

## Structure of Bis(phthalocyaninato)praseodymium ( $\beta$ 1 Phase)

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(Received 16 July 1990; accepted 5 March 1991)

**Abstract.**  $[\text{Pr}(\text{C}_{32}\text{H}_{16}\text{N}_8)_2]$ ,  $M_r = 1165.9$ , monoclinic,  $I2/c$ ,  $a = 13.383$  (2),  $b = 14.154$  (3),  $c = 25.644$  (7) Å,  $\beta = 83.32^\circ$ ,  $V = 4824.6$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.605$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.7093$  Å,  $\mu = 1.07$  mm<sup>-1</sup>,  $F(000) = 2348$ , room temperature,  $R = 0.026$  for 3562 observed reflections. The Pr atom has a distorted antiprism coordination with four N atoms from each of two ligands. A new type of molecular packing (hereafter the  $\beta$ 1 phase) is found in which the sandwich-like molecules are shifted in alternating directions from the molecular stack axis by 2.6 Å.

**Introduction.** This work is part of a series of investigations of the crystal and molecular structures of oxidized lanthanide (bis)phthalocyanines. Their electrical conductivity is thought to be related to their columnar structure which is favorable for quasi-one-dimensional conduction. The existence of several polymorphs for different (bis)phthalocyanines as well as for specific lanthanide derivatives (Darovskikh, Moskalev, Frank-Kamenetskaja, Sibilev, Trunov & Shapkin, 1982) indicates a complex phase diagram. The electrical and magnetic properties are likely to be strongly polymorph dependent.

**Experimental.** The title compound pcPrpcH, pc = phthalocyaninato =  $[\text{C}_{32}\text{H}_{16}\text{N}_8]^{2-}$ , has been synthesized by a well known method (Moskalev & Kirin, 1970). Crystals of a new phase have been prepared electrochemically (Moskalev, Shapkin & Darovskikh, 1979). They are supposed to have a composition pcPrpc<sub>ox</sub>, where pc<sub>ox</sub> =  $[\text{C}_{32}\text{H}_{16}\text{N}_8]^-$ . A dark prismatic crystal was cut and ground to a sphere of radius 0.2 mm. Enraf–Nonius CAD-4 diffractometer; cell parameters from least-squares treatment of setting angles of 25 reflections with  $2\theta < 40^\circ$ . No absorption correction; 4070 reflections with  $2\theta < 51^\circ$  measured in the range  $h: -15 \rightarrow 15$ ,  $k:$

$0 \rightarrow 16$ ,  $l: 0 \rightarrow 30$ ; no significant intensity variation (3%) for three standard reflections (532, 327, 20,1,2) recorded every 3 h. 3562 observed reflections with  $I > 2.5\sigma_f$ . Structure solved by ‘heavy-atom’ method and refinement performed with full-matrix least squares based on  $F^2$  with NRCVAX (Gabe, Le Page, Charland & Lee, 1989). Weights based on counting statistics;  $R = 0.026$ ,  $wR = 0.025$ ,  $S = 2.46$ ;  $(\Delta/\sigma)_{\text{max}} = 0.003$ ; Positions of H atoms all calculated and refined with isotropic thermal parameters; all non-H atoms were refined anisotropically; the deepest hole in the final difference Fourier map was  $-0.410 \text{ e } \text{Å}^{-3}$  and the highest peak  $0.530 \text{ e } \text{Å}^{-3}$ . Atomic parameters are given in Table 1.\*

**Discussion.** The molecule of  $\beta$ 1-pcPrpc<sub>ox</sub>, as in  $\beta$ -pcNdpc<sub>ox</sub> (Darovskikh, Tsitsenko, Frank-Kamenetskaja, Fundamenskii & Moskalev, 1984), is located at the special crystallographic position – praseodymium occupies the site of twofold symmetry (Fig. 1). pc ligands are related by symmetry but unlike the other (bis)phthalocyanines (except the  $\alpha$ -phase crystals) (Darovskikh, Frank-Kamenetskaja & Fundamenskii, 1986) in which all pyrrole and benzene rings are tilted so as to form a saucer-shaped ligand, the rings are not all bent in the same direction from the praseodymium ion. The atoms C(27), C(28), C(29), C(30) of the benzene ring (IX) are displaced from the plane of macrocycle (I) [C(1), C(8), C(9), C(16), C(17), C(24), C(25), C(32)] toward the metal ion by 0.033 (5), 0.116 (6), 0.103 (5) and 0.021 (5) Å, respectively. The deviations from planarity are smaller than in  $\beta$ -pcNdpc<sub>ox</sub> and pcThpc

