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Tetrakis[phthalocyaninato(2−)-antimony(III)] hexadecaiodotetra-antimony(III)

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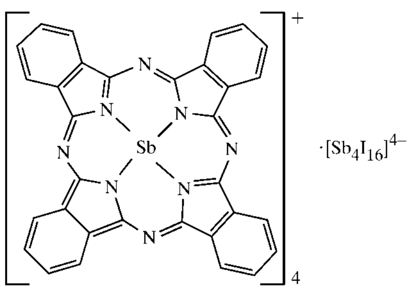
Crystals of a new antimony(III) phthalocyanine complex with the formula $[Sb(C_{32}H_{16}N_8)]_4(Sb_4I_{16})$, or $(SbPc)_4^+\cdot[Sb_4I_{16}]^{4-}$, where Pc is phthalocyaninate, have been obtained by the reaction of pure powdered antimony with phthalonitrile under a stream of iodine vapour. The crystals are built up from separate but interacting $(SbPc)^+$ cations and centrosymmetric $[Sb_4I_{16}]^{4-}$ anions. Each Sb atom of two independent $(SbPc)^+$ units is bonded to the four isoindole N atoms of the phthalocyaninate(2−) macrocycle and lies 1.0 Å out of the plane defined by four isoindole N atoms. The anionic part of the complex consists of four SbI_6 distorted octahedra joined together into a centrosymmetric $[Sb_4I_{16}]^{4-}$ anion. The arrangement of oppositely charged moieties in the crystal is mainly determined by ionic attraction and by a set of distinct donor–acceptor interactions between $(SbPc)^+$ and $[Sb_4I_{16}]^{4-}$ ions.

Comment

This study is part of an investigation on the synthesis and characterization of iodine-doped metallophthalocyanines. Earlier, we reported that besides the well characterized iodine-doped metallophthalocyanines and diphthalocyanines in which the iodine-doped atoms form chains of disordered symmetrical triiodide ions (Janczak *et al.*, 1998; Janczak, Kubiak & Jezierski, 1999; Janczak, Kubiak, Svoboda *et al.*, 2000; Janczak & Kubiak, 1999*a*; Janczak & Idemori, 2001*a*), and metallophthalocyanines in which the I atoms are directly joined to the central metal ion yielding mono- or diiodo-metallophthalocyanine complexes (Janczak & Kubiak, 1999*b*,*c*; Janczak & Idemori, 2001*b*), the I atoms can form a neutral I_2 molecule which is a bridge for the dimerization of monoiodometallophthalocyanines (Janczak, Kubiak & Hahn, 1999) or for the development of a polymeric supramolecular structure of diiodometallophthalocyanines (Janczak, Razik & Kubiak, 1999). Quite recently we reported that, depending on the synthesis conditions, iodine-doped atoms could form ordered but unsymmetrical triiodide ions (Janczak & Kubiak, 1999*d*; Kubiak *et al.*, 1999; Janczak & Idemori, 2002). The antimony(III) phthalocyanine–antimony(III) iodine complex, $[(SbPc)_4(Sb_4I_{16})]$, is isostructural with the bismuth(III) analog, $[(BiPc)_4(Bi_4I_{16})]$, (Kubiak & Ejsmont, 1999) and to our knowledge it is the second structurally characterized phthalocyaninato compound which contain the same metal in both ionic parts of the complex, *i.e.* in $(SbPc)^+$ as well as in $[Sb_4I_{16}]^{4-}$.

