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Diiodo[phthalocyaninato(2–)]germanium(IV) diiodine

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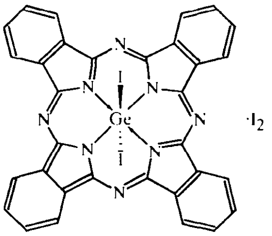
Abstract

The title germanium(IV) complex, $[GeI_2(C_{32}H_{16}N_8)]\cdot I_2$ or $(GePcI_2)I_2$, where Pc is phthalocyaninate(2−), was obtained from the reaction of pure germanium with 1,2-dicyanobenzene under a stream of iodine vapour. The phthalocyaninate residue is centrosymmetric and is not strictly planar. The two opposite isoindole rings are displaced below and the other two above the plane defined by the four isoindole N atoms. The Ge atom coordinates the four isoindole N atoms of the Pc ring and two I atoms (in *trans* positions). The I—Ge—I axis is tilted by 1.1 (2)° from the normal to the isoindole N_4 plane. Each $GePcI_2$ molecule in the crystal is bridged by a neutral I_2 molecule to two neighbouring molecules through the axial I atoms, forming a zigzag chain. The I—I bond length in the bridging I_2 molecule is comparable to the distance in pure iodine.

Comment

As a continuation of our studies on the synthesis and characterization of iodine-doped metallophthalocyanines, we have obtained several of these compounds (Kubiak & Janczak, 1997; Kubiak & Razik, 1998; Janczak *et al.*, 1999,1999*a*; Janczak & Kubiak, 1999*a*,*b*,*c*). The I atoms in most iodine-doped metallophthalocyanines form linear chains of symmetrical I_3^- ions, which are usually disordered in the crystal (Marks, 1980; Ibers *et al.*, 1982; Janczak *et al.*, 1999*a*,*b*; Janczak & Kubiak, 1999*a*,*b*). The I atoms can also be bonded directly to the central metal ion, yielding mono- or diiodometallophthalocyanines (Ejsmont & Kubiak, 1997; Janczak & Kubiak, 1999*c*; Schweiger *et al.*, 1998).

The crystal of the title compound, (I), is built up from centrosymmetric $GePcI_2$ molecules and neutral I_2 molecules (Fig. 1). Each $GePcI_2$ molecule is bridged by a neutral I_2 molecule to two neighbouring molecules through the axially coordinated I atoms. The central Ge atom is six-coordinated by the four isoindole N atoms of the phthalocyaninate(2−) macrocyclic ligand and by two I atoms (in *trans* positions) in an octahedral geometry. The tetradentate macrocyclic phthalocyaninate(2−) ligand is not strictly planar. The two opposite isoindole rings are displaced below and the other two above the plane defined by the four isoindole N atoms. The largest deviation (besides the H and I atoms) from the isoindole N_4 plane is for the C4 atom [0.492 (3) Å]. The I—Ge—I axis is tilted by 1.1 (2)° from the normal to the isoindole N_4 plane.



