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Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.011$ Å
 R factor = 0.048
 wR factor = 0.109
Data-to-parameter ratio = 21.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Bis[[phthalocyaninato(2-)]antimony(III)]
tetradecaiodotetraantimonate(III)

The structure of the title compound, $[\text{Sb}(\text{C}_{32}\text{H}_{16}\text{N}_8)]_2[\text{Sb}_4\text{I}_{14}]$ or $[\text{SbPc}]_2[\text{Sb}_4\text{I}_{14}]$, where Pc is the phthalocyaninato(2-) macrocycle, is built up from separate but interacting $[\text{SbPc}]^+$ cations and $[\text{Sb}_4\text{I}_{14}]^{2-}$ anions. The Sb atom of the $[\text{SbPc}]^+$ ion is bonded to four isoindole N atoms of the macrocycle and lies 0.974 (1) Å out of the plane defined by these four N atoms. The anion consists of $[\text{SbI}_3]$ and $[\text{SbI}_4]^-$ units which, through an inversion centre, form an $[\text{Sb}_4\text{I}_{14}]^{2-}$ anion. The anions interact with each other, forming $\{[\text{Sb}_4\text{I}_{14}]^{2-}\}_n$ chains. The arrangement of oppositely charged ions, *viz.* $[\text{SbPc}]^+$ and $[\text{Sb}_4\text{I}_{14}]^{2-}$, in the crystal structure is determined mainly by the ionic attractions between the $[\text{SbPc}]^+$ and $[\text{Sb}_4\text{I}_{14}]^{2-}$ units and by π - π interactions between the aromatic macrocycles.

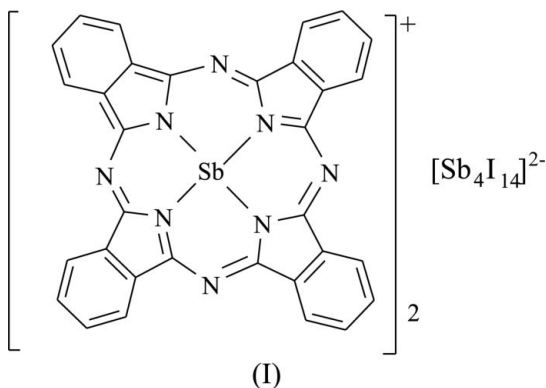
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Comment

The present study is a continuation of our investigations on the synthesis, characterization and stereochemistry of metallophthalocyaninate complexes, which have been obtained through oxidation by iodine vapour (Janczak & Idemori, 2001; Janczak, 2003). The title compound, (I), is an example of a complex containing the same metal ion in both parts of the complex, the cation and the anion, *i.e.* $[\text{SbPc}]^+$ and $[\text{Sb}_4\text{I}_{14}]^{2-}$. In addition, two isostructural complexes of $[(\text{SbPc})_4(\text{Sb}_4\text{I}_{16})]$ (Janczak & Idemori, 2002) and $[(\text{BiPc})_4(\text{Bi}_4\text{I}_{16})]$ (Kubiak & Ejsmont, 1999) have been structurally characterized to date. A search of the Cambridge Structural Database (Version 5.24; Allen, 2002) for structures containing both $[\text{MPc}]^+$ and $[\text{M}_4\text{I}_{14}]^{2-}$ units shows only one example, the complex $[\text{AsPc}][\text{As}_4\text{I}_{14}]$, (II) (Janczak & Kubiak, 2003), which is not isostructural with the present Sb complex; compound (I) crystallizes in the monoclinic system, while (II) is in the triclinic system.



Compound (I) is built up of separate but interacting $[\text{SbPc}]^+$ and $[\text{Sb}_4\text{I}_{14}]^{2-}$ units (Figs. 1 and 2). The $[\text{Sb}_4\text{I}_{14}]^{2-}$ units

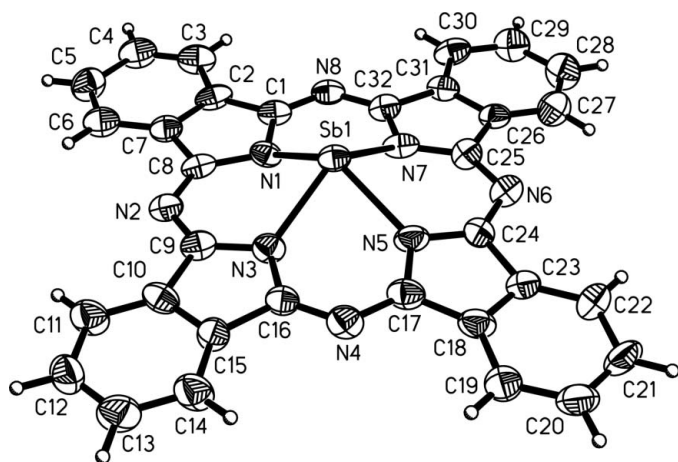


Figure 1
A view of the molecular structure of the $[\text{SbPc}]^+$ unit of (I), with the atom-labelling. Displacement ellipsoids are drawn at the 50% probability level.

