metal-organic compounds

Bis{[phthalocyaninato(2−)]-arsenic(III)} tetradecaiodotetra-arsenic(III)

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Crystals of the novel title arsenic(III) phthalocyanine complex, $[As(C_{32}H_{16}N_8)]_2[As_4I_{14}]$ or $[(AsPc)^+]_2 \cdot [As_4I_{14}]^{2-}$, where Pc is phthalocyaninate(2−), have been obtained by the reaction of pure powdered As with phthalonitrile under a stream of iodine vapour at 493 K. The crystals are built up of separate but interacting $[AsPc]^+$ cations and $[As_4I_{12}]^{2-}$ anions. The As atom of the $[AsPc]^+$ unit is bonded to the four isoindole N atoms of the Pc macrocycle and lies 0.743 (2) Å out of the plane defined by these four N atoms. The anionic part of the complex consists of AsI_3 and $[AsI_4]^-$ units joined together into an $[As_4I_{14}]^{2-}$ anion. The arrangement of the oppositely charged moieties, $[AsPc]^+$ and $[As_4I_{14}]^{2-}$, in the crystal is determined mainly by ionic attraction and by donor–acceptor interactions between the $[AsPc]^+$ and $[As_4I_{14}]^{2-}$ ions.

Comment

The present study is a continuation of our investigation of the synthesis and characterization of iodine-doped metallophthalocyanines. Earlier, we reported that, besides the well characterized I-doped metallophthalocyanines and diphthalocyanines, in which the I atoms form chains of disordered symmetrical triiodide ions (Janczak *et al.*, 1998, 2000; Janczak, Kubiak & Jezierski, 1999; Janczak & Kubiak, 1999a; Janczak & Idemori, 2001a), and metallophthalocyanines in which the I atoms are directly joined to the central metal ion, yielding mono- or diiodometallophthalocyanine complexes (Janczak & Kubiak, 1999b,c; Janczak & Idemori, 2001b), the I atoms can form a neutral I_2 molecule, which acts as a bridge for the dimerization of monoiodometallophthalocyanines (Janczak, Kubiak & Hahn, 1999) or for developing a polymeric supramolecular diiodometallophthalocyanine structure (Janczak, Razik & Kubiak, 1999; Janczak & Idemori, 2002a). More recently, we reported that, depending on the conditions of the synthesis, the I atoms could form ordered but unsymmetrical triiodide ions (Janczak & Kubiak, 1999d; Kubiak, Janczak &

Razik, 1999; Janczak & Idemori, 2002b). The title phthalocyanine–As^{III} iodine complex, (I), is unique and, to our knowledge, together with the two isostructural complexes of $[(SbPc)_4(Sb_4I_{16})]$ (Janczak & Idemori, 2002c) and $[(BiPc)_4(Bi_4I_{16})]$ (Kubiak & Ejsmont, 1999), it is only the third structurally characterized phthalocyaninate compound containing the same metal in both ionic parts of the complex, *i.e.* in the $[AsPc]^+$ moiety as well as in the $[As_4I_{14}]^{2-}$ moiety.

(I)
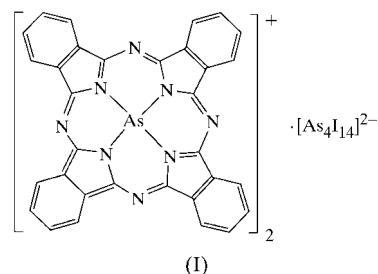
The crystal of (I) is built up of separate but interacting $[AsPc]^+$ and $[As_4I_{14}]^{2-}$ units (Fig. 1). The phthalocyaninate(2−) macrocyclic ring of the AsPc moiety is saucer-shaped, as a result of the interaction of the central As^{III} ion with the oppositely charged $[As_4I_{14}]^{2-}$ counter-ion. The greatest deviations from the plane defined by the four iso-indole N atoms of the phthalocyaninate(2−) macrocycle are observed for the C atoms of the phenyl rings: 0.039 (3)–0.219 (3) Å for C2–C7, 0.124 (3)–0.377 (3) Å for C10–C15, 0.061 (3)–0.228 (3) Å for C18–C23 and 0.103 (3)–0.377 (3) Å for C26–C31. The positively charged As^{III} atom, which is coordinated by the four isoindole N atoms, is significantly displaced from the N_4-isoindole plane [0.743 (3) Å] towards atom I3 of the $[As_4I_{14}]^{2-}$ counter-ion.

