) Å, respectively] from the N_4 -isoindole plane toward the I atoms of the $[\text{Sb}_6\text{I}_{22}]^{4-}$ counter-ion. The influence of the ionic attraction between the oppositely charged $[\text{SbPc}]^+$ and $[\text{Sb}_6\text{I}_{22}]^{4-}$ ions is clearly manifested in the Sb–N(isoindole) coordination, leading to the molecular symmetry of the Sb–N core being close to C_s , rather than the C_{4v} symmetry that characterizes the conformation in solution.

The anion of (I) consists of six deformed SbI_6 octahedra linked by bridging I atoms into a centrosymmetric $[\text{Sb}_6\text{I}_{22}]^{4-}$ ion (Fig. 1*b*). Generally, the Sb–I bond lengths fall into two groups, namely shorter Sb–I bonds with terminal I atoms and longer Sb–I bonds involving the bridging I atoms. However, in the $[\text{Sb}_6\text{I}_{22}]^{4-}$ anion, two different bridging I atoms exist. Atoms I1 and I2 bridge three Sb atoms, while atoms I3, I5 and I6 bridge only two Sb atoms. The distortion of the SbI_6 polyhedron from O_h symmetry is likely to be due to the electron lone pair on the Sb^{III} ion. Looking in more detail at the differences between the Sb–I bond lengths, and at the coordination geometry around atoms Sb1, Sb2 and Sb3, it is clear that the Sb atoms are coordinated to the I atoms through forces of different strength. Atom Sb1 links two I atoms with relatively short Sb–I bonds, two I atoms with intermediate Sb–I values and two I atoms with relatively long Sb–I bonds, the longest being the Sb1–I1 bond (Table 1). In the coordi-

nation environments of atoms Sb2 and Sb3, three short Sb—I bonds and three relatively long Sb—I bonds are observed. Thus the $[\text{Sb}_6\text{I}_{22}]^{4-}$ ion can be regarded as being composed of three symmetrically equivalent pairs of units, *viz.* one $[\text{SbI}_5]^{2-}$ and two crystallographically independent SbI_3 units. Atom Sb1 in the $[\text{SbI}_5]^{2-}$ unit has distorted square-pyramidal coordination, formed by four I atoms in the basal plane and one apical I atom with a relatively short Sb—I bond. The relatively long Sb1—I¹ bond in a position *trans* to the apical I atom indicates the stereochemical effect of the electron lone pair (Gillespie, 1992). In the coordination environments of atoms Sb2 and Sb3, it is not clear in which direction the electron lone pair points, since the three relatively long Sb—I bonds are very similar. However, the mutual orientation of the $[\text{SbI}_5]^{2-}$

and two SbI_3 units related by an inversion centre leads to the formation of an $[\text{Sb}_6\text{I}_{22}]^{4-}$ counter-ion, in which all Sb atoms have distorted octahedral coordination environments. A similar pattern concerning the Sb—I bond lengths is also observed in the $[\text{Sb}_4\text{I}_{16}]^{4-}$ (Janczak & Idemori, 2002) and $[\text{Sb}_4\text{I}_{14}]^{2-}$ (Perpétuo & Janczak, 2005) counter-ions of two antimony(III)–phthalocyanine complexes. In the first complex, the $[\text{Sb}_4\text{I}_{16}]^{4-}$ ion consists of four distorted SbI_6 octahedra, while in the second, the $[\text{Sb}_4\text{I}_{14}]^{2-}$ ion consists of two pairs of deformed SbI_6 octahedra and distorted square-pyramidal SbI_5 polyhedra.