interact to form chains of $\{(\text{Sb}_4\text{I}_{14})^{2-}\}_n$, which are different from (II), where the $[\text{As}_4\text{I}_{14}]^{2-}$ anions are more separated (Janczak & Kubiak, 2003). The Pc macrocycle of the $[\text{SbPc}]^+$ cation is saucer-shaped, as a result of the interaction of the central Sb^{III} ion with the I atoms of the oppositely charged $[\text{Sb}_4\text{I}_{14}]^{2-}$ counter-ion. The greatest deviations from the plane defined by the four isoindole N atoms of the macrocycle are observed for the C atoms of the benzene rings. The greatest range is 0.347 (1)–0.834 (1) Å for C18–C23. The Sb^{III} atom is significantly displaced from the N_4 -isoindole plane [0.974 (1) Å] towards atom I4 of the anion; the $\text{Sb1}\cdots\text{I4}$ distance of 3.693 (1) Å is shorter than the sum of the van der Waals radii of Sb and I (Shannon, 1976). The interaction of atom Sb1 of the $[\text{SbPc}]^+$ unit with two other I atoms (I1 and I7) of the anion is weaker, with $\text{Sb1}\cdots\text{I1}$ and $\text{Sb1}\cdots\text{I7}^i$ distances of 3.842 (1) and 3.999 (1) Å, respectively [symmetry code (i): $1 - x, 1 - y, 1 - z$]. The displacement of the Sb^{III} atom from the N_4 -isoindole plane is comparable with that in $[\text{SbPc}]^+\text{I}_3^-$ [0.966 (2) Å; Kubiak *et al.*, 1999] and in the $[\text{SbPc}]_4[\text{Sb}_4\text{I}_{16}]$ complex [1.000 (2) Å; Janczak & Idemori, 2002], but slightly shorter than that in $[\text{SbPcCl}]_2$ [1.057 (3) Å; Janczak & Kubiak, 2001]. The displacement of the As^{III} atom in $[(\text{AsPc})_2(\text{As}_4\text{I}_{14})]$ and other iodo-As-phthalocyaninato complexes is smaller by about 0.22 Å than in (I). This is quite reasonable, because of the difference in the ionic radii of Sb^{III} and As^{III} (Shannon, 1976). The influence of the $\text{Sb}\cdots\text{I}$ interaction is clearly manifested in the $\text{Sb}-\text{N}$ coordination, leading to the molecular symmetry of the $\text{Sb}-\text{N}_4$ core being close to C_s and not to C_{4v} , which corresponds to the conformation in solution.

The anion of (I), $[\text{Sb}_4\text{I}_{14}]^{2-}$, consists of two deformed SbI_6 octahedra joined together by two bridging I atoms and two deformed SbI_5 square pyramids, which are linked to the SbI_6 octahedra to form a centrosymmetric $[\text{Sb}_4\text{I}_{14}]^{2-}$ counter-ion (Fig. 2). The $\text{Sb}-\text{I}$ bond lengths fall into two groups, namely shorter $\text{Sb}-\text{I}$ bonds, which show that the $[\text{Sb}_4\text{I}_{14}]^{2-}$ ion consists of two pairs of SbI_3 and SbI_4 units, and longer $\text{Sb}-\text{I}$ bonds, with the I bridging atoms. The distortion of the SbI_6 octahedra and SbI_5 square-pyramidal polyhedra in the

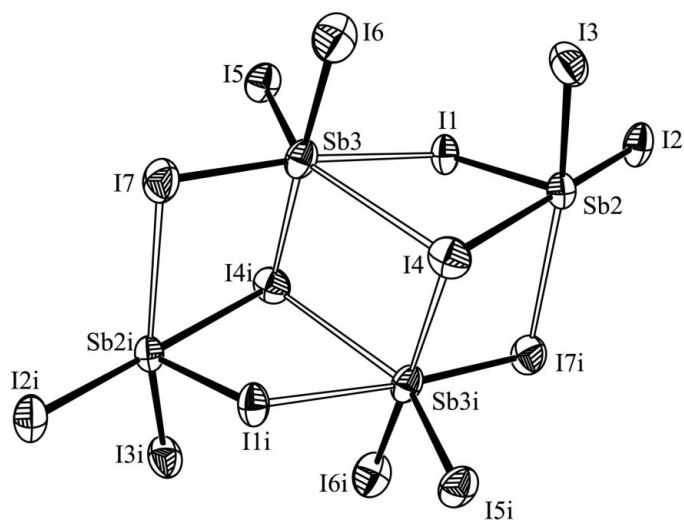


Figure 2
A view of the molecular structure of the $[\text{Sb}_4\text{I}_{14}]^{2-}$ counter-ion of (I), with the atom-labelling. Displacement ellipsoids are drawn at the 50% probability level [symmetry code: (i) $1 - x, 1 - y, 1 - z$].

