

[Phthalocyaninato(2-)]arsenic(III) triiodide

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Key indicators

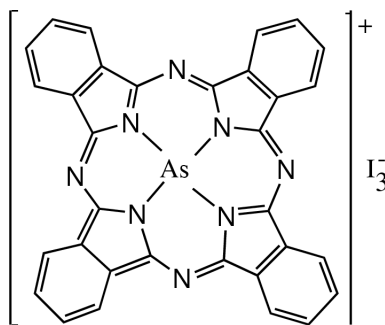
Single-crystal X-ray study
T = 295 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.048
wR factor = 0.041
Data-to-parameter ratio = 18.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

A new arsenic(III) phthalocyanine complex with the formula $[\text{As}(\text{C}_{32}\text{H}_{16}\text{N}_8)]\text{I}_3$, or AsPcI_3 ($\text{Pc} = \text{C}_{32}\text{H}_{16}\text{N}_8$), has been obtained by the reaction of pure powdered arsenic with phthalonitrile under a stream of iodine vapor. The four-coordinate As atom is bonded to the four isoindole N atoms of the phthalocyaninato(2-) macro-ring and lies significantly out of the plane defined by the four isoindole N atoms [0.757 (2) Å]. The I atoms form linear asymmetric triiodide I_3^- ions. In the crystal, the I_3^- ions related by an inversion center form $(\text{I}-\text{I}-\text{I} \cdots \text{I}-\text{I}-\text{I})^{2-}$ ions.

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Comment

The crystal of the title compound, (I), is built up from separate but interacting units of $(\text{AsPc})^+$ and I_3^- (Fig. 1). The arsenic phthalocyaninate unit is not planar, since in the crystal it interacts with the oppositely charged I_3^- ion. This interaction leads to the deviation of the arsenic cation from the phthalocyaninato(2-) macro-ring towards the I_3^- ion. The deviation of the arsenic cation from the weighted least-squares plane through the four isoindole N atoms is 0.757 (2) Å. For comparison, the deviation of the Sb^{3+} cation from the N_4 -isoindole plane in isostructural SbPcI_3 is 0.966 (2) Å (Kubiak *et al.*, 1999). The difference between the displacements of the central metal cations (As^{3+} and Sb^{3+}) correlates well with the difference between their ionic radii (Shannon, 1976).



(I)

The interaction of the arsenic cation with the I_3^- ion leads to the deformation of the phthalocyaninate macro-ring into a saucer-shaped form. The influence of the $\text{As} \cdots \text{I}$ interactions is manifested in the $\text{As}-\text{N}(\text{isoindole})$ coordination. The four $\text{As}-\text{N}(\text{isoindole})$ bonds are more asymmetrical and a little longer (0.03–0.06 Å) than the $\text{Sb}-\text{N}(\text{isoindole})$ bonds in SbPcI_3 (Kubiak *et al.*, 1999). Thus, the molecular symmetry of the $\text{As}-\text{N}$ core is close to C_s and not to C_{4v} , which is possible for saucer-shaped $M^{\text{II}}\text{Pc}$ complexes (Friedel *et al.*, 1970; Ukei,

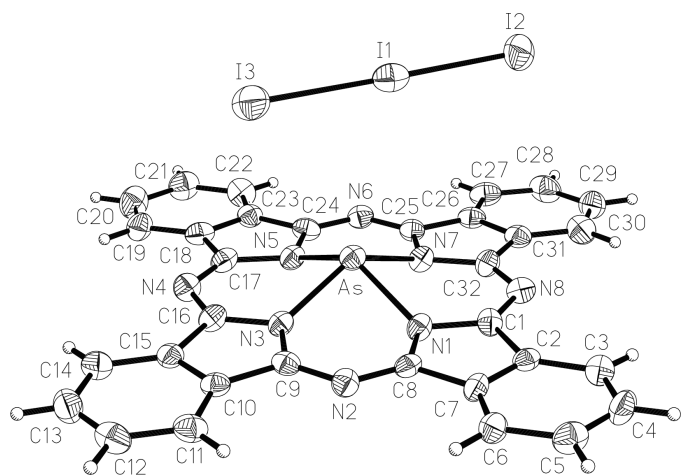


Figure 1
The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

1973; Iyechika *et al.*, 1982). The largest deviation from the N_4 -isoindole plane is observed for the outermost C atoms of the phenyl rings C18–C23 and C27–C31, as a result of the repulsive interaction of the delocalized π -electron system with the negatively charged I_3^- ion, which in the crystal is located close to the half of the Pc unit containing these two phenyl rings, not directly over the As atom of the AsPc cation.