\* Lists of structure factors, anisotropic thermal parameters, full lists of bond lengths and angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54057 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent B's for non-H atoms of the title compound with e.s.d.'s in parentheses

$$B_{eq} = (8\pi^2/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

	x	y	z	$B_{eq}(\text{\AA}^2)$
Pr	0	0.157415 (18)	1/4	2.616 (9)
N(1)	0.15592 (17)	0.24115 (19)	0.13524 (9)	3.41 (11)
N(2)	0.13741 (17)	-0.06652 (17)	0.21081 (9)	3.38 (11)
N(3)	0.07897 (17)	0.07112 (18)	0.37938 (9)	3.26 (11)
N(4)	0.10552 (17)	0.37915 (17)	0.30412 (9)	3.25 (10)
N(5)	0.13271 (17)	0.09924 (17)	0.18718 (9)	3.07 (10)
N(6)	0.09816 (16)	0.02838 (17)	0.28789 (8)	3.10 (10)
N(7)	0.08932 (16)	0.21321 (17)	0.32647 (8)	2.97 (10)
N(8)	0.12308 (16)	0.28339 (17)	0.22603 (8)	3.08 (10)
C(1)	0.15281 (19)	0.14827 (24)	0.14180 (11)	3.26 (13)
C(2)	0.17321 (21)	0.08100 (23)	0.09926 (11)	3.43 (13)
C(3)	0.1899 (3)	0.0932 (3)	0.04574 (13)	4.34 (16)
C(4)	0.2066 (3)	0.0130 (3)	0.01605 (15)	5.23 (20)
C(5)	0.2076 (3)	-0.0750 (3)	0.03821 (14)	5.07 (20)
C(6)	0.1881 (3)	-0.0879 (3)	0.09106 (16)	4.41 (17)
C(7)	0.17044 (21)	-0.00824 (23)	0.12128 (11)	3.54 (14)
C(8)	0.14523 (21)	0.00513 (22)	0.17708 (11)	3.24 (13)
C(9)	0.11830 (21)	-0.05449 (21)	0.26202 (12)	3.26 (13)
C(10)	0.11871 (22)	-0.13220 (20)	0.29964 (12)	3.49 (14)
C(11)	0.1355 (3)	-0.2277 (3)	0.29402 (15)	4.59 (18)
C(12)	0.1338 (3)	-0.2822 (3)	0.33812 (16)	5.55 (21)
C(13)	0.1162 (3)	-0.2424 (3)	0.38701 (16)	5.29 (19)
C(14)	0.0991 (3)	-0.1475 (3)	0.39293 (14)	4.40 (17)
C(15)	0.10145 (22)	-0.09229 (22)	0.34852 (12)	3.47 (13)
C(16)	0.09095 (21)	0.00948 (22)	0.34000 (11)	3.31 (14)
C(17)	0.08013 (19)	0.16466 (24)	0.37237 (10)	3.24 (13)
C(18)	0.07249 (21)	0.23146 (23)	0.41599 (11)	3.34 (14)
C(19)	0.0578 (3)	0.2182 (3)	0.46910 (13)	4.31 (17)
C(20)	0.0536 (3)	0.2979 (3)	0.49984 (14)	5.23 (19)
C(21)	0.0620 (3)	0.3866 (3)	0.47882 (14)	4.92 (19)
C(22)	0.0753 (3)	0.4001 (3)	0.42558 (14)	4.16 (16)
C(23)	0.08100 (20)	0.32106 (21)	0.39435 (11)	3.22 (13)
C(24)	0.09324 (21)	0.30766 (22)	0.33768 (11)	3.14 (13)
C(25)	0.11995 (21)	0.36681 (21)	0.25239 (12)	3.34 (13)
C(26)	0.13370 (21)	0.44564 (22)	0.21557 (12)	3.37 (13)
C(27)	0.1261 (3)	0.5422 (3)	0.22126 (15)	4.42 (17)
C(28)	0.1340 (3)	0.5969 (3)	0.17662 (16)	5.16 (20)
C(29)	0.1506 (3)	0.5564 (3)	0.12788 (16)	4.91 (19)
C(30)	0.1588 (3)	0.4595 (3)	0.12209 (14)	4.35 (16)
C(31)	0.14862 (21)	0.40477 (23)	0.16660 (12)	3.44 (13)
C(32)	0.14371 (21)	0.30289 (22)	0.17427 (11)	3.18 (13)

