

Two isomorphous complexes: dichloro[phthalocyaninato(2-)]tin(IV) and dichloro[phthalocyaninato(2-)]- germanium(IV)

Jan Janczak* and Ryszard Kubiak

W. Trzebiatowski Institute of Low Temperature and Structures Research, Polish Academy of Sciences, PO Box 1410, 50-950 Wrocław, Poland
Correspondence e-mail: janczak@int.pan.wroc.pl

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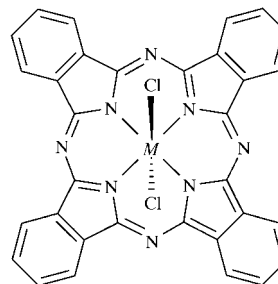
Isomorphous triclinic forms of dichloro[phthalocyaninato(2-)]tin(IV), $[\text{Sn}(\text{C}_{32}\text{H}_{16}\text{N}_8)\text{Cl}_2]$, and dichloro[phthalocyaninato(2-)]germanium(IV), $[\text{Ge}(\text{C}_{32}\text{H}_{16}\text{N}_8)\text{Cl}_2]$, and a monoclinic form of the latter have been obtained from the reaction of pure tin and germanium powder, respectively, with phthalonitrile under a stream of ICl vapour. All three crystal structures consist of centrosymmetric $[\text{SnPcCl}_2]$ and $[\text{GePcCl}_2]$ [Pc is phthalocyaninato(2-)] molecules, which are separated but interacting. In the triclinic forms (Sn and Ge), the Pc macrocycles are not staggered but slipped, and in the monoclinic form (Ge), the molecules are additionally inclined. In both cases, the central Sn or Ge atom is six-coordinated by the four isoindole N atoms of the Pc macrocyclic ligand and by two Cl atoms (located *trans*) into a tetragonal-bipyramidal structure. The arrangement of $[\text{SnPcCl}_2]$ and $[\text{GePcCl}_2]$ molecules in the crystal structure is determined mainly by intermolecular C—H...Cl, π – π and van der Waals interactions.

Comment

Continuing our investigation of the synthesis and characterization of metallophthalocyaninate complexes under a stream of halogen vapour (I_2 , IBr and ICl), we have obtained several metallophthalocyaninate complexes. Iodine-doped metallophthalocyaninate complexes have been reported previously (Kubiak & Janczak, 1997; Janczak *et al.*, 1998, 2000; Janczak & Kubiak, 1999a,b,d; Janczak, Kubiak & Hahn, 1999; Janczak, Kubiak & Jezierski, 1999; Janczak, Razik & Kubiak, 1999; Janczak & Idemori, 2001a,b, 2002; Janczak, 2003). Recently, we reported two Nb^{V} -diphthalocyaninate complexes, containing two inter-ring σ C—C bonds, obtained under IBr vapour (Janczak & Kubiak, 2003), and an $[\text{SbPcCl}]$ complex obtained under ICl vapour (Janczak & Kubiak, 2001).

Isomorphous triclinic crystals of $[\text{SnPcCl}_2]$, (Ia), and $[\text{GePcCl}_2]$, (IIa), have been obtained directly from the reac-

tions of powdered Sn and Ge, respectively, with phthalonitrile under a stream of ICl vapour at ~ 433 K, while at ~ 453 K, the monoclinic modifications of these complexes, (Ib) and (IIb), are formed (Kubiak & Janczak, 2003). We report here the crystal structures of the triclinic forms of $[\text{SnPcCl}_2]$, (Ia), and $[\text{GePcCl}_2]$, (IIa), and the monoclinic form of $[\text{GePcCl}_2]$, (IIb).