As two of the three I atoms of the I_3^- ion in the crystal of $AsPcI_3$ interact with the oppositely charged central arsenic cation of the $(AsPc)^+$ unit, the I_3^- ion is asymmetric. One of the terminal I atoms (I3) of the I_3^- ion interacts more strongly than the central iodine (I1). This interaction correlates well with the charge on the I atoms (-0.419 on both terminal I atoms and -0.163 on the central I atom) calculated by Landrum *et al.* (1997). The $As \cdots I_3$ (terminal) distance is ~ 0.1 Å shorter than the distance of $As \cdots I_1$ (I1 central). The interaction (repulsive force) between two triiodide ions related by an inversion center (with an $I_2 \cdots I_2$ distance of 3.72 Å) and the $As \cdots I$ interactions (attractive force) present in the crystal are responsible for the difference of the bond lengths within the I_3^- ions and are important for stacking interactions between the ring systems. The basic packing unit includes two $(AsPc)^+$ macrocycles and two interacting I_3^- ions, but each of those two macrocycles is closely associated with another macrocycle across an inversion center. The molecules related by a screw axis and glide plane are approximately perpendicular to each other (Fig. 2). A search of the Cambridge Structural Database (Allen & Kennard, 1993) for structures containing both $(I-I-I \cdots I-I-I)^{2-}$ and MN_4 groups showed only one example with $(I-I-I \cdots I-I-I)^{2-}$, but no comment was made on the $I_3 \cdots I_3$ interaction (Kubiak *et al.*, 1999). The I–I bond lengths in the $AsPcI_3$ complex are just slightly (0.02 Å), more nearly equal than those observed in the $SbPcI_3$ complex [2.861 (2) and 2.999 (2) Å; Kubiak *et al.*, 1999]. A similar asymmetric triiodide I_3^- ion is present in the crystal of oxomolybdenum(V) phthalocyanine triiodide, but

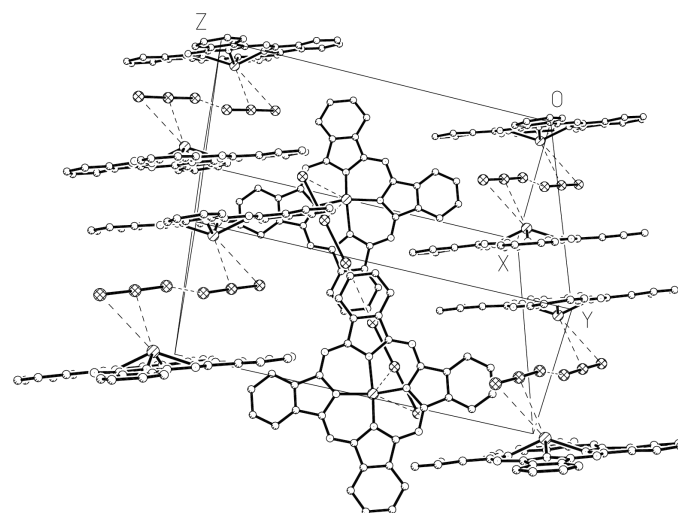


Figure 2
The molecular packing in the unit cell showing the $As \cdots I$ and $I_3^- \cdots I_3^-$ interactions (dashed lines).

the I–I distances are significantly larger [2.9737 (7) and 3.1934 (7) Å] than in the present As complex (Janczak & Kubiak, 1999).

Experimental

Crystals of $AsPcI_3$ were obtained by direct reaction of pure powdered arsenic with phthalonitrile (Kubiak & Janczak, 1993) under a stream of iodine vapor at about 493 K. At this temperature, the liquid phthalonitrile undergoes catalytic tetramerization with simultaneous transfer of two electrons from the As metal to form the Pc ring; the third electron from As is transferred to the I atoms forming an I_3^- ion.

Crystal data

$[As(C_{32}H_{16}N_8)]I_3$
 $M_r = 968.15$
 Monoclinic, $P2_1/n$
 $a = 8.652$ (2) Å
 $b = 17.558$ (4) Å
 $c = 19.668$ (4) Å
 $\beta = 95.42$ (3)°
 $V = 2974.4$ (11) Å³
 $Z = 4$
 $D_x = 2.162$ Mg m⁻³

$D_m = 2.16$ Mg m⁻³
 D_m measured by flotation
 Mo $K\alpha$ radiation
 Cell parameters from 2585 reflections
 $\theta = 5$ –26°
 $\mu = 4.30$ mm⁻¹
 $T = 295$ (2) K
 Parallelepiped, violet
 0.30 × 0.12 × 0.10 mm

Data collection

Kuma KM-4 diffractometer with CCD area detector
 ω scans
 Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990)
 $T_{min} = 0.359$, $T_{max} = 0.673$
 26611 measured reflections

7507 independent reflections
 4287 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.039$
 $\theta_{max} = 29.0^\circ$
 $h = -8 \rightarrow 11$
 $k = -23 \rightarrow 23$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.042$
 $S = 0.99$
 7507 reflections
 397 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0071P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.48$ e Å⁻³
 $\Delta\rho_{min} = -0.46$ e Å⁻³

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Table 1
Selected geometric parameters (Å, °).

I1—I2	2.8755 (7)	As—N3	2.071 (3)
I1—I3	2.9844 (7)	As—N1	2.082 (3)
As—N5	2.025 (3)	As—I1	3.7813 (9)
As—N7	2.060 (3)	As—I3	3.6948 (9)
I2—I1—I3	179.12 (2)	N5—As—N1	136.1 (1)
N5—As—N7	82.6 (1)	N7—As—N1	81.6 (1)
N5—As—N3	83.0 (1)	N3—As—N1	81.7 (1)
N7—As—N3	137.6 (1)		

Data collection: *Kuma KM-4 CCD Software* (Kuma, 2000); cell refinement: *Kuma KM-4 CCD Software*; data reduction: *Kuma 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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