The displacement of the As^{III} atom from the N_4-isoindole plane is comparable with that observed in [phthalocyaninato(2−)]arsenic(III) triiodide [0.757 (2) Å; Janczak & Idemori, 2002b]. In Sb^{III}–phthalocyanine iodine (Kubiak & Razik, 1998), Sb^{III}–phthalocyanine triiodide (Kubiak, Janczak & Razik, 1999) and the phthalocyanine–Sb^{III} iodine complex (Janczak & Idemori, 2002c), the displacement of the central Sb atom from the N_4-isoindole plane is about 0.22 Å greater than that observed for the As atom in As^{III}–phthalocyaninate(2−) complexes. This is quite reasonable, because of the difference between the ionic radii of As^{III} and Sb^{III} (Shannon, 1976), as well as because of the ionic attraction between the positively charged central As^{III} atom of the [AsPc] unit with the oppositely charged atom I3 of the $[As_4I_{14}]^{2-}$ counter-ion.

A similar interaction between the positively charged central atom and I exists in the Sb–phthalocyaninate structures. The influence of the As···I interaction is clearly manifested in the As—N coordination, leading to the molecular symmetry of the As—N_4 core being close to C_s and not to C_{4v}, which is consistent with the fully optimized *ab initio* molecular geometry calculations performed for the isolated and non-interacting $[AsPc]^+$ cation (Janczak, 2002), which corresponds to the conformation in solution. The displacement of the As atom from the N_4 plane is significantly greater [0.975 (3) Å] in the unique example of a partially oxidized I-doped As^{III}

phthalocyaninate–metal-free phthalocyanine complex (Janczak, Kubiak & Jezierski, 1999), due to the location of As between the two phthalocyanine rings.

The anionic part of (I), *viz.* $[As_4I_{14}]^{2-}$, consists of two deformed AsI_6 octahedra joined together by two bridging I atoms and two deformed AsI_5 square pyramids, that are linked to the AsI_6 octahedra to form the centrosymmetric $[As_4I_{14}]^{2-}$ counter-ion. The As—I bond lengths fall into two groups, namely shorter As—I bonds, which show that the $[As_4I_{14}]^{2-}$ counter-ion consists of two pairs of AsI_3 and AsI_4 units, and longer As—I bonds, with the I bridging atoms. The distortion of the two joined AsI_6 octahedra and the two AsI_5 square pyramidal polyhedra in the $[As_4I_{14}]^{2-}$ anion is likely to be due to the lone electron pair on the As^{III} atom. This is in agreement with the steric effect of a lone electron pair predicted by the valence-shell electron-pair repulsion model (VSEPR; Gillespie, 1963, 1992).

Looking in more detail at the differences in the As—I bond lengths, as well as in the coordination geometry around atoms As2 and As3, it is clear that they have different coordinations. Atom As2 joins to three I atoms with relatively short As—I bonds, and to two I atoms with significantly longer As—I bonds, resulting in a square-pyramidal coordination environment. Atom As3 joins to four I atoms with short As—I bonds and to two with longer As—I bonds. The longer As—I bonds
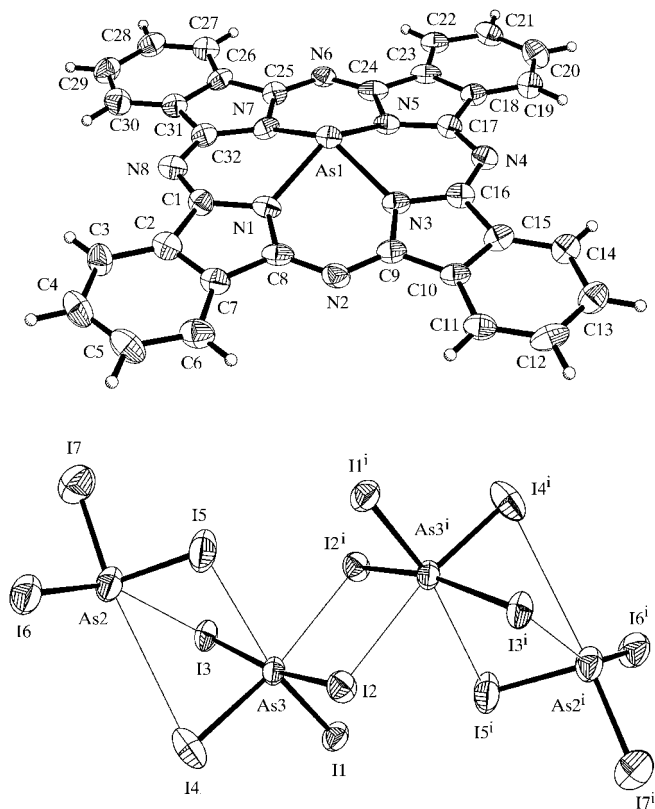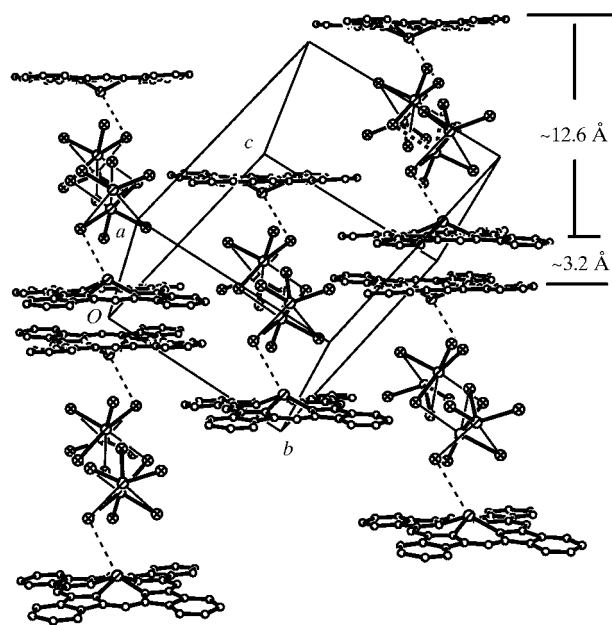
Figure 2
The molecular packing in the unit cell of (I), showing the As···I interactions (dashed lines).