$M = \text{Sn}$ (Ia) – triclinic, (Ib) – monoclinic
 $M = \text{Ge}$ (IIa) – triclinic, (IIb) – monoclinic

Crystals of (I) and (II) are composed of separate but interacting $[\text{SnPcCl}_2]$ and $[\text{GePcCl}_2]$ molecules (Fig. 1). The central Sn [in (Ia)] and Ge [in (IIa) and (IIb)] atoms are six-coordinated by four isoindole N atoms of the phthalocyaninato(2-) (Pc) macrocyclic ligand and by two Cl atoms (in a *trans* geometry) in a slightly distorted square bipyramid. This geometry agrees with the interpretation of the spectra of these compounds and related (4+2)-coordinated metallophthalocyaninate complexes (O'Rourke & Curran, 1970; Fujiki *et al.*, 1986). In both cases, the slightly buckled Pc ring resides on a crystallographic inversion centre. The largest displacements from the N_4 -isoindole plane are observed for the outermost C atoms, C4 and C5, which are displaced by ~ 0.53 , ~ 0.42 and ~ 0.21 Å in (Ia), (IIa) and (IIb), respectively. The Sn^{IV} and Ge^{IV} atoms are located at the centre of the N_4 -isoindole square. The Sn—N and Ge—N distances in (Ia) and (IIa) are comparable to those found in (Ib) (Rogers & Osborn, 1971) and (IIb), as well as to the distances observed in other Sn and Ge phthalocyaninate complexes (Krämer, 1985; Ejsmont & Kubiak, 1997; Janczak & Kubiak, 1999c; Janczak, Razik & Kubiak, 1999).

In (Ia) and (IIa), the axially coordinated Cl atoms are at comparable distances from the Sn and Ge atoms [2.470 (1) Å in (Ia) and 2.475 (1) Å in (IIa); Tables 1 and 2]. However, in the monoclinic modifications of these complexes, the axial

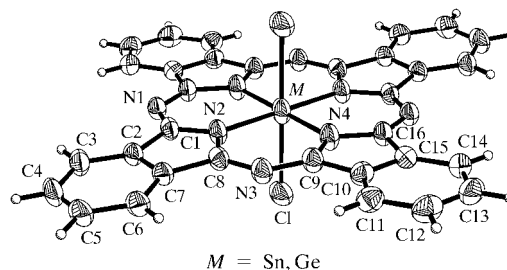


Figure 1
A view of the molecular structure of (I) and (II), showing displacement ellipsoids at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

Sn—Cl and Ge—Cl distances are different, viz. 2.448 (2) Å in (Ib) (Rogers & Osborn, 1971) and 2.299 (1) Å in (IIb) (Table 3). Thus, in the triclinic modification, the Ge—Cl bond is longer than that in the monoclinic modification, which indicates the different character of the Ge—Cl bond in these forms; the longer Ge—Cl bond in the triclinic form is more ionic than the shorter bond in the monoclinic modification. The Sn—Cl bond lengths in (Ia) and (Ib) are comparable, which implies that these bonds have the same character in both forms. The differences between the Ge—Cl bonds of (IIa) and (IIb) are consistent with far-IR spectroscopy, which shows the Ge—Cl band at a higher frequency for the monoclinic modification (shorter Ge—Cl bond) than for the triclinic modification (longer Ge—Cl bond), while the Sn—Cl vibrational bands are observed at almost the same frequency in (Ia) and (Ib) (Kubiak & Janczak, 2003).

The most remarkable feature of (Ia) and (IIa) is that the Pc macrocycles are not staggered but slipped. In the monoclinic form, the molecules are additionally inclined, the angle between the N₄-isindole planes of two neighbouring Pc macrocycles being 19.2 (2)°. In the unit cell (Figs. 2a and 2b) there are significant intermolecular C14—H14...Clⁱ [symmetry code: (i) 1 - x, 1 + y, 1 - z] hydrogen-bonding interactions, with H14...Clⁱ distances of 2.83 and 2.89 Å, C14...Clⁱ distances of 3.679 (2) and 3.747 (2) Å, and C4—H4...Clⁱ angles of 153 and 154° in (Ia) and (IIa), respectively. The corresponding C4—H4...Clⁱⁱ [symmetry code: (ii) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$] hydrogen-bonding interactions in (IIb) exhibit H4...Clⁱⁱ distances of 2.87 Å, C4...Clⁱⁱ distances of 3.579 (2) Å and C4—H4...Clⁱⁱ angles of 134°. This interaction

