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Iodo[phthalocyaninato(2–)]-manganese(III) bridged by a neutral I_2 molecule

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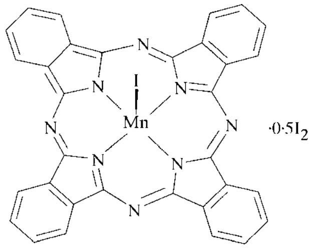
The title manganese(III) phthalocyaninate (Pc) complex, *viz.* iodo[phthalocyaninato(2−)]manganese(III) hemi(diiodine), $[Mn(C_{32}H_{16}N_8)I]\cdot0.5I_2$ or $(MnPcI)_2\cdot I_2$, was obtained from the reaction of pure powdered manganese with phthalonitrile under oxidation conditions of iodine vapour. The phthalocyaninato(2−) residue is not strictly planar and the Mn atom is five-coordinate, having distorted square-pyramidal geometry and residing 0.262 (2) Å above the plane defined by the four isoindole N atoms of the phthalocyaninate macrocycle. The neutral I_2 molecule bridges the iodo[phthalocyaninato-(2−)]manganese(III) molecules, forming a centrosymmetric dimeric structure.

Comment

The present study continues our investigations into the synthesis, characterization and stereochemistry of metallophthalocyaninate complexes, which have been obtained under oxidation conditions of iodine vapour. The I atoms in most iodine-doped metallophthalocyanines form linear chains of symmetrical I_3^- ions, which are usually disordered in the crystal (Janczak & Idemori, 2001). The I atoms can also be bonded directly to the central metal, yielding mono- or diiodometallophthalocyaninate complexes (Janczak & Kubiak, 1999*a*; Schweiger *et al.*, 1998). Additionally, it has been stated that, besides these disordered and symmetrical triiodide ions, I atoms can form ordered but unsymmetrical I_3^- ions (Janczak & Kubiak, 1999*b*; Janczak & Idemori, 2002*a*). Against this background, we present here the crystal structure of the title compound, (I).

Refinement of the crystal structure of (I), supported by a Raman experiment, clearly shows that this iodo[phthalocyaninato(2−)]manganese(III) complex (Fig. 1) crystallizes as a dimer, with a neutral I_2 molecule forming a bridge (Fig. 2). In the frequency region of 100–500 cm^{-1}, the Raman spectrum exhibits one expected band at ~180 cm^{-1}, for an I_2 molecule which interacts weakly with the axial I atoms of neighbouring MnPcI molecules (Pc is phthalocyaninate), forming a dimeric structure, $(MnPcI)_2\cdot I_2$. The absence of any observable peak at ~200 cm^{-1} eliminates pure iodine as an impurity (Anderson & Sun, 1970). The interaction of the I_2 molecule with two I atoms axially bonded to the central Mn results in the population of molecular orbitals with I—I antibonding character, and hence a slight increase in the I—I bond length, a decrease in bond order and constant stretching forces are observed (Cowie *et al.*, 1979; Marks *et al.*, 1976). This Raman spectrum is characteristic of complexes containing weakly interacting I_2 molecules (Teitelbaum *et al.*, 1978, 1980; Mizuno *et al.*, 1981).



(I)

The structure of (I) consists of two iodo[phthalocyaninato(2−)]manganese(III) molecules bridged by an I_2 molecule to form a dimer. The Mn atom is five-coordinate, involving the four isoindole N atoms and an axial I atom, resulting in a distorted square-pyramidal geometry for the metal. The Mn atom lies 0.262 (2) Å above the weighted mean plane defined by the four isoindole N atoms of the Pc macrocycle. The phthalocyaninate ring is not strictly planar but has a saucer shape, since the I atom axially bound to the central Mn atom leads to a deviation of the macroring from planarity.

The Pc macrocycles in the dimer are related by an inversion centre located at the centre of the I—I bond of the bridged I_2 molecule. The I—I bond length in the bridging I_2 molecule provides evidence for the existence of neutral I_2 molecules in the crystal that only weakly interact with the axial I atoms of the MnPcI molecules, since it is slightly longer than the I—I distance observed in pure iodine; in the solid state, this distance is 2.715 (6) Å (van Bolhuis *et al.*, 1967).

