

Bis[[phthalocyaninato(2-)]-
arsenic(III)] octaiododarsenic(III)Jan Janczak^{a*} and Genivaldo Júlio Perpétuo^{a,b}^aInstitute of Low Temperature and Structure Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland, and ^bDepartamento de Física, Instituto de Ciências Exatas e Biológicas, Universidade Federal de Ouro Preto, CEP 35.400-000 Ouro Preto, MG, Brazil

Correspondence e-mail: j.janczak@int.pan.wroc.pl

Received 29 November 2005

Accepted 15 December 2005

Online 14 January 2006

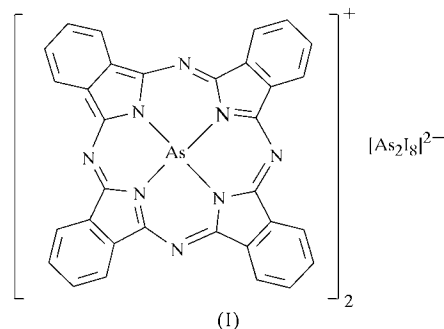
Crystals of the novel title arsenic(III)–phthalocyanine complex, $[\text{As}(\text{C}_{32}\text{H}_{16}\text{N}_8)]_2[\text{As}_2\text{I}_8]$ or $[\text{AsPc}]_2[\text{As}_2\text{I}_8]$, where Pc is the phthalocyaninate(2-) macrocycle, have been obtained from the reaction of pure powdered arsenic with phthalonitrile under oxidizing conditions (iodine vapour) at 463 K. The crystals are formed by separate but interacting $[\text{AsPc}]^+$ cations and centrosymmetric $[\text{As}_2\text{I}_8]^{2-}$ anions. The As atom of the $[\text{AsPc}]^+$ ion is bonded to the four isoindole N atoms of the Pc macrocycle and lies 0.762 (1) Å out of their plane. The anionic part of the complex consists of two $[\text{AsI}_4]^-$ units joined together into a centrosymmetric $[\text{As}_2\text{I}_8]^{2-}$ counter-ion. The arrangement of oppositely charged moieties, *viz.* $[\text{AsPc}]^+$ and $[\text{As}_2\text{I}_8]^{2-}$, in the crystal structure is determined mainly by their ionic attractions and by π – π interactions between the aromatic phthalocyaninate(2-) macrocycles.

Comment

The present study is part of an investigation of the synthesis, characterization and stereochemistry of metallophthalocyaninate complexes obtained under oxidizing conditions (iodine vapour). In the partially oxidized iodine-doped metallophthalocyanines and metallodiphthalocyanines, the I atoms form linear chains of symmetrical I_3^- ions, which are usually disordered (Janczak, Kubiak & Jezierski, 1999; Janczak & Idemori, 2001*b*) or ordered in the crystal structure (Janczak, 2003); in metallophthalocyanines, the I atoms are directly linked to the central metal ion, yielding mono- or diiodo-metallophthalocyanines (Janczak & Kubiak, 1999*a,b*; Janczak & Idemori, 2001*a*). Alternatively, the I atoms can form a neutral I_2 molecule, which acts as a bridge for dimerization (Janczak, Kubiak & Hahn, 1999; Janczak, 2004) or for developing a polymeric supramolecular structure (Janczak, Razik & Kubiak, 1999; Janczak & Idemori, 2002*c*).

Complexes of the metallophthalocyanines with group 15 metals are less well investigated. The title compound, (I), is an

example of a phthalocyaninate(2-) (Pc) complex containing the same metal in both the cation and the anion, *i.e.* $[\text{AsPc}]^+$ and $[\text{As}_2\text{I}_8]^{2-}$. A search of the Cambridge Structural Database (Version 5.24; Allen, 2002) for phthalocyaninate structures containing the same metal in both parts of the complex finds only $[(\text{SbPc})_4(\text{Sb}_4\text{I}_{16})]$ (Janczak & Idemori, 2002*a*), $[(\text{BiPc})_4(\text{Bi}_4\text{I}_{16})]$ (Kubiak & Ejsmont, 1999), $[(\text{AsPc})_2(\text{As}_4\text{I}_{14})]$ (Janczak & Kubiak, 2003) and $[(\text{SbPc})_2(\text{Sb}_4\text{I}_{14})]$ (Perpétuo & Janczak, 2005), none of which contain the $[\text{M}_2\text{I}_8]^{2-}$ ion. The present $[\text{AsPc}]_2[\text{As}_2\text{I}_8]$ structure is therefore the first example of this type of phthalocyaninate system.