involve the I atoms that are linked to two As atoms, while the shorter bonds involve mainly terminal I atoms. A similar pattern of short and long M—I bonds is observed in the $[Bi_4I_{16}]^{4-}$ and $[Sb_4I_{16}]^{-}$ counter-ions of the two isostructural Bi and Sb phthalocyaninate complexes (Kubiak & Ejsmont, 1999; Janczak & Idemori, 2002c). Alternatively, the $[As_4I_{14}]^{2-}$ anion can be regarded as composed of two pairs of symmetrically equivalent AsI_3 and AsI_4^{-} units. However, the mutual orientation and arrangement of both AsI_3 and AsI_4^{-} units related by an inversion centre in the crystal leads to the formation of an $[As_4I_{14}]^{2-}$ moiety.

The ionic attraction between the $[AsPc]^{+}$ and $[As_4I_{14}]^{2-}$ ions seems to be significant (Fig. 2). The basic packing unit includes two $[AsPc]^{+}$ macrocycles associated by an inversion centre and an $[As_4I_{14}]^{2-}$ ion. The central As1 atom of the AsPc moiety interacts with atom I3, since the As···I contact of 3.801 (3) Å is shorter than the sum of the van der Waals radii of As and I atoms (Pauling, 1960). In the crystal (Fig. 2), pairs of $[AsPc]^{+}$ macrocycles related by inversion are separated by 12.580 (5) Å (N_4-isoindole···N_4-isoindole distance). The centrosymmetric $[(AsPc)(As_4I_{14})(AsPc)]$ aggregates in the crystal form π–π interactions between adjacent pairs of Pc macrocycles. The stacks are inclined by 23.00 (3), 52.65 (3) and 43.83 (3)° to the *a*, *b* and *c* axes, respectively. The interplanar distance within the stack is 3.203 (5) Å. Strong π–π interactions are a common feature in the structures of phthalocyanine and its metal complexes (Nevin *et al.*, 1987; Terekhov *et al.*, 1996; Isago *et al.*, 1997, 1998).

The electrical conductivity of (I), measured on a single crystal along the stack, exhibits non-metallic character ($d\sigma/dT > 0$). At room temperature, the conductivity is 4.5–5 × 10^{-6} Ω^{-1} cm^{-1}.

Figure 1
A view of the molecular structure of (*a*) the $[AsPc]^{+}$ unit and (*b*) the $[Ab_4I_{14}]^{2-}$ counter-ion of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii [symmetry code: (i) $-x$, $1 - y$, $1 - z$].