A search of the Cambridge Structural Database (Version 5.25; Allen, 2002) shows that relatively few structures have

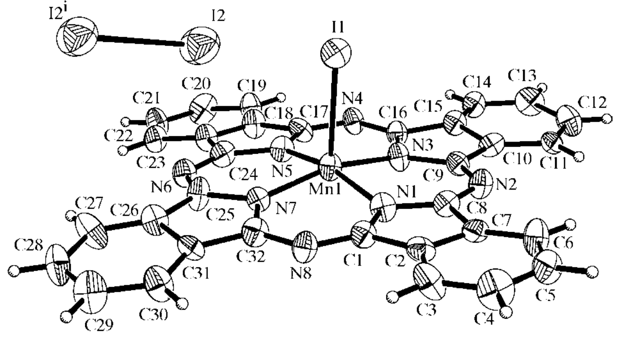


Figure 1
A view of the molecular structure of the independent unit of (I), with the atom-labelling scheme (the I_2 dimer is shown). Displacement ellipsoids are shown at the 50% probability level.

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been reported having a neutral I_2 molecule coordinated between two I atoms, and only three are metallophthalocyanine structures: $GePcI_2{\cdot}I_2$ (Janczak, Razik & Kubiak, 1999) and $CrPcI_2{\cdot}I_2$ (Janczak & Idemori, 2002*b*), in which the neutral I_2 molecules develop polymeric structures, and $(FePcI)_2{\cdot}I_2$ (Janczak, Kubiak & Hahn, 1999), which is isostructural with the present Mn complex, (I).

The I—I distance of the bridging I_2 molecule in (I) is comparable with those found in the $GePcI_2{\cdot}I_2$ [2.770 (2) Å], $CrPcI_2{\cdot}I_2$ [2.773 (1) Å] and $(FePcI)_2{\cdot}I_2$ [2.766 (2) Å] systems, three phthalocyaninate complexes with a bridging I_2 molecule between the two I atoms. Besides these complexes, a new iodine-doped phthalocyaninate complex has been reported in which the neutral I_2 molecules interact with unsymmetrical I_3^- ions, forming zigzag $\cdots I_3^- \cdots I_2 \cdots I_3^- \cdots I_2 \cdots$ chains (Janczak, 2003). An interesting example of an I_2 molecule interacting with two I_3^- ions and forming $I_3^- \cdots I_2 \cdots I_3^-$ aggregates is in the crystal structure of iodine-doped bis(phthalocyaninato)niobium(IV) (Donzello *et al.*, 1998). A neutral I_2 molecule acting as a bridge can also be found in the iodine-doped chloro[phthalocyaninato(2−)]iron(III) complex $(FePcCl)_2{\cdot}I_2$ (Palmer *et al.*, 1985). Additionally, the I_2 molecule is present and 'stapled' by two inter-ring C—C σ bonds in the (diphthalocyaninato)niobium(V) complex obtained in an IBr_2 atmosphere. However, in that crystal, the I_2 molecule interacts with the Br atom of the IBr_2^- ion *via* only one I atom, forming $[I{-}I \cdots Br{-}I{-}Br]^-$ aggregates (Janczak & Kubiak, 2003).

The I···I distance between the neutral I_2 molecule and the I atom coordinated to the central Mn atom in (I) is a little shorter than the intermolecular distance in pure iodine in the solid state (~3.50 Å; van Bolhuis *et al.*, 1967). This value demonstrates the interaction between the I_2 molecule and the two MnPcI molecules, which are related by an inversion centre to form a dimeric structure. The $I1 \cdots I2{-}I2^i \cdots I1^i$ sequence is almost linear. The Mn···Mn distance in the dimer is 12.045 (2) Å, while the shortest Mn···Mn distance of 5.610 (2) Å is observed between back-to-back partially overlapping neighbouring iodo[phthalocyaninato(2−)]manganese(III) molecules.