$GePcI_2$

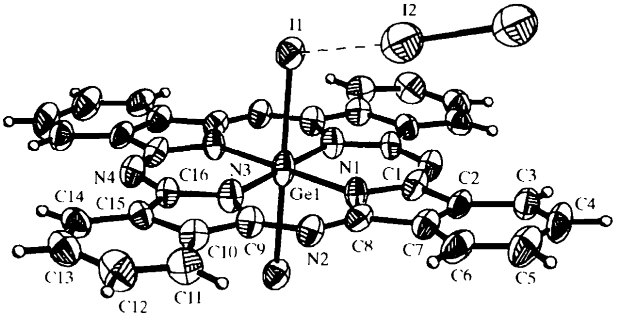


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

The I—I bond length in the bridging diiodine molecule is 2.770 (2) Å. This value is comparable to the I—I distance in pure iodine. The I—I bond length is 2.66 Å in gaseous I_2 (Karle, 1955), and 2.715 (6) Å in the solid state (at 110 K) (van Bolhuis *et al.*, 1967). The I—I bond distance in the present germanium complex provided evidence of the existence of neutral diiodine molecules in the crystal, in contrast to the known tetragonal iodine-doped metallophthalocyanines in which the iodine-doped atoms form a linear chain of I_3^- ions. The neutral diiodine molecule in the crystal has also been detected by Raman spectroscopy; the Raman spectrum shows the expected vibrational band (at $\simeq 200\,cm^{-1}$) of the I_2 molecule, which interacts weakly with the axial I atoms of the $GePcI_2$ molecules. Relatively few structures have been reported of compounds having a neutral I_2 molecule coordinated between two I atoms (Tebbe & Plewa, 1982; Millan *et al.*, 1982; Ray *et al.*, 1983), and only one is a metallophthalocyanine structure, namely, $(FePcI)_2I_2$ (Janczak *et al.*, 1999*b*). In contrast to $(FePcI)_2I_2$, in which the neutral molecule [with an I—I distance of 2.766 (2) Å] is a bridge for dimerization, in the present germanium phthalocyanine, the neutral I_2 molecule links the $GePcI_2$ molecules into zigzag chains (Fig. 2). A neutral diiodine molecule acting as a bridge can also be found in the structure of iodine-doped chloro[phthalocyaninato(2−)]iron(III), $(FePcCl)_2I_2$ (Palmer *et al.*, 1985). In the germanium complex, the distance between the axially coordinated I atoms and the I atom of the bridging I_2 molecule in the chains is 3.494 (2) Å, which is longer than that in the structure of $(FePcI)_2I_2$ [3.418 (2) Å] and is comparable to the intermolecular distance in pure iodine in the solid state (~3.50 Å; van Bolhuis *et al.*, 1967).

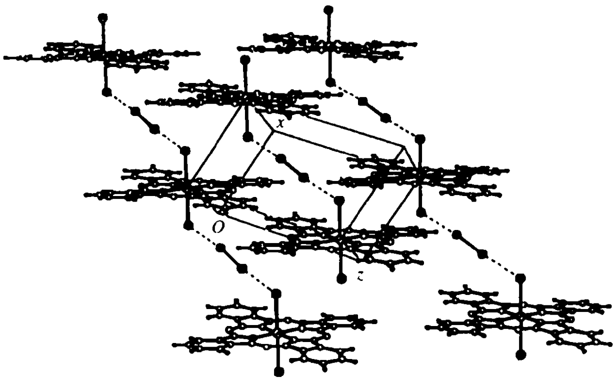


Fig. 2. The molecular packing in the unit cell showing the chains of $GePcI_2$ molecules bridged by neutral I_2 molecules.

The Ge—I distance in (I) is 2.762 (2) Å, which is shorter than the corresponding distance in $GePcI_2$ [2.687 (2) Å; Ejsmont & Kubiak, 1997]. This is most likely due to the interactions of the axially coordinated I atoms and the neutral bridging I_2 molecules. The large anisotropic displacement parameters of the I atom (I2) of the bridging diiodine molecule [especially U^{33} of 0.0890 (3) Å^2] can be explained by oscillation of the I_2 molecule, since the I_2 molecule interacts weakly with the two axial I atoms.

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

Experimental

Crystals of $(GePcI_2)I_2$ were obtained from the reaction of pure germanium with 1,2-dicyanobenzene (Kubiak & Janczak, 1993) under a stream of iodine vapour at 473 K.

Crystal data

$[GeI_2(C_{32}H_{16}N_8)]\cdot I_2$
$M_r = 1092.72$
Triclinic
$P\bar{1}$
$a = 7.716\,(2)$ Å
$b = 8.597\,(2)$ Å
$c = 12.540\,(3)$ Å
$\alpha = 80.19\,(3)°$
$\beta = 74.83\,(3)°$
$\gamma = 81.74\,(3)°$
$V = 786.8\,(3)$ Å^3
$Z = 1$
$D_x = 2.306$ Mg m^{-3}
$D_m = 2.28$ Mg m^{-3}
D_m measured by floation in dibromoethylene–tribromoethylene

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30 reflections
$\theta = 16–24°$
$\mu = 4.936$ mm^{-1}
$T = 293\,(2)$ K
Plate
0.42 × 0.18 × 0.12 mm
Black–violet