causes a slight tilt of the Sn—Cl [1.3 (1)° in (Ia) and 2.5° in (Ib); Rogers & Osborn, 1971] and Ge—Cl [0.9 (1)° in (IIa) and 1.2 (1)° in (IIb)] axes from the normal to the N₂/M/N₄ plane (M = Sn and Ge). The C—H...Cl intermolecular interactions link the [SnPcCl₂] and [GePcCl₂] molecules into two-dimensional sheets, the distance between the halves of the Pc rings of neighbouring molecules being less than ~3.4 Å. This value indicates a π - π interaction between the phenyl rings of neighbouring Pc macrocycles, since this distance is shorter than the van der Waals distance for an aromatic C atom (Pauling, 1960). This π - π interaction (Figs. 2a and 2b) is significant and, together with the van der Waals and C—H...Cl interactions, is responsible for the molecular arrangement and the crystal packing. Such intermolecular π - π interactions are a common feature in the field of phthalocyanine chemistry, since the molecules of phthalocyanine and its metal complexes tend to aggregate as a result of strong π - π intermolecular interactions (Nevin *et al.*, 1987; Terekhov *et al.*, 1996; Isago *et al.*, 1997, 1998). The solubility of the [SnPcCl₂] and [GePcCl₂] complexes in polar solvents, such as water, methanol and ethanol, is insignificant, but the complexes are slightly soluble in pyridine, dimethylformamide, dimethyl sulfoxide, tetrahydrofuran and high-boiling aromatic solvents, such as chloronaphthalene or quinoline. As can be seen from the crystal structures of [SnPcCl₂] and [GePcCl₂], molecules with polar Sn—Cl and Ge—Cl bonds on both sides of the Pc ring are surrounded by the hydrophobic peripheral phenyl rings of neighbouring molecules, which prevent the interactions of polar solvents with the polar Sn—Cl or Ge—Cl bonds, thus leading to the limited solubility of the crystals in polar solvents.

Experimental

Triclinic and monoclinic crystals of [SnPcCl₂] and [GePcCl₂] were obtained by the direct reaction of pure powdered tin or germanium with phthalonitrile under a stream of ICl vapour at ~433 and ~453 K, respectively (Kubiak & Janczak, 2003). At these temperatures, the liquid 1,2-dicyanobenzene undergoes catalytic tetramerization, with the simultaneous transfer of two electrons from the Sn or Ge atom to the Pc ring; the other two electrons are transferred from the Sn or Ge atom to ICl to form I⁻ and Cl⁻ ions. Crystals of [SnPcCl₂] and [GePcCl₂] were grown, together with crystals of their iodine analogues, viz. [SnPcI₂] and [GePcI₂].

Triclinic compound (Ia)

Crystal data

[Sn(C₃₂H₁₆N₈)Cl₂]
 $M_r = 702.12$
 Triclinic, $P\bar{1}$
 $a = 7.363$ (1) Å
 $b = 8.676$ (2) Å
 $c = 11.048$ (2) Å
 $\alpha = 74.21$ (3)°
 $\beta = 80.33$ (3)°
 $\gamma = 85.47$ (3)°
 $V = 669.1$ (2) Å³
 $Z = 1$
 $D_x = 1.743$ Mg m⁻³

$D_m = 1.74$ Mg m⁻³
 D_m measured by flotation in
 CHCl₃/CHBr₃
 Mo K α radiation
 Cell parameters from 2604
 reflections
 $\theta = 3.7$ – 27.6 °
 $\mu = 1.20$ mm⁻¹
 $T = 293$ (2) K
 Parallelepiped, violet
 0.36 × 0.18 × 0.12 mm