The crystal of the title complex, (I), is built up from separate but interacting units of $(SbPc)^+$ and $[Sb_4I_{16}]^{4-}$ (Fig. 1). The two crystallographically independent $(SbPc)^+$ cation units have essentially the same geometry. In both SbPc cation moieties, each of the phthalocyaninate(2−) macrocycles shows a saucer-shaped form, as a result of the interaction of the central Sb^{III} ion with the oppositely charged $[Sb_4I_{16}]^{4-}$ unit. The greatest deviation from the planes defined by the four isoindole N atoms of the Pc macrocycles is observed for the outermost C atoms of phenyl rings C26–C31 [0.157 (3)–0.464 (3) Å] and C34–C39 [0.286 (3)–0.634 (3) Å] for the Sb1Pc and Sb2Pc units, respectively. The positively charged Sb1 and Sb2 atoms are significantly displaced from the N_4-isoindole planes towards the I atoms of the $[Sb_4I_{16}]^{4-}$ counter-ion. The displacements of Sb1 and Sb2 are almost equal, *viz.* 0.999 (3) and 1.010 (3) Å for Sb1 and Sb2, respectively. This is quite reasonable because the large ionic radius of antimony(III) (about 0.90 Å) prevents it fitting inside the cavity of the phthalocyaninate(2−) macrocycle (Shannon, 1976), in addition to the ionic attraction between the positively charged Sb^{III} atoms with I atoms of $[Sb_4I_{16}]^{4-}$. The influence of the interaction is clearly manifested in the $Sb-N_{isoindole}$ coordination leading to the molecular symmetry of the Sb—N core being close to C_s and not to C_{4v}. A similar deviation of the antimony(III) ion from the N_4-isoindole plane has been observed in other iodine-doped antimony(III) monophthalocyaninate complexes (Kubiak & Razik, 1998; Kubiak *et al.*, 1999). However, in diphthalocyaninato(2−)antimony(III) complexes, in which the Sb^{III} atom is sandwiched between two phthalocyaninate macrocycles, the displacement of Sb^{III} (about 1.45 Å) is mainly determined by the Pc–Pc interaction of the $SbPc_2$ units, for instance, in $(n\text{-}Bu_4N)[Sb^{III}Pc_2]\cdot 2THF$ and $(PNP)_2[Sb^{III}Pc_2]Br\cdot 2Et_2O$, which are the two sandwich-type antimony(III) diphthalocyaninate(2−) complexes that have been recently structurally characterized (Hückstädt *et al.*, 2001). For a comparison, the deviation of the Bi^{III} cation from



(I)

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the N_4-isoindole plane in the isostructural Bi^{III} analog complex is 1.137 (7) Å (Kubiak & Ejsmont, 1999). The difference between the displacement of the Sb^{III} and Bi^{III} cations from the N_4 planes of the Pc macro-rings is consistent with the difference between their ionic radii (Shannon, 1976).

The anionic part of the complex consists of four deformed SbI_6 octahedra joined together into a centrosymmetric $[Sb_4I_{16}]^{4-}$ counter-ion. The Sb—I bond lengths fall into two groups: shorter Sb—I bonds with the iodine terminal and longer with the iodine bridging. However, in the $[Sb_4I_{16}]^{4-}$ anionic complex, two different bridging I atoms exist. The I2 and I3 atoms bridge two Sb ions, while I1 is a bridge for the three Sb ions. The distortion of the SbI_6 polyhedron from O_h symmetry is likely to be due to the electron lone pair on the Sb ion. Looking in more detail at the differences between the Sb—I bond lengths, as well as at the coordination geometry around the Sb3 and Sb4 atoms (and symmetrically equivalents), it is clear that they have different coordinations. The Sb3 atom joins five I atoms with relatively short Sb—I bonds, the sixth Sb—I bond length being relatively long. In the coordination sphere of the second Sb atom, Sb4, three short Sb—I bonds and three relatively long Sb—I bonds are observed. In conclusion, it could be said that the $[Sb_4I_{16}]^{4-}$ counter-ion is composed from two pairs of symmetrically equivalent units: $[SbI_5]^{2-}$ and $[SbI_3]$. The Sb3 atom in the $[SbI_5]^{2-}$ ion has distorted square-pyramidal coordination, four I atoms in a plane (I1, I2, I3 and I4) and one apical I5 atom. The relatively long Sb3—I1^i bond in a *trans* position to the apical I atom indicates the stereochemical effect of the electron lone pair. In the coordination sphere of the Sb4 atom, it is not clear in which direction the electron lone pair points, since the three relatively long Sb—I bond lengths are very similar. However, the mutual orientation of both $[SbI_5]^{2-}$ and SbI_3 units related by an inversion centre in the crystal leads to the formation of an $[Sb_4I_{16}]^{4-}$ counter-ion. A similar pattern of short and long M—I bond lengths is observed in the $[Bi_4I_{16}]^{4-}$ ion of the bismuth(III) phthalocyaninate analog complex, but no comment was made on this fact (Kubiak & Ejsmont, 1999).

