

Iodo(phthalocyaninato)chromium(III)

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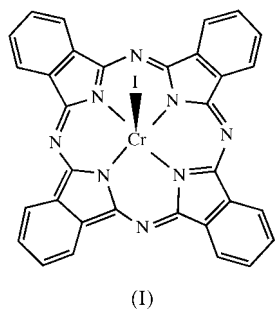
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A new chromium(III)–phthalocyanine complex with the formula $[\text{Cr}(\text{C}_{32}\text{H}_{16}\text{N}_8)\text{I}]$, or CrPcI where Pc is phthalocyanate(2[−]), has been obtained by the reaction of pure Cr powder with phthalonitrile under a stream of iodine vapour. The five-coordinate Cr atom is bonded to the four isoindole N atoms of the phthalocyaninate(2[−]) ligand and to one apical iodine ligand, and has a square-pyramidal coordination geometry. The Cr^{III} cation is significantly displaced [0.456 (2) Å] from the N_4 -isoindole plane towards the I atom. The Cr–I bond is tilted 2.51 (4)° to the N_4 -isoindole plane.

Comment

This study forms part of an investigation on the synthesis and characterization of metallophthalocyanines obtained under a stream of iodine vapour. Previously, we reported that under these conditions crystals of iodine-doped metallophthalocyaninate complexes, in which the iodine-doped atoms form chains of disordered symmetrical triiodide ions (Janczak *et al.*, 1998, 2000; Janczak, Kubiak & Jezierski, 1999; Janczak & Kubiak, 1999a; Janczak & Idemori, 2001) or ordered but unsymmetrical triiodide ions (Janczak & Kubiak, 1999b; Kubiak *et al.*, 1999), are usually formed. The I atoms can also be directly joined to the central metal ion yielding mono- or

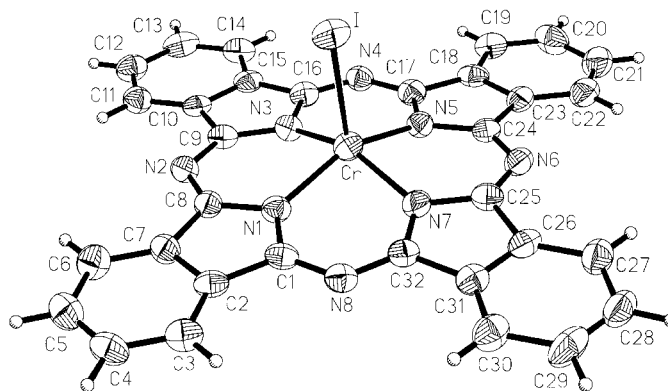


diiodometallophthalocyanine complexes (Janczak & Kubiak, 1999c,d), as well as forming a neutral molecule of I₂ which is a bridge for dimerization or for developing a polymeric structure of mono- and diiodometallophthalocyanine complexes

(Janczak, Razik & Kubiak, 1999; Janczak, Kubiak & Hahn, 1999).

The crystal of the title compound, (I), is built up from discrete molecules (Fig. 1). The central Cr^{III} cation is five-coordinated by four isoindole N atoms of the phthalocyaninate(2[−]) macrocyclic ligand and by one apical I atom in a square-pyramidal geometry. The Cr^{III} cation is significantly displaced [0.456 (2) Å] from the plane defined by four isoindole N atoms towards the I atom. For comparison, the displacement of the central metal ion in other iodo-[phthalocyaninate(2[−])]metal(III) complexes is 0.258 (2) Å in FePcI (Janczak, Razik & Kubiak, 1999), 0.322 (2) Å in VPcI (Ejsmont & Kubiak, 1998), 0.738 (3) Å in InPcI (Janczak & Kubiak, 1999c) and 0.959 (3) Å in TlPcI (Schweiger *et al.*, 1998). In this series of $M^{\text{III}}\text{PcI}$ complexes, the displacement of the metal ion from the N_4 -isoindole plane correlates with the $M\text{—N}_{\text{iso}}$ distances. However, the effective ionic radii for Cr³⁺ and Fe³⁺ are not significantly different (Shannon, 1976), but the displacement of the Cr atom from the N_4 -isoindole plane is significantly greater than the corresponding displacement in the FePcI complex, since according to the calculation by Whangbo & Stewart (1983), the 3d electrons of chromium are more localized and higher in energy than the ring π electrons, whereas the Fe levels are much closer. This will result in better orbital overlaps and more covalency for Fe–N_{iso} than Cr–N_{iso}. In both the InPcI and TlPcI complexes, the displacement of the central metal cation is significantly greater in relation to the Cr, Fe and V analogues, since both In³⁺ and Tl³⁺ are closed-shell (d^{10}) ions, and the displacement of In³⁺ and Tl³⁺ from the N_4 -isoindole plane correlates well with the effective ionic radius, *viz.* In³⁺ \sim 0.71 Å and Tl³⁺ \sim 0.82 Å (Shannon, 1976).

