I thank EPSRC for funds to purchase the diffractometer and access to the Chemical Database Service at Daresbury Laboratory.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1211). Services for accessing these data are described at the back of the journal.

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(1,2-Benzenedicarbonitrile-κN)diiodo(phthalocyaninato-$\kappa^4 N$)zirconium(IV)

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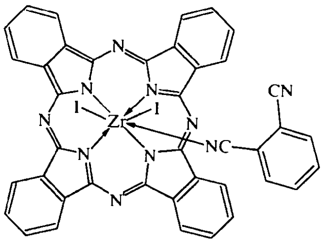
Abstract

A new zirconium phthalocyanine complex [$ZrI_2(Pc)\{C_6H_4(CN)_2\}$] (Pc = $C_{32}H_{16}N_8$) was obtained in crystalline form by the reaction of zirconium with 1,2-dicyanobenzene (*o*-DCB) under a stream of iodine. The molecule is a reaction product of zirconium, I atoms and *o*-DCB molecules, four of which form the Pc macrocycle. The crystal structure of this compound consists of discrete molecules in which seven-coordinate Zr^{IV} is surrounded by four N atoms of the phthalocyaninato ligand, two *cis*-I atoms and an N atom from one of the cyano groups of the fifth *o*-DCB molecule. A set of hydrogen-bonded interactions links the molecules in the crystal lattice.

Comment

The iodination of metallophthalocyanines provides a large class of materials with potentially useful properties (Kasuga & Tsutsui, 1980). We present here a portion of our work in this area which is related to the synthesis and structures of iodometallophthalocyanines (Ejsmont & Kubiak, 1997; Kubiak & Janczak, 1997).

The chemical composition of the title compound $I_2Zr(C_8H_4N_2)_5$, (1), is analogous to $O_2U(C_8H_4N_2)_5$, (2) (Day *et al.*, 1975). However, in (2), all five *o*-DCB units are part of the macrocycle and a super-phthalocyanine (SPc = $C_{40}H_{20}N_{10}$) is formed so that the conjugated π-electron ring system comprises all C and N atoms. In (1), a normal phthalocyanine ring involving four $C_8H_4N_2$ subunits does exist, but the fifth *o*-DCB molecule is ligated to the central Zr atom through the N atom of one of its two cyano groups. Thus (1) could also be written in the form $(PcZrI_2)(NC)C_6H_4(CN)$. There are also five *o*-DCB molecules in the compound $[(PcNb)_2O_2Br]^+.Br_3^-$. However, in this case, the fifth *o*-DCB residue is a discrete molecule of crystallization (Gingl & Strähle, 1989).



(1)

The seven-coordinate Zr^{IV} atom in (1) is surrounded by the four isoindole N atoms (N_4) of the Pc ring, two *cis*-I atoms and an N atom from one of the cyano groups of the fifth *o*-DCB molecule. The Zr atom lies 1.067 (2) Å above the N_4 plane. This value is slightly smaller than that observed in $ZrPc_2$ (1.10 Å; Silver *et al.*, 1991). The average interatomic distances in the phthalocyanine ring are 1.388 (3) for C—N_4, 1.315 (3) for C—N_{azam} (N_{azam} is an azamethine N atom) and 1.399 (6) Å for C—C. These distances are in agreement with other phthalocyanine macrocycles and, in particular, those for $ZrPc_2$ (Silver *et al.*, 1991).

The ligated fifth *o*-DCB unit evidently differs in structure from free *o*-DCB (Janczak & Kubiak, 1995) where two equivalent and practically linear cyano groups are *cisoid*-tilted from the benzene plane. In contrast, the cyano groups in (1) are *transoid* and the coordinated C34—C33—N9 group deviates slightly more from linearity than does the C39—C40—N10 group (see Table 1 and Fig. 1). The redistribution of the π-electron density resulting from the N9→Zr1 donor–acceptor bond involves a marginal shortening of the C33—N9 bond relative to C40—N10. The C40—N10 and mean aromatic C—C bond lengths are consistent with analogous values for crystalline *o*-DCB (Janczak & Kubiak, 1995).

There are intermolecular I···H contacts in the crystal lattice; the distances I1···H37($-x-1$, $-y$, $-z$) and I2···H28($-x-\frac{1}{2}$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) are 3.146 (7) and 3.207 (5) Å, respectively.