In the unit cell (Fig. 2), there seems to be significant ionic attraction between the $[\text{SbPc}]^+$ cations and $[\text{Sb}_6\text{I}_{22}]^{4-}$ counter-ions. The basic packing unit includes two pairs of $[\text{SbPc}]^+$

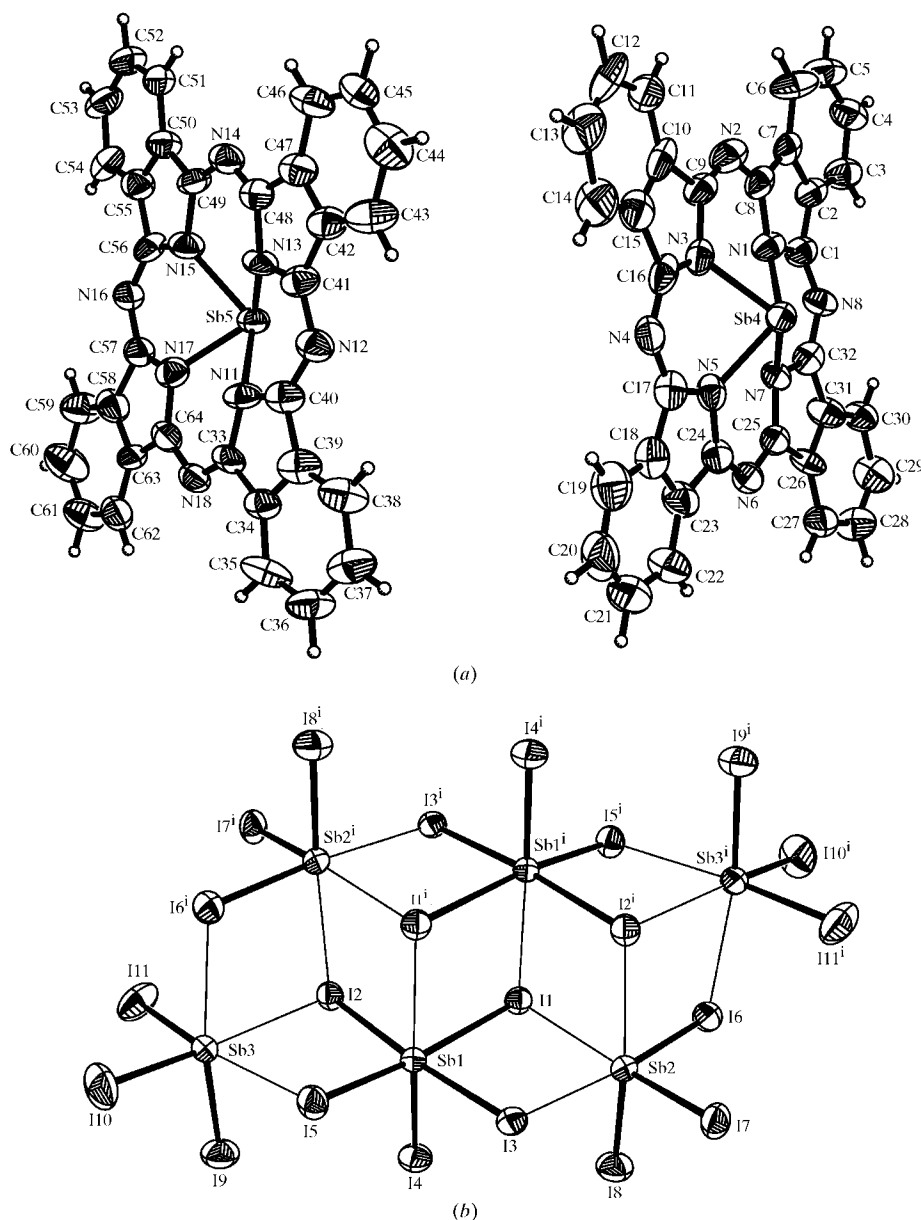


Figure 1 Views of the molecular structures of (a) the two independent $[\text{SbPc}]^+$ cations and (b) the $[\text{Sb}_6\text{I}_{22}]^{4-}$ unit, showing the atom labelling and displacement ellipsoids at the 50% probability level. [Symmetry code: (i) $-x, -y, -z$.]