The Cr–I bond length [2.5769 (7) Å] is the shortest $M\text{—I}$ bond in this class of $M^{\text{III}}\text{PcI}$ complexes. The equivalent $M\text{—I}$ bond lengths are 2.628 (1), 2.665 (1), 2.672 (1) and 2.674 (1) Å in the VPcI, FePcI, InPcI and TlPcI complexes, respectively. The Cr–N_{iso} bond lengths are slightly longer than those found in the dichloro derivative (Moubaraki *et al.*, 1990), since in CrPcCl₂^{iv}, the Cr^{III} cation lies close to the centre of one oxidized phthalocyaninate(1[−]) ring and the Cl atoms are


Figure 1

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

joined axially to the Cr atom on both sides of the phthalocyaninate(1⁻) ring.

The bonding interaction of the central Cr^{III} cation with the apically joined I atom leads to the deformation of the phthalocyaninate(2⁻) macro-ring as a saucer-shaped form. The greatest deviation from the N₄-isoindole plane is observed for the outermost C atoms of phenyl rings C18–C23 and C26–C31, as a result of the face-to-face orientation and overlapping of the neighbouring CrPcI molecules, which are slightly joined by I...H intermolecular donor–acceptor interactions. This results in pairs of face-to-face but stepped CrPcI molecules in the crystal (Fig. 2), and is also the reason for the 2.51 (4)° tilt of the Cr–I bond with respect to the normal to the N₄-isoindole plane. Thus, the CrPcI molecule is close to C_s symmetry and not to C_{4v}, which is expected in solution. In the face-to-face pairs of CrPcI molecules, there are two equivalent I...H

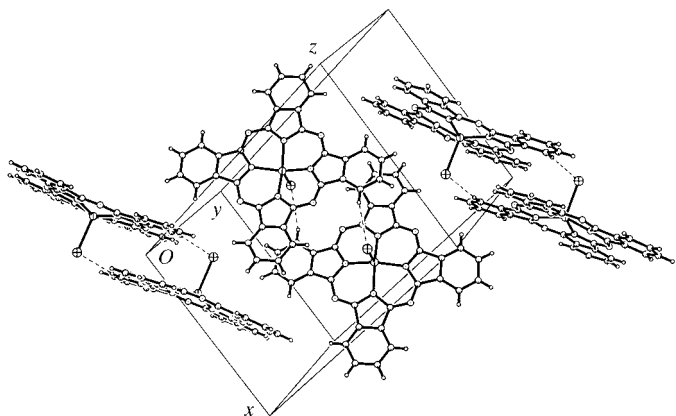


Figure 2
The molecular packing in the unit cell showing the pseudo-dimers of CrPcI molecules.

intermolecular hydrogen bonds. Both I...H3ⁱ and Iⁱ...H3 distances are 3.109 Å and the I...H3ⁱ–C3ⁱ angle [symmetry code: (i) $-x, -y, -z$] is 164°. The isoindole moieties of the phthalocyaninate(2⁻) macro-ring are almost planar. The dihedral angles between the N₄-isoindole plane and the planes of four isoindole moieties are 4.2 (1), 2.8 (1), 4.1 (1) and 6.6 (1)°, for N1/C1/C8, N3/C9/C16, N5/C17/C24 and N7/C25/C32, respectively.

Although there is no imposed crystallographic symmetry on the phthalocyaninate(2⁻) macro-ring, the bond distances and angles for the chemically equivalent bonds do not differ significantly and compare well with the equivalent bond lengths and angles of the other metallophthalocyanine structures.

Experimental

The crystals of CrPcI were obtained by the direct reaction of pure powdered chromium with 1,2-dicyanobenzene (Kubiak & Janczak, 1993) under a stream of iodine vapour at about 495 K. At this temperature, the liquid 1,2-dicyanobenzene undergoes catalytic tetramerization with simultaneous transfer of two electrons from the Cr metal to form the Pc ring; the third electron from Cr is transferred to the I atom to form an I⁻ ion.

Crystal data

[Cr(C₃₂H₁₆N₈)I]
M_r = 691.43
Monoclinic, P2₁/n
a = 13.173 (3) Å
b = 10.424 (2) Å
c = 19.435 (4) Å
β = 99.76 (3)°
V = 2630.1 (10) Å³
Z = 4
D_x = 1.746 Mg m⁻³
D_m = 1.74 Mg m⁻³

D_m measured by flotation in a mixture of CH₂Cl₂ and CH₂Br₂
Mo Kα radiation
Cell parameters from 458 reflections
θ = 5–25°
μ = 1.65 mm⁻¹
T = 293 (2) K
Parallelepiped, black–violet
0.16 × 0.12 × 0.10 mm

Data collection

Kuma KM-4 diffractometer with CCD area-detector
ω scans
Absorption correction: face-indexed analytical (SHELXTL; Sheldrick, 1990)
T_{min} = 0.778, T_{max} = 0.852
22036 measured reflections

6441 independent reflections
3350 reflections with I > 2σ(I)
R_{int} = 0.043
θ_{max} = 28.5°
h = -13 → 17
k = -13 → 13
l = -25 → 25

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.050
wR(F²) = 0.049
S = 0.96
6441 reflections
379 parameters

H-atom parameters constrained
w = 1/[σ²(F_o²) + (0.0088P)²]
where P = (F_o² + 2F_c²)/3
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.32 e Å⁻³
Δρ_{min} = -0.33 e Å⁻³

H atoms were refined as riding with C–H distances of 0.93 Å.

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, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1528). Services for accessing these data are described at the back of the journal.

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