The crystal structure of (I) is built up of separate but interacting $[\text{AsPc}]^+$ and $[\text{As}_2\text{I}_8]^{2-}$ units (Fig. 1). The Pc macrocycle of the $[\text{AsPc}]^+$ moiety is saucer-shaped as a result of the interaction of the central As^{III} ion with the oppositely charged $[\text{As}_2\text{I}_8]^{2-}$ counter-ion. The greatest deviations from the plane defined by the four isoindole N atoms of the macrocycle are observed for the outermost C atoms of the benzene rings, ranging from 0.074 (1) to 0.346 (1) Å for the C2–C7 ring. The positively charged As^{III} ion of the $[\text{AsPc}]^+$ cation, which is coordinated by the four isoindole N atoms, is significantly displaced from the isoindole N_4 plane [0.762 (1) Å] towards atoms I2, I3 and I4 of the $[\text{As}_2\text{I}_8]^{2-}$ anion. The $\text{As}_2 \cdots \text{I}_2^i$ [symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$], $\text{As}_2 \cdots \text{I}_4$ and $\text{As}_2 \cdots \text{I}_3$ distances of 3.5376 (9), 3.5655 (8) and 3.7941 (9) Å, respectively, are shorter than the sum of the van der Waals radii of As and I atoms (Shannon, 1976). The displacement of the As^{III} atom from the isoindole N_4 plane is comparable to that observed in both phthalocyaninato(2-)arsenic(III) triiodide [0.757 (2) Å; Janczak & Idemori, 2002*b*] and bis[phthalocyaninato(2-)arsenic(III)] tetradeca-iodotetraarsenic(III) [0.743 (3) Å; Janczak & Kubiak, 2003]. In the Sb^{III} –phthalocyanine (Kubiak & Razik, 1998), Sb^{III} –phthalocyanine triiodide (Kubiak *et al.*, 1999) and two Sb^{III} –phthalocyanine Sb^{III} –iodine complexes (Janczak & Idemori, 2002*a*; Perpétuo & Janczak, 2005), the displacement of the central Sb atom from the isoindole N_4 plane is ~ 0.25 Å greater than that observed in the As^{III} –phthalocyaninate(2-) complexes. This difference is quite reasonable because of the difference between the ionic radii of As^{III} and Sb^{III} (Shannon, 1976). The ionic attraction between the $[\text{AsPc}]^+$ and $[\text{As}_2\text{I}_8]^{2-}$ ions is clearly manifested in the As–N coordination, leading to the molecular symmetry of the AsN_4 core being close to C_s , rather than C_{4v} , which corresponds to the conformation in solution. The displacement of the As^{III} atom from the isoindole

dole N₄ plane is significantly greater in the unique example of a partially oxidized I-doped As^{III}-phthalocyaninate metal-free phthalocyanine complex [0.975 (2) Å; Janczak, Kubiak & Jezierski, 1999], as a result of the location of the As atom between the two phthalocyaninate rings.

The anionic part of (I) consists of two [AsI₄][−] moieties linked by two bridging I atoms to form the centrosymmetric [As₂I₈]^{2−} anion. The As—I bond lengths fall into two groups, namely shorter As—I bonds, which join the terminal I atoms, and longer As—I bonds, involving the bridging I atoms. Thus, the [As₂I₈]^{2−} counter-ion can be viewed as two distorted square-pyramidal AsI₅ polyhedra linked together by one edge. The distortion of the AsI₅ units from ideal square-pyramidal geometry is probably due to the lone electron pair on the As^{III} atoms predicted by the valence-shell electron-pair repulsion model (Gillespie, 1963, 1992), as well as the interaction with the oppositely charged [AsPc]⁺ counter-ion. Looking in more detail at the As—I bond lengths in the [As₂I₈]^{2−} ion, it is clear that the I atoms are linked to the As atoms with different strengths; atom I3 is linked more strongly than atom I1, and atom I1 more strongly than atom I4 (Table 1). These differences correlate with the strength of the interactions between the I atoms in the [As₂I₈]^{2−} anion and the oppositely charged As^{III} atom of the [AsPc]⁺ moiety. The strongest interaction

