Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A low-temperature polymorph of [5,10,15,20-*meso*-tetrakis(4-chlorophenyl)porphyrinato-$\kappa^4 N$]zinc(II) nitrobenzene clathrate

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Received 30 June 2003
Accepted 1 July 2003
Online 10 July 2003

The title compound, $[Zn(C_{44}H_{24}Cl_4N_4)]\cdot C_6H_5NO_2$, crystallizes in several polymorphic forms. We report in this paper the third known polymorph of this compound, which can be obtained at temperatures below *ca* 195 K.

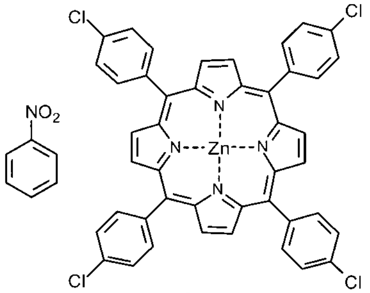
Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.005 Å
R factor = 0.053
wR factor = 0.134
Data-to-parameter ratio = 16.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In earlier studies, we reported two different room-temperature polymorphs of the title compound, (I), namely a monoclinic form [$P2_1$, $Z = 2$; CSD (Allen, 2002) refcode ZITLUJ01; Goldberg *et al.*, 1994] and a triclinic form ($P\overline{1}$, $Z = 4$, $Z' = 2$; CSD refcode ZITLUJ; Krupitsky *et al.*, 1995). Semi-empirical calculations have indicated only minor differences of 0.4–0.8 kJ mol^{-1} between the two crystal structures (Krupitsky *et al.*, 1995).


(I)

The third polymorph described below was obtained by cooling crystals of the triclinic form below *ca* 195 K. The low-temperature structure is also triclinic ($P\overline{1}$), but with $Z = 2$ and

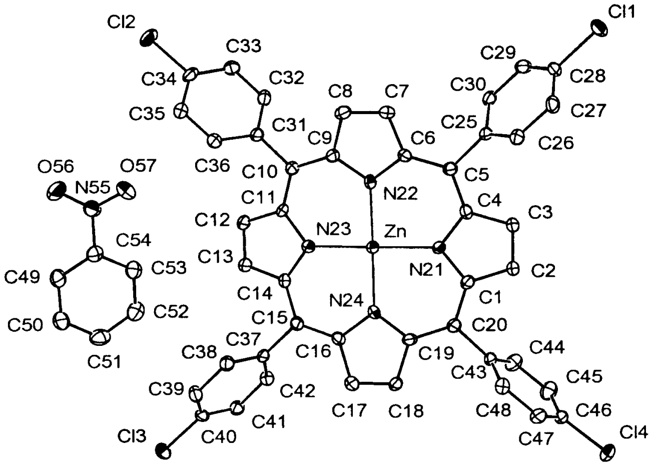


Figure 1
The molecular structure of the constituent species, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

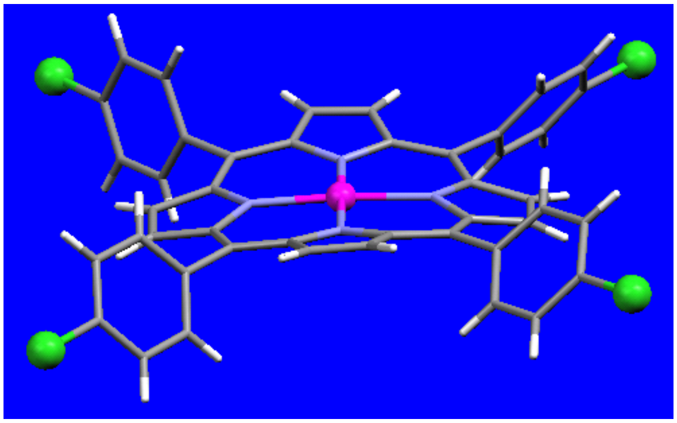


Figure 2
Perspective view of the porphyrin species, showing the four-saddle conformation. The Zn and Cl atoms are represented by small spheres. Color code: C gray, H white, Cl green, N light blue and Zn purple.

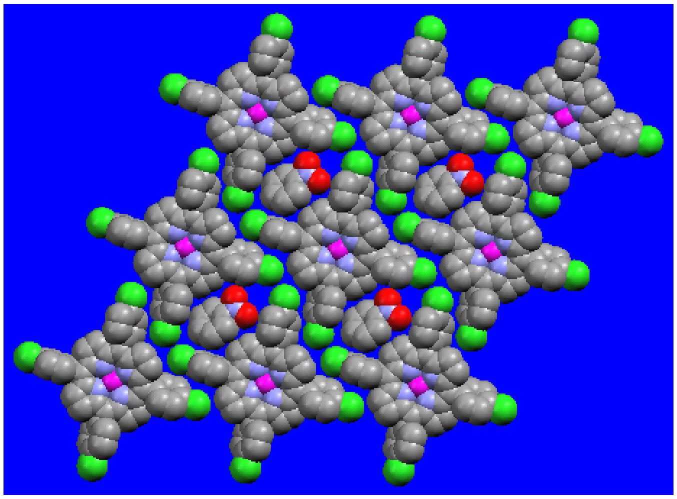


Figure 3
Space-filling illustration of a single porphyrin layer with the guest nitrobenzene molecules conveniently included within the interporphyrin voids. These layers are normal to the [$1\overline{1}0$] direction. H atoms have been omitted for clarity and the O atoms are red.