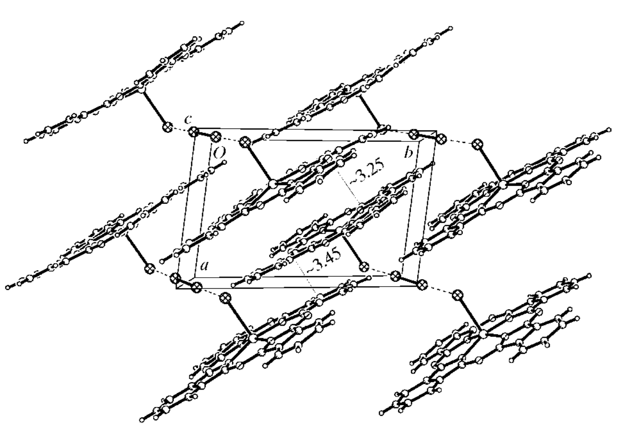

Figure 2
The molecular packing in the unit cell of (I), showing the $(MnPcI)_2{\cdot}I_2$ dimeric unit. Distances are given in Å.

The two distances of ~3.25 and ~3.45 Å between ring systems indicate the presence of π–π interactions between the back-to-back and face-to-face oriented and partially overlapping Pc units (Fig. 2), since these values are comparable with the van der Waals distance of ~3.4 Å for an aromatic ring system (Pauling, 1960). Pc···Pc interactions overlapping with π–π interactions are a common feature in such structures (Nevin *et al.*, 1987; Terekhov *et al.*, 1996; Isago *et al.*, 1997). The overlapping of π electrons between the Pc rings which form the conduction band (Ibers *et al.*, 1982) is responsible for the relatively high observed electrical conductivity measured on a polycrystalline sample pressed into pellets (at room temperature, the conductivity is 3.3–4.8 × 10^{-4} Ω^{-1}cm^{-1}). Anisotropy of the conductivity and investigations of the magnetic and spectroscopic properties of (I) are in progress.

Experimental

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

Crystal data

$[Mn(C_{32}H_{16}N_8)I]{\cdot}0.5I_2$
M_r = 821.27
Triclinic, $P\overline{1}$
a = 8.447 (2) Å
b = 13.051 (2) Å
c = 13.218 (2) Å
α = 102.11 (2)°
β = 91.61 (2)°
γ = 96.81 (2)°
V = 1412.6 (5) Å^3
Z = 2
D_x = 1.931 Mg m^{-3}
D_m = 1.93 Mg m^{-3}
D_m measured by flotation in a $CHBr_3/CHCl_3$ mixture
Mo $K\alpha$ radiation
Cell parameters from 2544 reflections
θ = 3.0–28°
μ = 2.69 mm^{-1}
T = 293 (2) K
Parallelepiped, black–violet
0.24 × 0.21 × 0.17 mm

Data collection

Kuma KM-4 with CCD area-detector diffractometer
ω scans
Absorption correction: analytical face-indexed (*SHELXTL*; Sheldrick, 1990)
T_{min} = 0.563, T_{max} = 0.656
16 124 measured reflections
6769 independent reflections
4580 reflections with $I > 2\sigma(I)$
R_{int} = 0.045
θ_{max} = 28.0°
$h = -8 \rightarrow 11$
$k = -17 \rightarrow 16$
$l = -17 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.079$
S = 1.00
6769 reflections
388 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0162P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.82 e Å^{-3}
$\Delta\rho_{min}$ = −1.07 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I1—Mn1	2.7312 (11)	Mn1—N1	1.974 (4)
Mn1—N7	1.953 (4)	I2—I2^i	2.7827 (12)
Mn1—N5	1.969 (4)	I1—I2	3.4238 (10)
Mn1—N3	1.969 (4)		
N7—Mn1—N5	89.51 (17)	N7—Mn1—I1	99.69 (12)
N7—Mn1—N3	164.40 (17)	N5—Mn1—I1	100.08 (12)
N5—Mn1—N3	88.61 (17)	N3—Mn1—I1	95.89 (12)
N7—Mn1—N1	89.30 (17)	N1—Mn1—I1	94.83 (12)
N5—Mn1—N1	165.03 (17)	I1—I2—I2^i	178.97 (3)
N3—Mn1—N1	88.54 (17)		

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

H atoms were placed in calculated positions and treated as riding, with C—H distances of 0.93 Å and with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

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: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1221). Services for accessing these data are described at the back of the journal.

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