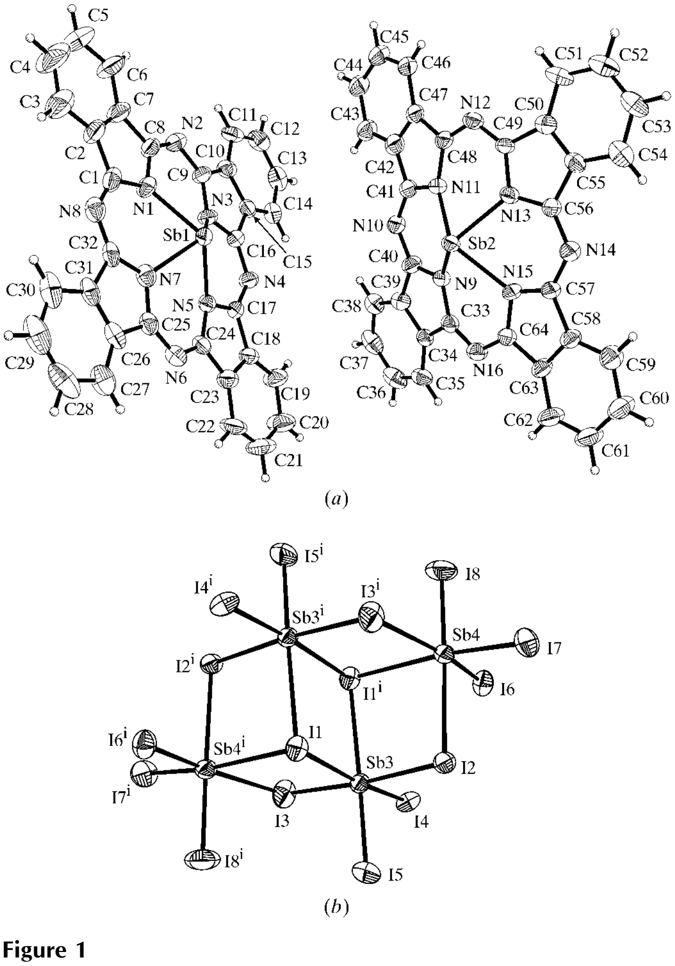

Figure 1
The molecular structure of (*a*) the two independent $SbPc^+$ units and (*b*) the $[Sb_4I_{16}]^{4-}$ counter-ion [symmetry code: (i) $1-x$, $1-y$, $-z$]. Ellipsoids show 50% probability displacement and H atoms are shown as spheres of an arbitrary radius.

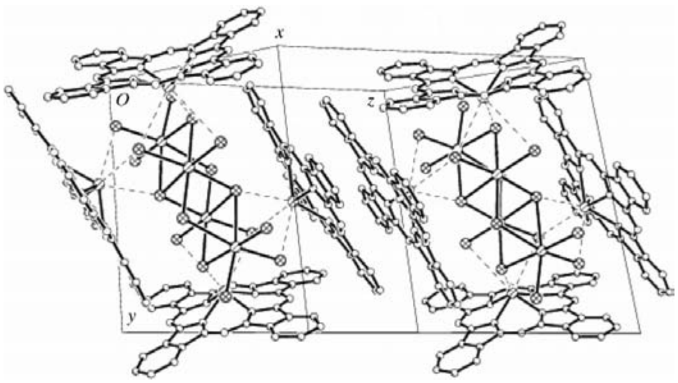

Figure 2
The molecular packing in the unit cell showing the Sb···I interactions (dashed lines).