$[\text{Sb}_4\text{I}_{14}]^{2-}$ anion is likely to be due to stereochemical activity of the lone electron pair on the Sb^{III} atom, as predicted by the valence-shell electron-pair repulsion (VSEPR) model (Gillespie, 1963, 1992). A similar pattern in $M-\text{I}$ bond lengths is also observed in $[\text{Bi}_4\text{I}_{16}]^{4-}$ (Kubiak & Ejsmont, 1999), $[\text{Sb}_4\text{I}_{16}]^{4-}$ (Janczak & Idemori, 2002) and $[\text{As}_4\text{I}_{14}]^{2-}$ ions (Janczak & Kubiak, 2003). The $[\text{Sb}_4\text{I}_{14}]^{2-}$ anion can also be described as composed of two symmetrically equivalent pairs of SbI_3 and SbI_4^- units. However, the mutual orientation and arrangement of both SbI_3 and SbI_4^- units, related by an inversion centre in the crystal structure, leads to the formation of an $[\text{Sb}_4\text{I}_{14}]^{2-}$ ion, in contrast with the As complex, (II) (Janczak & Kubiak, 2003).

The ionic attraction between the $[\text{SbPc}]^+$ and $[\text{Sb}_4\text{I}_{14}]^{2-}$ ions seems to be significant (Fig. 3). The basic packing unit includes two $[\text{SbPc}]^+$ macrocycles associated by an inversion centre and an $[\text{Sb}_4\text{I}_{14}]^{2-}$ counter-ion. The central Sb1 atom of the $[\text{SbPc}]^+$ cation interacts strongly with atom I4 and weakly with two other I atoms (I1 and I7). In the crystal structure, the pairs of $[\text{SbPc}]^+$ metallomacrocycles related by the inversion centre are separated by 14.15 Å (N_4 -isoindole $\cdots\text{N}_4$ -isoindole distance), covering two sides of the $[\text{Sb}_4\text{I}_{14}]^{2-}$ counter-ion (one SbPc covered on the side of atoms I4/I7/I1ⁱ and the other on the side of atoms I1/I4ⁱ/I7ⁱ) [symmetry code (i) is as in Fig. 2].

The asymmetric distortion of the Pc macrocycle of $[\text{SbPc}]^+$ from the N_4 -isoindole plane and the deviation from C_{4v} symmetry mentioned above can be understood by taking into account the interaction of the central positively charged atom Sb1 with the $[\text{Sb}_4\text{I}_{14}]^{2-}$ counter-ion, as well as the interaction of the π -cloud of the phthalocyaninato macrocycle with the I atoms of the $[\text{Sb}_4\text{I}_{14}]^{2-}$ anion.

The centrosymmetric $\{[\text{SbPc}]^+\cdots[\text{Sb}_4\text{I}_{14}]^{2-}\cdots[\text{SbPc}]^+\}$ aggregates in the crystal structure form stacks, with $\pi-\pi$ interactions between adjacent back-to-back oriented pairs of Pc macrocycles. The interplanar N_4 -isoindole $\cdots\text{N}_4$ -isoindole distance within the stack is 3.45 Å, indicating a $\pi-\pi$ inter-

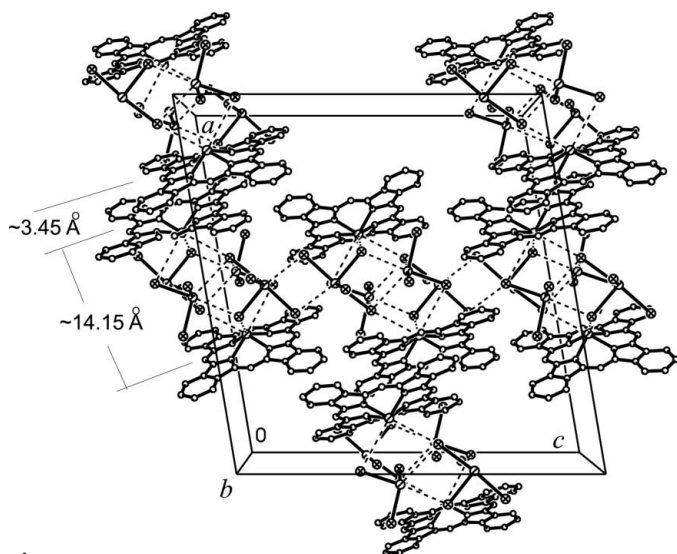


Figure 3
The molecular packing in the unit cell, showing the Sb...I interactions (dashed lines).

action. Strong π - π interactions are a common feature in the structures of phthalocyanine and its metal complexes, determining their crystal architectures.