(Darovskikh, Frank-Kamenetskaja, Fundamenskii & Golinskaja, 1985). The pyrrole nitrogen atoms N(5), N(6), N(7) and N(8) (bound to the metal) are displaced from plane (I) towards Pr by 0.06–0.14 Å, N(6) having the largest distortion. The bridge nitrogen atoms N(1), N(2), N(3) and N(4) are displaced in pairs in the opposite direction from plane (I) as in  $\beta$ -pcNdpc<sub>ox</sub>. The bond lengths and bond angles which are related by the local symmetry  $4mm$  of the pc ligand are equivalent according to a  $\chi^2$  test. The interatomic distances within the pc ligand of  $\beta$ 1-pcPrpc<sub>ox</sub> are comparable with those of  $\beta$ -pcNdpc<sub>ox</sub>. As in other (bis)phthalocyanines the metal atom occupies the center of the square antiprism formed by the eight pyrrole N atoms. The bases of the coordination polyhedron are staggered by  $\psi = 42^\circ$  ( $38^\circ$  in  $\beta$ -pcNdpc<sub>ox</sub>), but they are not parallel. The distinctive feature of the praseodymium antiprism is the inclination of the base planes towards each other (by  $2^\circ$ ). The contraction of symmetry-equivalent edges N(6)⋯N'(5) and N(5)⋯N'(6) in comparison with N(7)⋯N'(8) and N(8)⋯N'(7) by 0.19 Å results in a distortion of the polyhedron (Table 2). The

Table 2. Interatomic distances (Å) of coordination polyhedra of  $\beta$ 1-pcPrpc<sub>ox</sub> and  $\beta$ -pcNdpc<sub>ox</sub>

$M^*—N$	$\beta$ 1-pcPrpc <sub>ox</sub>	$\beta$ -pcNdpc <sub>ox</sub>
$M—N(5)$	2.400 (2)	2.48
$M—N(6)$	2.511 (2)	2.46
$M—N(7)$	2.539 (2)	2.49
$M—N(8)$	2.457 (2)	2.46
Average	2.477	2.47

$N\cdots N$	Base	
N(5)—N(6)	2.759 (3)	2.81
N(6)—N(7)	2.795 (3)	2.82
N(7)—N(8)	2.749 (3)	2.79
N(8)—N(5)	2.788 (3)	2.80
Average	2.773	2.805

$N\cdots N'$	Edge	$N\cdots N' \dagger$
N(6)—N(6)'	3.445 (4)	3.20
N(6)—N(5)'	3.241 (3)	3.42
N(7)—N(5)'	3.435 (3)	3.21
N(7)—N(8)'	3.431 (3)	3.44
N(8)—N(8)'	3.380 (4)	3.27

\*  $M$  = metal; the numbering of the N atoms is according to Fig. 2.

† The numbering of the N atoms is according to Darovskikh *et al.* (1984).

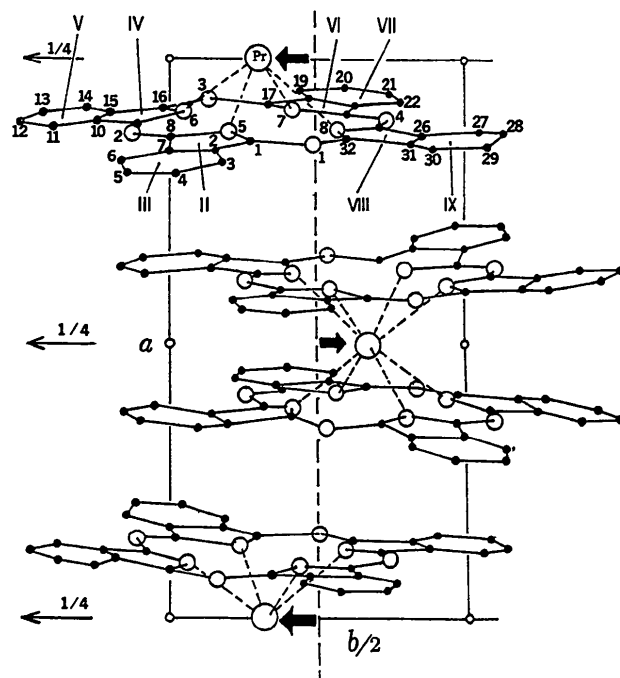


Fig. 1. View of layer ( $z = 0.5$ ) of the  $\beta$ 1-pcPrpc<sub>ox</sub> structure along [001]. C and N atoms are represented by shaded and opened spheres of arbitrary size, respectively. The heavy arrows emphasize the displacement of the molecule from the molecular stack axis.