Data collection

Kuma KM-4 diffractometer
ω–2θ scans
Absorption correction: face-indexed analytical (*SHELXTL*; Sheldrick, 1990*b*)
$T_{min} = 0.264$, $T_{max} = 0.816$
6077 measured reflections
3985 independent reflections
2411 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 30.06°$
$h = -5 \rightarrow 10$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 17$
2 standard reflections frequency: 50 min intensity decay: 0.9%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.077$
$S = 0.925$
3985 reflections
205 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.97$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Ge1—N1	1.948 (3)	I2—I2^{i}	2.7698 (13)
Ge1—N3	1.953 (4)	I1—I2	3.494 (2)
Ge1—I1	2.7622 (11)		
N1—Ge1—N3	90.25 (15)	N1^{ii}—Ge1—I1	90.48 (12)
N1—Ge1—N3^{ii}	89.75 (15)	N3—Ge1—I1	89.45 (12)
N1—Ge1—I1	89.52 (12)	N3^{ii}—Ge1—I1	90.55 (12)

Symmetry codes: (i) $-1-x, -y, 1-z$; (ii) $-x, -y, -z$.

Data collection: *KM*-4 *Software* (Kuma, 1997). Cell refinement: *KM*-4 *Software*. Data reduction: *KM*-4 *Software*. Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1249). Services for accessing these data are described at the back of the journal.

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(η^6-Arylhimachalene)tricarbonylchromium(0)

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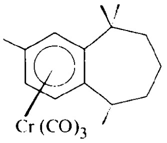
Abstract

The reaction of $Cr(CO)_6$ with arylhimachalene yields the title aryl organometallic compound, tricarbonyl[(1,2,3,4,4a,9a-η)-(7*S*)-3,5,5,9-tetramethyl-6,7,8,9-tetrahydro-5*H*-benzocycloheptene]chromium(0), $[Cr(C_{15}H_{22})(CO)_3]$, with the hydrocarbon linked to a $Cr(CO)_3$ tripod group. The crystal structure of one of the stereoisomeric products, *i.e.* that with the tripod *anti* to the methyl group on the asymmetric carbon, is presented here.

Comment

Organic molecules complexed with tricarbonylchromium have attracted much attention in recent years (Solladie-Cavallo, 1989; Sardone *et al.*, 1996). In order to establish the stereochemistry of the final metal-free targets, it is essential to know the spatial structure of the complexes. In a previous work, we have shown that the formation of π-allylpalladium complexes of a natural sesquiterpenic series occurs with high regio- and stereoselectivity (Chiaroni *et al.*, 1993: El Firdoussi *et al.*, 1997).

The reaction of arylhimachalene with hexacarbonylchromium(0) yields two stereoisomers of the corresponding organometallic compound, the existence of which has been established using high resolution NMR spectroscopy. The relative proportions are 60/40, respectively, for the *syn* and *anti* dispositions of the $Cr(CO)_3$ group with respect to the methyl group (C15) at the asymmetric carbon. Good quality single crystals could be obtained for the *anti* isomer, (I), the structure of which is presented here.



(I)

The molecular structure of this compound consists of a Cr atom in the zero oxidation state coordinated by three carbon monoxide molecules and the phenyl ring of arylhimachalene in a η^6 manner. The tricarbonyl–phenyl–chromium(0) residue is a well known motif in organometallic chemistry (see Bentele *et al.*, 1997) and it is even a textbook example for building molecular orbitals (Cotton, 1990), but we have not found a reference to any other compound in which the phenyl ring belongs to a natural product derivative. A view of the molecular structure of (I) is shown in Fig. 1.

The coordination sphere displays the expected linear Cr—C—O disposition, with the carbon monoxide molecules perpendicular to one another and the three C atoms defining a plane parallel to the phenyl ring. The Cr atom is 1.721 (2) Å above the average phenyl plane and is virtually exactly over the centroid of the ring, despite the different Cr—C distances shown in Table 1; such small differences among these distances have also been observed in analogous compounds (Oike *et al.*,