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 473 K. Compound (I) is not soluble in polar solvents such as H_2O , CH_3OH and $\text{C}_2\text{H}_5\text{OH}$. It is only sparingly soluble in pyridine, dimethylformamide, dimethyl sulfoxide and related solvents. The electrical conductivity of (I), measured on a single crystal along the stacking direction of the $\{[\text{SbPc}]^+ \cdots [\text{Sb}_4\text{I}_{14}]^{2-} \cdots [\text{SbPc}]^+\}$ aggregates (the a axis), as well as along the c axis, exhibits non-metallic character ($d\sigma/dT > 0$). At room temperature, the conductivity is $2.4\text{--}4.2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ (along the a axis) and $6.8\text{--}8.2 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ (along the c axis).

Crystal data

$[\text{Sb}(\text{C}_{32}\text{H}_{16}\text{N}_8)]_2[\text{Sb}_4\text{I}_{14}]$
 $M_r = 3532.16$
 Monoclinic, $C2/c$
 $a = 25.179$ (4) Å
 $b = 13.822$ (3) Å
 $c = 24.112$ (4) Å
 $\beta = 99.58$ (1)°
 $V = 8275$ (3) Å³
 $Z = 4$
 $D_x = 2.835 \text{ Mg m}^{-3}$
 $D_m = 2.83 \text{ Mg m}^{-3}$

D_m measured by flotation in a mixture of CHCl_3 and CHBr_3
 Mo $K\alpha$ radiation
 Cell parameters from 2852 reflections
 $\theta = 3.4\text{--}27.8^\circ$
 $\mu = 7.20 \text{ mm}^{-1}$
 $T = 295$ (2) K
 Prism, black-violet
 $0.32 \times 0.16 \times 0.12 \text{ mm}$

Data collection

Kuma KM-4 diffractometer with CCD area detector
 ω scans
 Absorption correction: analytical (face-indexed; *SHELXTL*, Sheldrick, 1990)
 $T_{\min} = 0.215$, $T_{\max} = 0.486$
 34609 measured reflections

9652 independent reflections
 6039 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\text{max}} = 27.8^\circ$
 $h = -32 \rightarrow 27$
 $k = -18 \rightarrow 18$
 $l = -31 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.109$
 $S = 1.00$
 9652 reflections
 451 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0578P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.45 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.09 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Sb2—I3	2.7385 (10)	Sb3—I1	3.4363 (9)
Sb2—I1	2.8479 (8)	Sb3—I4	3.712 (1)
Sb2—I2	2.9079 (8)	Sb3—I4 ⁱ	3.358 (1)
Sb2—I4	3.1966 (8)	Sb1—N1	2.172 (5)
Sb2—I7 ⁱ	3.658 (1)	Sb1—N3	2.181 (6)
Sb3—I5	2.7655 (8)	Sb1—N5	2.188 (6)
Sb3—I6	2.7859 (10)	Sb1—N7	2.197 (5)
Sb3—I7	2.8438 (9)		
I3—Sb2—I1	94.97 (2)	I1—Sb3—I5	79.89 (2)
I3—Sb2—I2	97.39 (3)	I1—Sb3—I6	95.83 (2)
I1—Sb2—I2	88.59 (2)	I4—Sb3—I7	111.99 (2)
I3—Sb2—I4	88.25 (2)	Sb2—I1—Sb3	106.53 (2)
I1—Sb2—I4	85.55 (2)	Sb2—I4—Sb3	93.60 (2)
I2—Sb2—I4	172.21 (2)	Sb2—I4—Sb3 ⁱ	94.09 (2)
I1—Sb2—I7 ⁱ	84.93 (2)	Sb3—I4—Sb3 ⁱ	86.34 (2)
I2—Sb2—I7 ⁱ	96.11 (2)	N1—Sb1—N3	78.7 (2)
I4—Sb2—I7 ⁱ	78.28 (2)	N1—Sb1—N5	127.6 (2)
I5—Sb3—I6	94.71 (3)	N3—Sb1—N5	78.1 (2)
I5—Sb3—I7	98.16 (3)	N1—Sb1—N7	78.3 (2)
I6—Sb3—I7	93.57 (3)	N3—Sb1—N7	126.5 (2)
I1—Sb3—I4	70.13 (2)	N5—Sb1—N7	79.0 (2)

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

H atoms were positioned geometrically and treated as riding, with $\text{C—H} = 0.93$ Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The highest peak is located 0.90 Å from atom I2 and the deepest hole is 0.89 Å from atom Sb1 atom.

Data collection: *KM-4 CCD Software* (Kuma, 2001); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); 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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