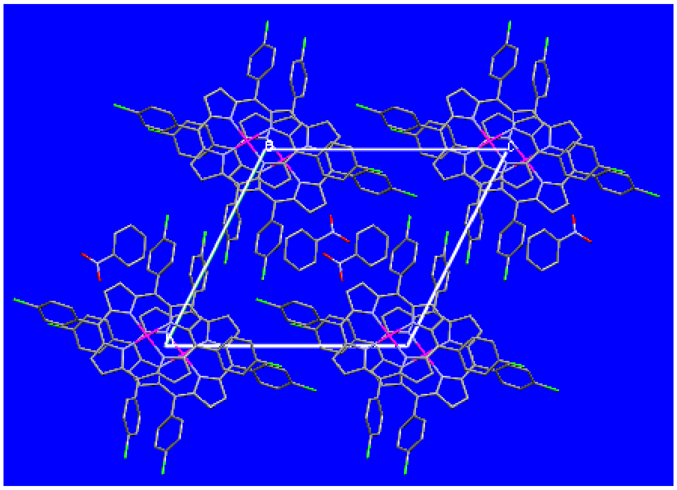


Figure 4
View of the crystal structure, approximately down *a* (*c* is horizontal), illustrating the offset between parallel layers displaced along the *a* axis of the crystal, and location of the nitrobenzene guest molecules in interporphyrin channels which propagate along *a*.

$Z' = 1$. It has been precisely analysed from data collected at *ca* 110 K (Fig. 1). Gradual cooling of the crystals from 298 to 110 K, monitored by unit-cell determination at temperature intervals of 10 K (5 K near the transition point) and examination of the diffraction pattern frames, revealed that the phase transformation occurs at 190–200 K. It is continuous and reversible, and it can be detected by the appearance and disappearance on the detector of the relevant reflections corresponding to the two different phases. The phase transformation occurs without any apparent change in the crystal morphology, but is associated with an increase of the crystal mosaicity in the vicinity of the transition temperature. Interestingly, all three polymorphs reveal similar features of the porphyrin molecular structure (Fig. 2; slight saddle conformation) and the porphyrin–porphyrin interaction scheme (Fig. 3). The latter is characterized by Cl···Cl contact distances of 3.638 (3) and 3.710 (3) Å, and an antiparallel arrangement of the proximate C—Cl dipoles of adjacent molecules. The zinc ion is four-coordinate in all structures. The three polymorphs differ slightly in the relative disposition of the nitrobenzene guest molecule with respect to the porphyrin host lattice. In this structure, the porphyrin and nitrobenzene components are nearly coplanar. Fig. 3 illustrates a typical layered organization of the component porphyrin and nitrobenzene species, and the convenient accommodation of the nitrobenzene guest within the interporphyrin voids. Adjacent layers, which stack parallel along the [$1\overline{1}0$] direction, are related by the crystallographic inversion. These layers pack in the crystal in an offset manner (Fig. 4), revealing characteristic features of the 'porphyrin sponges' described previously in the literature for the tetraarylporphyrin species (Byrn *et al.*, 1991, 1993; Krishna Kumar *et al.*, 1998). The average perpendicular distance between the partly overlapping porphyrin macrocycles is 3.930 (4) Å.

Experimental

Crystals of the title compound were obtained by dissoving the zinc–tetra(4-chlorophenyl)porphyrin in a mixture of THF and nitrobenzene, followed by slow evaporation of the solvent at ambient temperature.

Crystal data

$[Zn(C_{44}H_{24}Cl_4N_4)]\cdot C_6H_5NO_2$
$M_r = 938.95$
Triclinic, $P\overline{1}$
$a = 8.9390$ (4) Å
$b = 15.2220$ (4) Å
$c = 16.8100$ (6) Å
$\alpha = 115.7470$ (19)°
$\beta = 97.316$ (2)°
$\gamma = 96.671$ (2)°
$V = 2005.47$ (13) Å^3

$Z = 2$
$D_x = 1.555$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8956 reflections
$\theta = 2.3$–27.5°
$\mu = 0.93$ mm^{-1}
$T = 110$ (2) K
Prism, red
0.30 × 0.15 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.768$, $T_{\max} = 0.955$
19 096 measured reflections
8956 independent reflections
5732 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 27.5^\circ$
$h = -11 \rightarrow 11$
$k = -19 \rightarrow 19$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.134$
$S = 1.01$
8956 reflections
559 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.40$ e Å^{-3}
$\Delta\rho_{\min} = -0.65$ e Å^{-3}

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski, 1985); data reduction: *DENZO*; program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *MERCURY* (Cambridge Crystallographic Data Centre, 2002); software used to prepare material for publication: *SHELXL*97.

This research was supported in part by The Israel Science Foundation, founded by the Israel Academy of Sciences and Humanities (grant No. 68/01), as well as by grant No. 1999082 from the US–Israel Binational Science Foundation (BSF), Jerusalem, Israel.

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