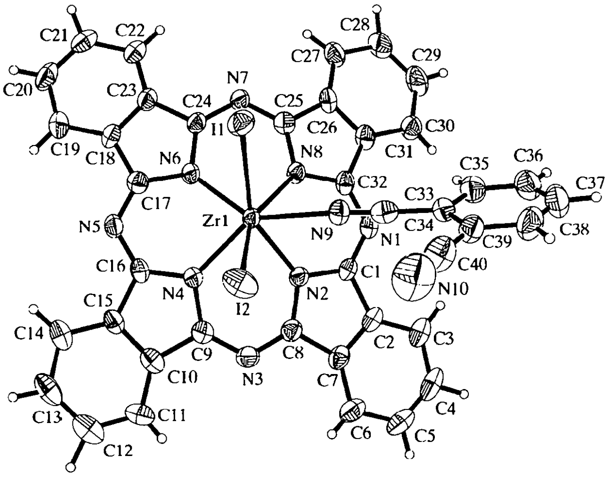


Fig. 1. The molecular structure of $(PcZrI_2)C_6H_4(CN)_2$. Displacement ellipsoids are plotted at the 50% probability level. H atoms are shown as spheres of arbitrary size.

Experimental

The compound $(PcZrI_2)C_6H_4(CN)_2$ was obtained in crystalline form by the reaction of zirconium with 1,2-dicyanobenzene (Kubiak & Janczak, 1993) under a stream of iodine.

Crystal data

$[ZrI_2(C_{32}H_{16}N_8)(C_8H_4N_2)]$
$M_r = 985.694$
Monoclinic
$P2_1/n$
$a = 9.965$ (2) Å
$b = 21.188$ (4) Å
$c = 16.792$ (3) Å
$\beta = 93.10$ (3)°
$V = 3540.3$ (12) Å^3
$Z = 4$
$D_x = 1.8493$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 10$–15°
$\mu = 2.101$ mm^{-1}
$T = 293$ (2) K
Parallelepiped
0.90 × 0.30 × 0.25 mm
Red–violet

Data collection

Kuma KM-4 diffractometer
ω–2θ scans
Absorption correction: *XABS*2 (Parkin *et al.*, 1995)
$T_{\min} = 0.482$, $T_{\max} = 0.591$
14 327 measured reflections
7906 independent reflections
4529 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.049$
$\theta_{\max} = 28.06°$
$h = 0 \rightarrow 13$
$k = -28 \rightarrow 28$
$l = -22 \rightarrow 22$
2 standard reflections every 50 reflections intensity decay: <1.02%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.074$
$S = 1.151$
7906 reflections
558 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = -0.005$
$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$\Delta\rho_{\min} = -0.55$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

I1—Zr1	2.9164 (8)	Zr1—N9	2.381 (5)
I2—Zr1	2.8801 (8)	N9—C33	1.130 (7)
Zr1—N2	2.207 (4)	N10—C40	1.139 (9)
Zr1—N6	2.208 (4)	C33—C34	1.447 (8)
Zr1—N8	2.208 (4)	C39—C40	1.414 (10)
Zr1—N4	2.218 (4)		
N2—Zr1—N6	122.0 (2)	N8—Zr1—I2	152.34 (11)
N2—Zr1—N8	76.7 (2)	N4—Zr1—I2	79.17 (11)
N6—Zr1—N8	77.2 (2)	N9—Zr1—I2	76.74 (11)
N2—Zr1—N4	76.6 (2)	N2—Zr1—I1	150.50 (11)
N6—Zr1—N4	75.6 (2)	N6—Zr1—I1	80.05 (11)
N8—Zr1—N4	122.5 (2)	N8—Zr1—I1	91.29 (11)
N2—Zr1—N9	74.2 (2)	N4—Zr1—I1	131.34 (12)
N6—Zr1—N9	143.6 (2)	N9—Zr1—I1	76.78 (11)
N8—Zr1—N9	75.6 (2)	I2—Zr1—I1	84.09 (3)
N4—Zr1—N9	140.3 (2)	C33—N9—Zr1	169.0 (5)
N2—Zr1—I2	94.17 (11)	N9—C33—C34	176.6 (6)
N6—Zr1—I2	128.23 (11)	N10—C40—C39	178.2 (8)

Before correction for absorption, $R_{\rm int}$ had a value of 0.0491 and the $\Delta\rho$ values ranged from 0.79 to -0.56 e Å^{-3}. The absorption correction was made using the *XABS*2 program (Parkin *et al.*, 1995) since an accident precluded any alternative. It lowered the R indices slightly and produced little change in the parameters.