In the unit cell (Fig. 2), there seems to be significant ionic attraction between the $(SbPc)^+$ and $[Sb_4I_{16}]^{4-}$ counter-ions. Each $[Sb_4I_{16}]^{4-}$ anion is surrounded by four $(SbPc)^+$ units. The Sb1 and Sb2 atoms of the $(SbPc)^+$ moieties interact with three I atoms of $[Sb_4I_{16}]^{4-}$ (Sb1 with I4, I6 and I1, and Sb2 with I2, I4 and I5), since the Sb···I contacts are shorter than 4.35 Å from the Sb atoms, that value being the sum of the van der Waals radii of Sb and I (Pauling, 1960). The dihedral angle between mean planes through the Pc macrocycle of the $(Sb1Pc)^+$ and $(Sb2Pc)^+$ units is 106.4°. The centrosymmetric $[(SbPc)_4(Sb_4I_{16})]$ aggregates in the crystal form π–π-interacted stacks in a back-to-back manner of the Pc macrocycle. The back-to-back distance in the stack of two neighbouring $[(SbPc)_4(Sb_4I_{16})]$ molecules is shorter than 3.0 Å. This value indicates the interaction and overlapping of the π clouds of the phthalocyaninate macrocycle. The π–π intermolecular interaction is a common feature in the field of phthalocyanine chemistry, since the phthalocyanine and its metal complexes tend to aggregate the molecules to each other due to the strong π–π interaction (Nevin *et al.*, 1987; Terekhov *et al.*, 1996; Isago *et al.*, 1997, 1998).

Although the crystals of $[(SbPc)_4(Sb_4I_{16})]$ are built up from oppositely charged $(SbPc)^+$ and $(Sb_4I_{16})^{4-}$ ions, the compound does not possess the characteristic properties of ionic crystals.

The solubility of this compound in the polar solvents, water, methanol, ethanol *etc.*, is insignificant and it is slightly soluble in pyridine, DMSO, THF and chloronaphthalene. As can be seen from the crystal structure architecture of $[(\mathrm{SbPc})_4(\mathrm{Sb}_4\mathrm{I}_{16})]$ that both hydrophilic parts of this complex in the crystal are surrounded by the hydrophobic peripheral phenyl rings of the Pc macrocycle.

Experimental

Crystals of $[(\mathrm{SbPc})_4(\mathrm{Sb}_4\mathrm{I}_{16})]$ were obtained by the direct reaction of pure powdered antimony with phthalonitrile (Kubiak & Janczak, 1993) under a stream of iodine vapour at 513 K.

Crystal data

$[\mathrm{Sb}(\mathrm{C}_{32}\mathrm{H}_{16}\mathrm{N}_8)]_4[\mathrm{Sb}_4\mathrm{I}_{16}]$
$M_r = 5054.62$
Triclinic, $P\bar{1}$
$a = 15.963\ (3)$ Å
$b = 16.051\ (3)$ Å
$c = 16.552\ (3)$ Å
$\alpha = 88.59\ (3)^\circ$
$\beta = 62.54\ (3)^\circ$
$\gamma = 69.16\ (3)^\circ$
$V = 3466.9\ (11)$ Å^3
$Z = 1$

$D_x = 2.421$ Mg m^{-3}
$D_m = 2.42$ Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
Cell parameters from 10 265 reflections
$\theta = 3$–27°
$\mu = 5.16$ mm^{-1}
$T = 293\ (2)$ K
Parallelepiped, dark violet
$0.20 \times 0.12 \times 0.08$ mm

Data collection

Kuma KM-4 with two-dimensional area CCD detector
ω scans
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 1990)
$T_{\min} = 0.425$, $T_{\max} = 0.683$
29 594 measured reflections

14 695 independent reflections
10 265 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.026$
$\theta_{\max} = 27.2^\circ$
$h = -20 \rightarrow 17$
$k = -20 \rightarrow 20$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.079$
$S = 1.01$
14695 reflections
829 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.0131P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 1.21$ e Å^{-3}
$\Delta\rho_{\min} = -1.17$ e Å^{-3}

The ω-scan technique was used, with $\Delta\omega = 0.75^\circ$ for one image. The 960 images for six different runs covered about 95% of the Ewald sphere. The lattice parameters were calculated using 458 reflections obtained from 50 images for 10 runs with different orientations in reciprocal space and after data collection were refined on 10 265 reflections.