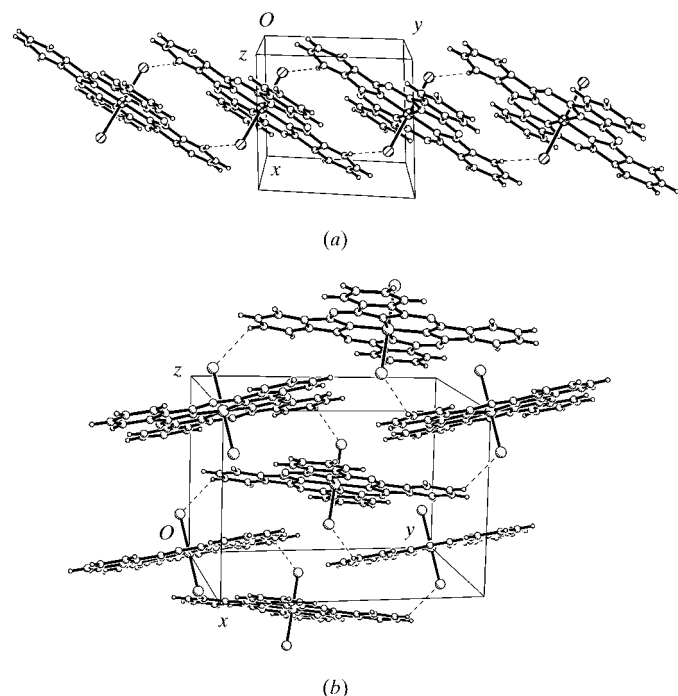


Figure 2

A view of the molecular packing in the unit cell, showing the intermolecular C—H...Cl interactions between the [M^{IV}PcCl₂] molecules [M = Sn in (I) and Ge in (II)] in the triclinic form (a) and in the monoclinic form (b).

Data collection

Kuma KM-4 CCD area-detector diffractometer	2968 independent reflections
ω scans	2604 reflections with $I > 2\sigma(I)$
Absorption correction: analytical face-indexed (<i>SHELXTL</i> ; Sheldrick, 1990)	$R_{\text{int}} = 0.025$
$T_{\text{min}} = 0.673$, $T_{\text{max}} = 0.870$	$\theta_{\text{max}} = 27.6^\circ$
6020 measured reflections	$h = -9 \rightarrow 9$
	$k = -10 \rightarrow 11$
	$l = -12 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2 + 0.8816P]$
$R[F^2 > 2\sigma(F^2)] = 0.030$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.078$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.53 \text{ e } \text{\AA}^{-3}$
2968 reflections	$\Delta\rho_{\text{min}} = -0.54 \text{ e } \text{\AA}^{-3}$
197 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (\AA , $^\circ$) for triclinic (Ia).

Sn—Cl	2.470 (1)	Sn—N4	2.047 (3)
Sn—N2	2.063 (2)		
N2—Sn—Cl	91.36 (8)	N4—Sn—N2 ⁱⁱⁱ	89.91 (10)
N4—Sn—Cl	89.42 (8)	N4—Sn—Cl ⁱⁱⁱ	90.58 (8)

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

Triclinic compound (IIa)

Crystal data

[Ge(C ₃₂ H ₁₆ N ₈)Cl ₂]	$D_m = 1.63 \text{ Mg m}^{-3}$
$M_r = 656.02$	D_m measured by flotation in CHCl ₃ /CHBr ₃
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.3650 (10) \text{ \AA}$	Cell parameters from 3082 reflections
$b = 8.704 (2) \text{ \AA}$	$\theta = 2.8\text{--}28^\circ$
$c = 10.966 (2) \text{ \AA}$	$\mu = 1.39 \text{ mm}^{-1}$
$\alpha = 73.85 (3)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 80.61 (3)^\circ$	Parallelepiped, violet
$\gamma = 86.39 (3)^\circ$	$0.36 \times 0.25 \times 0.18 \text{ mm}$
$V = 666.1 (2) \text{ \AA}^3$	
$Z = 1$	
$D_x = 1.635 \text{ Mg m}^{-3}$	