distance  $h$  between the centers of the bases (Fig. 2) is equal to 3.0 Å. The distance between parallel pcPrpc<sub>ox</sub> molecules along the [100] direction is 6.7 Å, but in contrast to the  $\alpha$ -phase structure the units are not coaxial. The adjacent molecules along  $a$  are displaced in opposite directions along the  $b$  axis by 2.6 Å (Fig. 1). The choice of the non-conventional space group  $I2/c$  reveals the ratio  $T_{[100]}^{\beta 1} = 2T_{[001]}^{\alpha}$  and

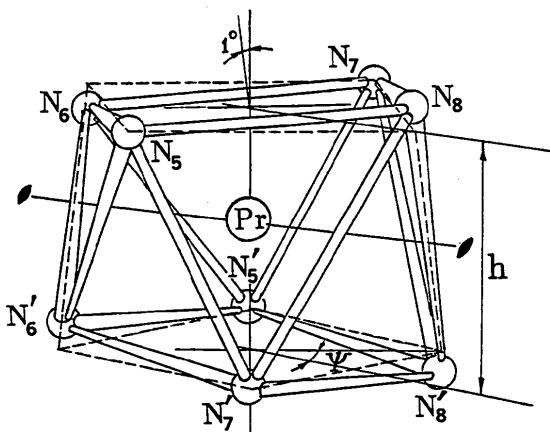


Fig. 2. The coordination polyhedron of praseodymium in the structure of the  $\beta$ 1 phase. The undistorted square antiprism is represented by a dashed line. The angle is shown between the normals to the base planes of distorted and undistorted polyhedra.

$T_{[100]}^{\beta 1} = T_{[100]}^{\alpha}$  between the  $\beta$ 1 phase and the  $\alpha$  phase of the neodymium derivative, indicating the close structural relationship of these phases.

We thank Professor P. Coppens for valuable discussions during the preparation of this paper. This work was supported by the National Science Foundation under Grant No. CHE8711736 and by the US Department of Energy under Grant No. DEF60286ER5231.

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*Acta Cryst.* (1991). **C47**, 1838–1842

## Structures of Zinc(II) and Copper(II) Chloride *N,N*-Dimethylformamide Solvates

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(Received 21 January 1991; accepted 6 March 1991)

**Abstract.** (I) Dichlorobis(*N,N*-dimethylformamide)-zinc(II),  $[\text{ZnCl}_2(\text{C}_3\text{H}_7\text{NO})_2]$ ,  $M_r = 282.5$ , monoclinic,  $C2/c$ ,  $a = 13.296(4)$ ,  $b = 13.254(4)$ ,  $c = 14.702(6)$  Å,  $\beta = 113.76(3)^\circ$ ,  $V = 2371(2)$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.583$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu(\text{Mo } K\alpha) = 25.5$  cm<sup>-1</sup>,  $F(000) = 1152$ ,  $T = 226$  K,  $R = 0.035$  for 2825 independent reflections. The Zn atom has a tetrahedral environment of two O atoms from two *N,N*-dimethylformamide (DMF) molecules and two Cl atoms, with Zn—O distances of 2.003(2) and 1.993(2) Å and Zn—Cl distances of 2.203(1) and 2.214(1) Å. (II) Di- $\mu$ -chloro-bis[chlorobis(*N,N*-

dimethylformamide)copper(II)],  $[\text{CuCl}_2(\text{C}_3\text{H}_7\text{NO})_2]_2$ ,  $M_r = 561.3$ , monoclinic,  $P2_1/n$ ,  $a = 11.568(5)$ ,  $b = 11.617(7)$ ,  $c = 8.992(4)$  Å,  $\beta = 111.87(5)^\circ$ ,  $V = 1121(1)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.662$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu(\text{Mo } K\alpha) = 24.1$  cm<sup>-1</sup>,  $F(000) = 572$ ,  $T = 265$  K,  $R = 0.054$  for 2577 independent reflections. The structure consists of centrosymmetric chlorine-bridged dimers, the bridging Cu—Cl distance being 2.661(2) Å. The coordination around copper is distorted tetragonal pyramidal with two *cis* O atoms [Cu—O = 1.973(3) and 1.989(3) Å] and two Cl atoms [Cu—Cl = 2.247(2) and 2.284(1) Å] in the basal plane and the bridging Cl atom axial. The Cu...Cu separation in the dimer is 3.613(2) Å. In

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