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Although the crystal of (I) is built up from oppositely charged $[AsPc]^+$ and $[As_4I_{14}]^{2-}$ moieties, the compound does not possess the characteristic properties of ionic crystals. The solubility of this compound in polar solvents, such as water, methanol or ethanol, is insignificant, and it is only slightly soluble in pyridine, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, chloronaphthalene and other aromatic solvents. A search of the Cambridge Structural Database (Version 5.24; Allen, 2002) for structures containing both $[MPc]^+$ and $[M_4I_{14}]^{2-}$ units showed no similar examples of phthalocyaninate complexes, so the title As–phthalocyaninate complex is the first of this type to be structurally characterized.

Experimental

Crystals of (I) were obtained by the direct reaction of pure powdered arsenic with phthalonitrile (Kubiak & Janczak, 1993) under a stream of iodine vapour at 493 K.

Crystal data

$[As(C_{32}H_{16}N_8)]_2[As_4I_{14}]$
$M_r = 3251.18$
Triclinic, $P\bar{1}$
$a = 12.081 (2)$ Å
$b = 12.600 (2)$ Å
$c = 13.950 (3)$ Å
$\alpha = 82.32 (3)°$
$\beta = 71.63 (3)°$
$\gamma = 83.05 (3)°$
$V = 1990.2 (7)$ Å^3
$Z = 1$
$D_x = 2.713$ Mg m^{-3}

$D_m = 2.71$ Mg m^{-3}
D_m measured by flotation in a mixture of CHBr$_3$ and CHCl$_3$
Mo $K\alpha$ radiation
Cell parameters from 6210 reflections
$\theta = 3.3–26.7°$
$\mu = 7.97$ mm^{-1}
$T = 293 (2)$ K
Parallelepiped, black–violet
$0.44 \times 0.15 \times 0.14$ mm

Data collection

Kuma KM-4 diffractometer with a two-dimensional CCD area detector
ω scans
Absorption correction: analytical face-indexed (SHELXTL-Plus; Sheldrick, 1990)
$T_{min} = 0.127$, $T_{max} = 0.402$

15 578 measured reflections
8037 independent reflections
6210 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 26.7°$
$h = -12 \rightarrow 15$
$k = -15 \rightarrow 15$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.057$
$S = 1.00$
8037 reflections
452 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.60$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}
Extinction correction: SHELXL97 (Sheldrick, 1997)
Extinction coefficient: 0.00059 (6)

H atoms were treated as riding, with a C—H distance of 0.93 Å.

Data collection: KM-4 CCD Software (Kuma Diffraction, 1999); 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-Plus (Sheldrick, 1990); software used to prepare material for publication: SHELXL97.

Table 1
Selected geometric parameters (Å, °).

I1—As3	2.5963 (7)	As1—N5	2.039 (3)
I2—As3	2.8133 (10)	As1—N3	2.068 (3)
I3—As3	2.9182 (11)	As1—N1	2.073 (3)
I4—As3	2.6742 (8)	As1—I3	3.8004 (13)
I5—As2	2.5533 (12)	As2—I3	3.7011 (10)
I6—As2	2.5868 (9)	As2—I4	4.1238 (15)
I7—As2	2.5816 (12)	As3—I5	3.5590 (10)
As1—N7	2.028 (3)	As3—I2^i	3.1964 (9)
N7—As1—N5	83.18 (12)	I4—As3—I3	90.53 (4)
N7—As1—N3	137.15 (11)	I2—As3—I3	168.59 (2)
N5—As1—N3	82.03 (11)	I1—As3—I5	168.89 (2)
N7—As1—N1	82.21 (12)	I1—As3—I2^i	90.83 (3)
N5—As1—N1	137.90 (11)	I3—As2—I6	155.07 (2)
N3—As1—N1	82.43 (12)	I3—As2—I7	103.73 (3)
N1—As1—I3	113.51 (9)	I3—As2—I5	88.36 (3)
N3—As1—I3	149.95 (8)	I3—As2—I4	60.80 (3)
N5—As1—I3	99.02 (8)	I4—As2—I6	96.74 (3)
N7—As1—I3	72.21 (8)	I4—As2—I7	164.53 (2)
I5—As2—I7	99.50 (4)	I4—As2—I5	81.16 (3)
I5—As2—I6	99.29 (3)	I2—As3—I2^i	86.47 (3)
I7—As2—I6	98.39 (3)	As1—I3—As3	110.72 (3)
I1—As3—I4	99.68 (3)	As2—I3—As3	78.83 (2)
I1—As3—I2	95.52 (3)	As2—I4—As3	73.87 (3)
I4—As3—I2	92.79 (4)	As2—I5—As3	86.36 (3)
I1—As3—I3	94.68 (3)		

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

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