Data collection

Kuma KM-4 CCD area-detector diffractometer	3082 independent reflections
ω scans	1936 reflections with $I > 2\sigma(I)$
Absorption correction: analytical face-indexed (<i>SHELXTL</i> ; Sheldrick, 1990)	$R_{\text{int}} = 0.013$
$T_{\text{min}} = 0.634$, $T_{\text{max}} = 0.787$	$\theta_{\text{max}} = 28.0^\circ$
5657 measured reflections	$h = -9 \rightarrow 9$
	$k = -11 \rightarrow 10$
	$l = -14 \rightarrow 13$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\text{max}} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.053$	$\Delta\rho_{\text{max}} = 0.35 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.151$	$\Delta\rho_{\text{min}} = -0.29 \text{ e } \text{\AA}^{-3}$
$S = 1.06$	Extinction correction: <i>SHELXL97</i>
3082 reflections	Extinction coefficient: 0.110 (10)
197 parameters	
H-atoms parameters constrained	
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2 + 0.2297P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 2

Selected geometric parameters (\AA , $^\circ$) for triclinic (IIa).

Ge—Cl	2.475 (1)	Ge—N4	1.968 (3)
Ge—N2	1.979 (3)		
N2—Ge—Cl	89.09 (10)	N4 ⁱⁱⁱ —Ge—N2	89.83 (13)
N4—Ge—Cl	90.71 (11)	N2—Ge—N4	90.17 (13)

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

Monoclinic compound (IIb)

Crystal data

[Ge(C ₃₂ H ₁₆ N ₈)Cl ₂]	D_m measured by flotation in CHCl ₃ /CHBr ₃
$M_r = 656.02$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 2102 reflections
$a = 9.124 (2) \text{ \AA}$	$\theta = 3.4\text{--}29^\circ$
$b = 14.810 (3) \text{ \AA}$	$\mu = 1.36 \text{ mm}^{-1}$
$c = 10.233 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 98.50 (3)^\circ$	Parallelepiped, violet
$V = 1367.6 (5) \text{ \AA}^3$	$0.30 \times 0.22 \times 0.18 \text{ mm}$
$Z = 2$	
$D_x = 1.593 \text{ Mg m}^{-3}$	
$D_m = 1.59 \text{ Mg m}^{-3}$	

Data collection

Kuma KM-4 CCD area-detector diffractometer	3561 independent reflections
ω scans	2102 reflections with $I > 2\sigma(I)$
Absorption correction: analytical face-indexed (<i>SHELXTL</i> ; Sheldrick, 1990)	$R_{\text{int}} = 0.040$
$T_{\text{min}} = 0.687$, $T_{\text{max}} = 0.792$	$\theta_{\text{max}} = 29.0^\circ$
12 868 measured reflections	$h = -12 \rightarrow 10$
	$k = -20 \rightarrow 20$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.2270P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 1.04 \text{ e } \text{\AA}^{-3}$
3561 reflections	$\Delta\rho_{\text{min}} = -0.33 \text{ e } \text{\AA}^{-3}$
196 parameters	
H-atom parameters constrained	

Table 3

Selected geometric parameters (\AA , $^\circ$) for monoclinic (IIb).

Ge—Cl	2.299 (1)	Ge—N4	1.954 (2)
Ge—N2	1.959 (2)		
N2—Ge—Cl	88.83 (6)	N4—Ge—N2 ^{iv}	89.98 (8)
N4—Ge—Cl	89.80 (6)	N4—Ge—Cl ^{iv}	90.20 (6)
N2—Ge—N4	90.02 (8)	N2—Ge—Cl ^{iv}	91.17 (6)

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

The 960 images for six different runs covered more than 95% of the Ewald sphere. All H atoms were treated as riding, with C—H distances of 0.93 \AA .

For all three compounds, data collection: *KM-4 Software* (Kuma, 2000); cell refinement: *KM-4 Software*; data reduction: *KM-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1161). Services for accessing these data are described at the back of the journal.

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