macrocycles associated by an inversion centre and an $[\text{Sb}_6\text{I}_{22}]^{4-}$ counter-ion; thus, each anion is surrounded by four $[\text{SbPc}]^+$ cations. Atoms Sb4 and Sb5 of two crystallographically independent $[\text{SbPc}]^+$ cations each interact with three I atoms of the $[\text{Sb}_6\text{I}_{22}]^{4-}$ counter-ion (Sb4 with I1, I2 and I3, and Sb5 with I6, I7 and I11), the Sb—I contacts being considerably shorter than the sum of the van der Waals radii of Sb and I of 4.35 Å (Shannon, 1976). The centrosymmetric $[(\text{SbPc})_4(\text{Sb}_6\text{I}_{22})]$ aggregates in the crystal structure form stacks along [111], with π - π interactions between adjacent back-to-back-oriented pairs of Pc macrocycles. The interplanar N_4 -isoindole- N_4 -isoindole distance within the stack is ~ 3.4 Å, which indicates a strong π - π interaction and overlapping of the π clouds of the phthalocyanine macrocycle, since this distance is comparable to the van der Waals distance of 3.4 Å for aromatic C atoms (Pauling, 1960). Strong π - π interaction is a common feature in the structures of phthalocyanine and its metal complexes, and determines their crystal architectures. The π - π interactions also play an important role in association of metallophthalocyanines in solution (Nevin *et al.*, 1987; Terekhov *et al.*, 1996; Isago *et al.*, 1997, 1998).

Although the crystal structure of (I) is built up from oppositely charged $[\text{SbPc}]^+$ and $[\text{Sb}_6\text{I}_{22}]^{4-}$ species, the compound does not possess the characteristic properties of ionic crystals. The solubility of this compound in polar

solvents, such as water, methanol and ethanol, is insignificant, and it is only slightly soluble in pyridine, dimethylformamide, dimethyl sulfoxide, chloronaphthalene, quinoline and diazabicycloundecane. As can be seen from the crystal structure architecture (Fig. 2), both hydrophilic parts of this complex are surrounded by the hydrophobic peripheral benzene rings of the Pc macrocycle.

The electronic spectrum of this salt in pyridine solution exhibits two bands characteristic of the phthalocyaninate(2-) macrocycle, *viz.* at 680 nm (*Q*-band) and at 350 nm (*B*-band) (Stillman & Nyokong, 1989). The electrical conductivity of (I), measured on a single crystal along the stacking direction of $[(\text{SbPc})_4(\text{Sb}_6\text{I}_{22})]$ aggregates (*viz.* along the [111] direction), exhibits non-metallic character ($d\sigma/dT > 0$). At room temperature, the conductivity is ~ 1.7 – $2.2 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$.

Experimental

Crystals of the title compound were obtained by the direct reaction of pure powdered antimony with phthalonitrile (Kubiak & Janczak, 1993) under a stream of iodine vapour at 533 K.

Crystal data

$[\text{Sb}(\text{C}_{32}\text{H}_{16}\text{N}_8)_4][\text{Sb}_6\text{I}_{22}]$
 $M_r = 6059.42$
 Triclinic, $P\bar{1}$
 $a = 14.708$ (3) Å
 $b = 15.633$ (3) Å
 $c = 19.158$ (4) Å
 $\alpha = 94.99$ (3)°
 $\beta = 96.62$ (3)°
 $\gamma = 114.88$ (3)°
 $V = 3924.4$ (18) Å³
 $Z = 1$

$D_x = 2.564$ Mg m⁻³
 $D_m = 2.56$ Mg m⁻³
 D_m measured by flotation in a mixture of bromoform and chloroform
 Mo $K\alpha$ radiation
 $\mu = 6.08$ mm⁻¹
 $T = 295$ (2) K
 Parallelepiped, black-violet
 $0.23 \times 0.15 \times 0.12$ mm

Data collection

Kuma KM-4 diffractometer with a CCD detector
 ω scan
 Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990b)
 $T_{\min} = 0.334$, $T_{\max} = 0.527$

34137 measured reflections
 19326 independent reflections
 10908 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$
 $\theta_{\max} = 28.3^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.074$
 $S = 1.02$
 19326 reflections
 865 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0181P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 1.65 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -1.15 \text{ e \AA}^{-3}$