between the [AsPc]⁺ and [As₂I₈]^{2−} ions takes place between the As atom of the [AsPc]⁺ ion and the bridging I atom of the [As₂I₈]^{2−} ion [As2···I2ⁱ = 3.5376 (9) Å].

The ionic attraction between the [AsPc]⁺ and [As₂I₈]^{2−} ions seems to be significant in the crystal structure (Fig. 2). The basic packing unit includes two [AsPc]⁺ complexes related by an inversion centre and one centrosymmetric [As₂I₈]^{2−} counter-ion. The positively charged [AsPc]⁺ moieties are attached to the [As₂I₈]^{2−} anion on both sides, forming centrosymmetric [(AsPc)(As₂I₈)(AsPc)] aggregates with a distance of ~10.11 (1) Å between the isoindole N₄ planes. These aggregates form stacks that are propagated along the [101] direction. The distance of ~3.41 (1) Å between the isoindole N₄ planes of two neighbouring [AsPc]⁺ units within the stack indicates strong π–π interaction between Pc macrocycles (Pauling, 1960). The π–π intermolecular interaction is a common feature of phthalocyanine chemistry, and it leads phthalocyanine and its metal complexes to form supramolecular aggregates (Nevin *et al.*, 1987; Terekhov *et al.*, 1996; Isago *et al.*, 1997, 1998).

Although the crystal of (I) is built up from oppositely charged [AsPc]⁺ and [As₂I₈]^{2−} ions, the compound does not possess the characteristic properties of ionic crystals. The solubility of this compound in most polar solvents, such as water, methanol, ethanol and acetone, is insignificant, and it is slightly soluble in pyridine, dimethyl sulfoxide, tetrahydrofuran, chloronaphthalene and other aromatic solvents. This is in agreement with the crystal structure, in which both hydrophilic parts of the complex are surrounded by the hydrophobic phenyl rings of the Pc macrocycle.

The electrical conductivity of (I), measured from a single crystal along the stacking direction of the {[AsPc]⁺···[As₂I₈]^{2−}···[AsPc]⁺} aggregates (along the [101] direction) and along the *b* axis (perpendicular to the stacks), exhibits non-metallic character ($d\sigma/dT > 0$). At room temperature the conductivity is ~4.4–5.1 × 10^{−6} Ω^{−1} cm^{−1} along [101] and ~5.8–6.5 × 10^{−7} Ω^{−1} cm^{−1} along the *b* axis.