Data collection: *KM*-4 *CCD Software* (Kuma, 1999); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1539). Services for accessing these data are described at the back of the journal.

Table 1
Selected geometric parameters (Å, °).

Sb3—I1	3.179 (1)	Sb1—N7	2.189 (4)
Sb3—I2	3.046 (1)	Sb1—N3	2.191 (4)
Sb3—I3	2.984 (1)	Sb1—N5	2.209 (4)
Sb3—I4	2.957 (1)	Sb1—I4	3.653 (1)
Sb3—I5	2.834 (1)	Sb1—I6	3.729 (1)
Sb3—I1$^{\mathrm{i}}$	3.400 (1)	Sb1—I1$^{\mathrm{i}}$	3.546 (1)
Sb4—I6	2.849 (1)	Sb2—N11	2.185 (4)
Sb4—I7	2.814 (1)	Sb2—N13	2.189 (4)
Sb4—I8	2.779 (1)	Sb2—N9	2.212 (4)
Sb4—I2	3.354 (1)	Sb2—N15	2.217 (4)
Sb4—I1$^{\mathrm{i}}$	3.362 (1)	Sb2—I2	3.5426 (9)
Sb4—I3$^{\mathrm{i}}$	3.3705 (9)	Sb2—I4	3.548 (1)
Sb1—N1	2.181 (4)	Sb2—I5	3.918 (1)

I1—Sb3—I3	88.53 (4)	I7—Sb4—I3$^{\mathrm{i}}$	94.86 (4)
I1—Sb3—I2	90.36 (4)	I8—Sb4—I1$^{\mathrm{i}}$	92.25 (4)
I1—Sb3—I5	95.39 (4)	I8—Sb4—I3$^{\mathrm{i}}$	87.32 (4)
I1—Sb3—I4	172.56 (2)	Sb3—I2—Sb4	96.53 (3)
I1—Sb3—I1$^{\mathrm{i}}$	77.15 (4)	Sb3—I1—Sb4$^{\mathrm{i}}$	94.08 (4)
I2—Sb3—I1$^{\mathrm{i}}$	88.77 (3)	Sb3—I3—Sb4$^{\mathrm{i}}$	97.61 (4)
I2—Sb3—I3	175.08 (2)	N1—Sb1—N7	78.7 (2)
I2—Sb3—I4	91.79 (4)	N1—Sb1—N3	78.0 (2)
I2—Sb3—I5	87.81 (3)	N7—Sb1—N3	126.6 (2)
I3—Sb3—I4	88.73 (4)	N1—Sb1—N5	125.0 (2)
I3—Sb3—I5	97.06 (3)	N7—Sb1—N5	77.3 (2)
I4—Sb3—I5	91.81 (4)	N3—Sb1—N5	78.0 (2)
I6—Sb4—I7	96.70 (4)	N11—Sb2—N13	77.7 (2)
I6—Sb4—I8	91.32 (4)	N11—Sb2—N9	78.0 (2)
I6—Sb4—I1$^{\mathrm{i}}$	89.12 (4)	N13—Sb2—N9	124.4 (2)
I6—Sb4—I2$^{\mathrm{i}}$	113.17 (4)	N11—Sb2—N15	126.4 (2)
I6—Sb4—I3$^{\mathrm{i}}$	168.44 (2)	N13—Sb2—N15	78.3 (2)
I7—Sb4—I8	96.66 (4)	N9—Sb2—N15	77.4 (2)

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

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