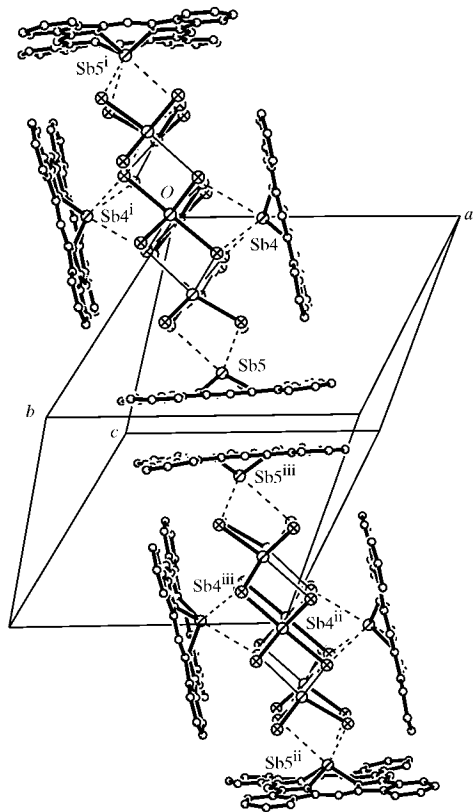


Figure 2

The molecular packing in the unit cell, showing the Sb...I and back-to-back π - π interactions. [Symmetry codes: (i) $-x, -y, -z$; (ii) $x + 1, y + 1, z + 1$; (iii) $-x + 1, -y + 1, -z + 1$].

All H atoms were positioned geometrically ($\text{C}-\text{H} = 0.93$ Å) and treated as riding, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. The structure contains voids of 187 and 84 Å³ at $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, 0, \frac{1}{2})$, respectively. Since the crystals were obtained directly from phthalonitrile and powdered antimony under iodine vapour, no solvents are expected. This was confirmed by the experimental and X-ray densities.

Data collection: *KM-4 CCD Software* (Kuma, 2002); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL97*.

Table 1

Selected geometric parameters (Å, °).

Sb1—I1	3.2186 (10)	Sb3—I10	2.7600 (10)
Sb1—I2	3.0451 (15)	Sb3—I11	2.7985 (14)
Sb1—I3	3.0344 (15)	Sb4—I3	3.6984 (10)
Sb1—I4	2.7903 (8)	Sb4—I1 ⁱ	3.5750 (15)
Sb1—I5	2.8781 (9)	Sb4—I2 ⁱ	3.6640 (11)
Sb1—I1 ⁱ	3.3864 (9)	Sb4—N5	2.175 (6)
Sb2—I6	2.9001 (9)	Sb4—N1	2.189 (5)
Sb2—I7	2.8428 (12)	Sb4—N3	2.195 (5)
Sb2—I8	2.7630 (9)	Sb4—N7	2.195 (5)
Sb2—I1	3.2402 (16)	Sb5—I6	3.6598 (18)
Sb2—I3	3.2563 (10)	Sb5—I7	3.5843 (11)
Sb2—I2 ⁱ	3.4734 (9)	Sb5—I11 ⁱ	3.6696 (10)
Sb3—I2	3.3696 (10)	Sb5—N17	2.165 (6)
Sb3—I5	3.3402 (9)	Sb5—N15	2.180 (6)
Sb3—I6 ⁱ	3.4527 (10)	Sb5—N13	2.203 (5)
Sb3—I9	2.7638 (9)	Sb5—N11	2.210 (5)
I4—Sb1—I5	98.07 (3)	N5—Sb4—N3	79.0 (2)
I5—Sb1—I2	93.97 (4)	N1—Sb4—N3	77.5 (2)
I3—Sb1—I1	89.31 (4)	N5—Sb4—N7	77.8 (2)
I8—Sb2—I7	97.48 (4)	N1—Sb4—N7	78.7 (2)
I7—Sb2—I6	98.05 (4)	N17—Sb5—N15	78.4 (2)
I3—Sb2—I1	85.19 (4)	N15—Sb5—N13	78.5 (2)
I10—Sb3—I9	98.51 (4)	N17—Sb5—N11	77.8 (2)
I10—Sb3—I11	97.36 (4)	N13—Sb5—N11	77.7 (2)
I2—Sb3—I5	80.44 (4)		

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3021). Services for accessing these data are described at the back of the journal.

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