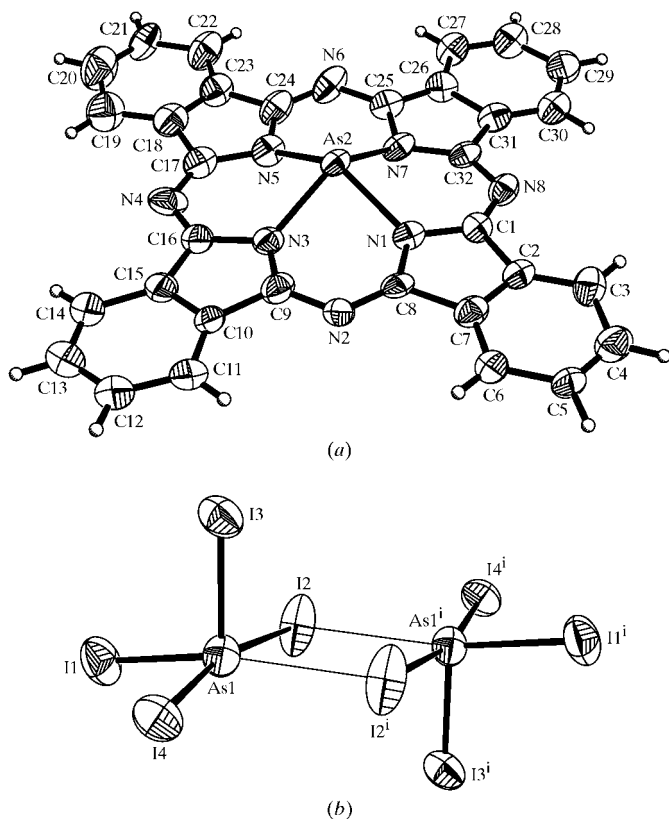


Figure 1

A view of the molecular structure of (a) the [AsPc]⁺ and (b) the [As₂I₈]^{2−} units with the labelling of the atoms. Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]

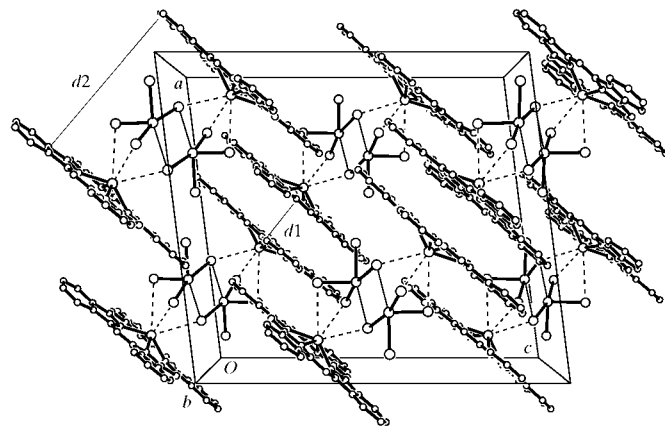


Figure 2

The molecular stacking in the extended structure. The dashed lines represent the As···I interactions between the [AsPc]⁺ and [As₂I₈]^{2−} units. The distances *d*1 and *d*2 are 3.41 and 10.11 Å, respectively.

Experimental

Crystals of the title compound were obtained by the direct reaction of pure powdered arsenic (99.9%) with phthalonitrile (99.0%) (Kubiak & Janczak, 1993) under a stream of iodine vapour (99.8%) at 463 K.

Crystal data

[As(C₃₂H₁₆N₈)₂][As₂I₈]
M_r = 2339.94
 Monoclinic, *C*2/*c*
a = 19.357 (3) Å
b = 16.537 (2) Å
c = 21.783 (3) Å
 β = 97.09 (1)°
V = 6919.6 (17) Å³
Z = 4
D_x = 2.246 Mg m⁻³
D_m = 2.24 Mg m⁻³

D_m measured by flotation in a mixture of bromoform and chloroform
 Mo *K*α radiation
 Cell parameters from 5312 reflections
 θ = 3.3–28.3°
 μ = 5.54 mm⁻¹
T = 295 (2) K
 Parallelepiped, black–violet
 0.42 × 0.24 × 0.24 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
 ω scans
 Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990b)
T_{min} = 0.212, *T_{max}* = 0.273
 37315 measured reflections

8498 independent reflections
 5312 reflections with *I* > 2σ(*I*)
R_{int} = 0.028
 θ_{max} = 28.3°
 $h = -25 \rightarrow 25$
 $k = -22 \rightarrow 21$
 $l = -28 \rightarrow 28$

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.049
wR (*F*²) = 0.139
S = 1.00
 8498 reflections
 416 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0806P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.72 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -1.07 \text{ e } \text{Å}^{-3}$

The greatest positive and negative residual electron densities are located at the positions (0.1871, 0.2648, 0.3078) and (0.1269, 0.6243, 0.3007), respectively.

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, 1990a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL97*.

GJP thanks the CNPq foundation (Brazil) for a scholarship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1174). Services for accessing these data are described at the back of the journal.

Table 1

Selected geometric parameters (Å, °).