Data collection: *Kuma KM*-4 *Users Guide* (Kuma, 1995). Cell refinement: *Kuma KM*-4 *Users Guide*. Data reduction: *Kuma KM*-4 *Users Guide*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXL*93.

We would like to thank Professor Z. Gałdecki, Technical University of Łódź, Poland, for the opportunity to make calculations using the *SHELXTL* program system in his laboratory. This research was supported by a grant (No. 3 T09A 083 13) from the Polish State Committee for Scientific Research.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1357). Services for accessing these data are described at the back of the journal.

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Di-μ-chloro-bis[(2-ammoniobenzenethiolato-*S*)chloromercury(II)]

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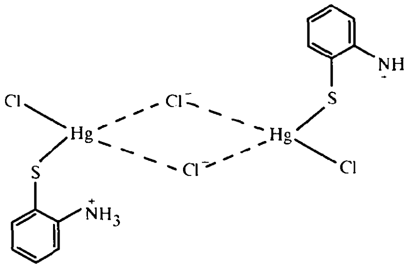
Abstract

The title compound, [$Hg_2Cl_4(C_6H_7NS)_2$], was obtained from the reaction of $HgCl_2$ with benzothiazole and studied by X-ray diffraction and IR spectroscopy. The molecule is centrosymmetric, with Hg—μ-Cl distances of 2.720 (1) and 2.976 (1) Å. The 2-aminobenzenethiol ligand (existing in a zwitterionic form) is bonded to mercury through the S atom, with an Hg—S distance of 2.340 (2) Å. There are N—H···Cl hydrogen bonds involving the bridging Cl atoms, as well as a bifurcated hydrogen bond involving the terminal Cl atoms.

Comment

As the activities of many enzymes depend upon the interaction of an imidazole or thiazole group with a metal ion, the coordination behaviour of benzothiazole towards mercury(II) is of particular interest since this molecule contains both S and N heteroatoms, and a π-donor aromatic system. The title compound, (I), was obtained from the reaction of $HgCl_2$ with benzothiazole. Ring opening of 2-(2-pyridyl)benzothiazoline by mercury(II) cations (Capitan *et al.*, 1979) and similar metal-ion-induced rearrangements of bis(benzothiazolines) to Schiff base chelates (Bayer, 1961; Jadamus *et al.*, 1964) have been reported. The reaction of 2-aminobenzenethiol and mercury(II) acetate gave bis(2-aminobenzenethiolato)mercury(II) (Jadamus *et al.*, 1964).



(I)

In (I), the 2-aminobenzenethiol ligand is bonded to mercury through the S atom. The Hg—S distance of 2.340 (2) Å is equal to the sum of the covalent radii of sulfur and two-coordinate mercury (Grdenić, 1981), but is the shortest of its kind found in the Cambridge Structural Database (1996) (Romero *et al.*, 1996; Brotherton *et al.*, 1974; Herbstein *et al.*, 1986). The Hg—Cl1 distance of 2.383 (1) Å is longer than expected for two-coordination, though it is comparable to that of 2.391 (2) Å found in $C_{24}H_{36}Cl_4Hg_2S_4$ (Romero *et al.*, 1996), and there is a large deviation from linearity [S—Hg—Cl1 148.31 (5)°]. These deformations are caused by two additional Hg···Cl interactions with distances shorter than the sum of the van der Waals radii [Hg···Cl2 2.720 (1) and Hg···Cl2^i 2.976 (1) Å; see Table 1 for symmetry code]. These two Cl atoms bridge the monomeric molecules related by a centre of symmetry. The Hg···Cl2 and Hg···Cl2^i distances fall within the range found for other chloro-bridged dimeric mercury structures (Biscarini & Pelizzi, 1988).

The molecules are interconnected by four hydrogen bonds of the N—H···Cl type, leading to an infinite two-dimensional network parallel to the (100) plane. Atom H13 forms a bifurcated hydrogen bond with two terminal Cl1 atoms. The geometries of the hydrogen bonds are given in Table 2.

The strong and broad absorption bands at 3300–2910 cm^{-1} in the IR spectrum are indicative of asymmetric and symmetric NH_3^+ stretching modes. Two main