I1–As1	2.6595 (7)	As2–N7	2.028 (6)
I2–As1	2.9910 (8)	As2–N5	2.063 (6)
I3–As1	2.5953 (8)	As2–N1	2.086 (5)
I4–As1	2.7680 (7)	As2–N3	2.088 (6)
I3–As1–I1	99.86 (3)	N7–As2–N5	82.6 (2)
I3–As1–I4	96.95 (2)	N7–As2–N1	82.1 (2)
I1–As1–I4	93.94 (2)	N5–As2–N1	137.3 (2)
I3–As1–I2	92.38 (2)	N7–As2–N3	136.0 (2)
I1–As1–I2	92.41 (2)	N5–As2–N3	81.4 (2)
I4–As1–I2	167.65 (3)	N1–As2–N3	82.5 (2)

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
 Gillespie, R. J. (1963). *J. Chem. Educ.* **40**, 295–301.
 Gillespie, R. J. (1992). *Chem. Soc. Rev.* **21**, 59–69.
 Isago, H., Leznoff, C. C., Ryan, M. F., Metcalfe, R. A., Davis, R. & Lever, A. B. P. (1998). *Bull. Chem. Soc. Jpn.* **71**, 1039–1047.
 Isago, H., Terekhov, D. S. & Leznoff, C. C. (1997). *J. Porphyrins Phthalocyanines*, **1**, 135–140.
 Janczak, J. (2003). *Inorg. Chem.* **42**, 3549–3558.
 Janczak, J. (2004). *Acta Cryst.* **C60**, m330–m332.
 Janczak, J. & Idemori, Y. M. (2001a). *Acta Cryst.* **C57**, 924–925.
 Janczak, J. & Idemori, Y. M. (2001b). *Inorg. Chim. Acta*, **325**, 85–93.
 Janczak, J. & Idemori, Y. M. (2002a). *Acta Cryst.* **C58**, m23–m25.
 Janczak, J. & Idemori, Y. M. (2002b). *Acta Cryst.* **E58**, m36–m38.
 Janczak, J. & Idemori, Y. M. (2002c). *Inorg. Chim. Acta*, **41**, 5059–5065.
 Janczak, J. & Kubiak, R. (1999a). *Inorg. Chim. Acta*, **288**, 174–180.
 Janczak, J. & Kubiak, R. (1999b). *Pol. J. Chem.* **73**, 1587–1592.
 Janczak, J. & Kubiak, R. (2003). *Acta Cryst.* **C59**, m70–m72.
 Janczak, J., Kubiak, R. & Hahn, F. (1999). *Inorg. Chim. Acta*, **287**, 101–104.
 Janczak, J., Kubiak, R. & Jezierski, A. (1999). *Inorg. Chim. Acta*, **38**, 2043–2049.
 Janczak, J., Razik, M. & Kubiak, R. (1999). *Acta Cryst.* **C55**, 359–361.
 Kubiak, R. & Ejsmont, K. (1999). *J. Mol. Struct.* **474**, 275–281.
 Kubiak, R. & Janczak, J. (1993). *J. Alloys Compd.* **204**, L7–L8.
 Kubiak, R., Janczak, J. & Razik, M. (1999). *Inorg. Chim. Acta*, **293**, 155–159.
 Kubiak, R. & Razik, M. (1998). *Acta Cryst.* **C54**, 483–485.
 Kuma (2001). *KM-4-CCD Software*. Version 171. Kuma Diffraction, Wrocław, Poland.
 Nevin, W. A., Liu, W. & Lever, A. B. P. (1987). *Can. J. Chem.* **65**, 855–858.
 Pauling, L. (1960). *The Nature of the Chemical Bond*, p. 262. Ithaca: Cornell University Press.
 Perpétuo, G. J. & Janczak, J. (2005). *Acta Cryst.* **E61**, m2003–m2005.
 Shannon, R. D. (1976). *Acta Cryst.* **A32**, 751–767.
 Sheldrick, G. M. (1990a). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1990b). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Terekhov, D. S., Nolan, K. J. M., McArthur, C. R. & Leznoff, C. C. (1996). *J. Org. Chem.* **61**, 3034–3040.