Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

[5,10,15,20-Tetrakis(4-pyridyl)porphyrinato]zinc(II) acetic acid clathrate, and its unique polymeric honeycomb architecture

Sumod George and Israel Goldberg*

School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel

Correspondence e-mail:
goldberg@chemsg7.tau.ac.il

Received 7 June 2005
Accepted 10 June 2005
Online 6 July 2005

The crystal structure of the title compound, [Zn($C_{40}H_{24}N_8$)]·1.6$C_2H_4O_2$ has been determined at *ca* 110 K. The centrosymmetric metalloporphyrin compound forms a self-assembled honeycomb architecture, with open channels extending parallel to the *c* axis of the unit cell. The compound crystallizes as an acetic acid clathrate. The guest species, which are included in the interporphyrin channels, hydrogen bond to the porphyrin framework.

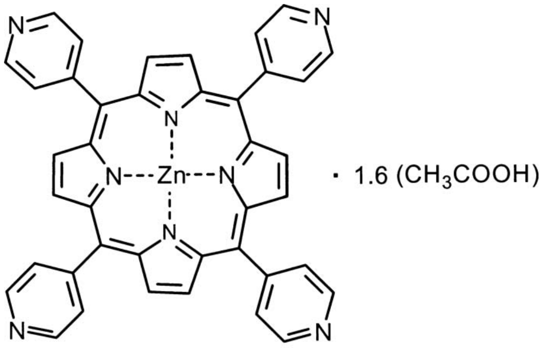
Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.055
wR factor = 0.165
Data-to-parameter ratio = 17.3

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

Comment

The supramolecular self-assembly of metallated *meso*-tetrapyridylporphyrin scaffolds (MTPyPs) may lead to the formation of one-, two- and three-dimensional multiporphyrin architectures (Krupitsky *et al.*, 1994; Lin, 1999; Pan *et al.*, 2002). Of particular interest are the three-dimensional frameworks which reveal an open honeycomb structure, wherein every metalloporphyrin building block coordinates to four neighboring units (Krupitsky *et al.*, 1994; Lin, 1999). The metal ion core (Zn, Co or Mn) is six-coordinate and binds axially from above and below to the pyridyl functions of two adjacent porphyrins. Two of the *trans*-related pyridyl groups coordinate to the metal centers of two other units. This binding pattern, obtained by crystallizing the MTPyP from small polar and protic solvents, leads to crystallization of the corresponding compounds in the trigonal space group $R\overline{3}$ (Krupitsky *et al.*, 1994; Lin, 1999), yielding a robust single-framework coordination polymer that resembles a molecular-sieve material. The metalloporphyrin molecules are arranged around the threefold axes of the crystal, creating 6 Å wide interporphyrin channel voids around them. The latter promote incorporation of the crystallization solvent into the crystal structure.



(I)

Only a small number of examples of this structure type are known, namely ZnTPyP with water and with a mixture of methanol and water (Krupitsky *et al.*, 1994), CoTPyP with a

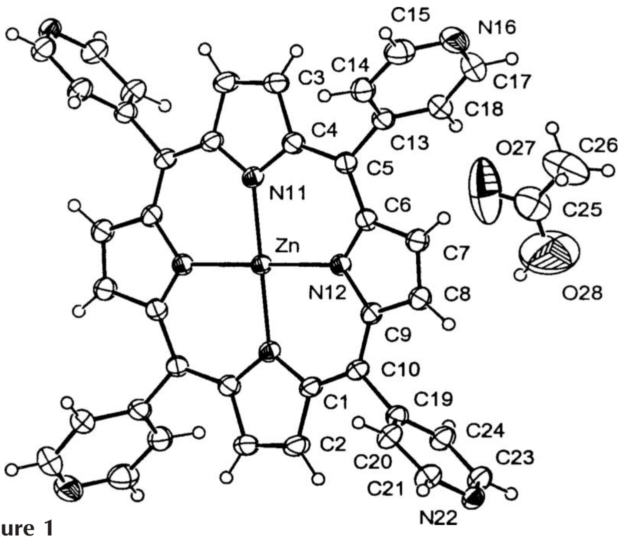


Figure 1
Molecular structure of (I), showing the atom labeling scheme. Displacement ellipsoids are shown at the 40% probability level at *ca* 110 K. The porphyrin molecule resides on a crystallographic inversion center at ($\frac{1}{6}$, $\frac{1}{3}$, $\frac{1}{3}$).

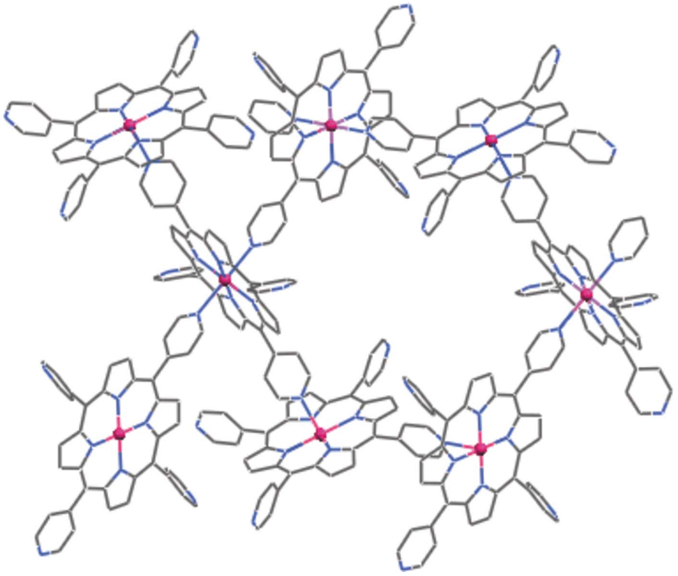


Figure 2
Illustration of the coordination environment of the ZnTPyP unit and the supramolecular polymerization around the trigonal axis. Color code: C gray, N blue, Zn pink. H atoms have been omitted for clarity.

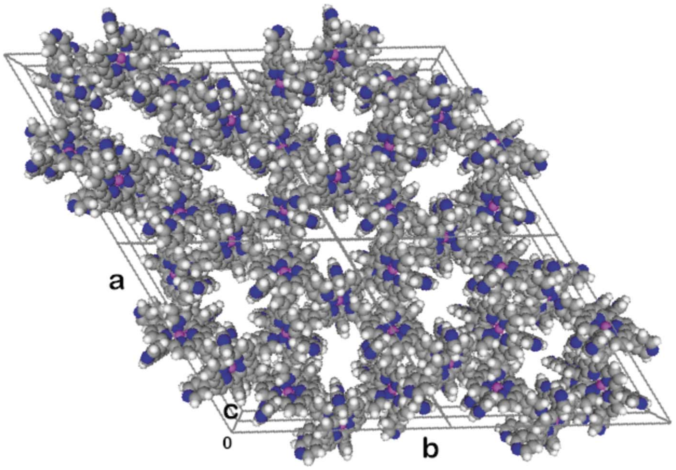


Figure 3
Space-filling illustration of the crystal structure, viewed down the *c* axis of the unit cell. Eight unit cells are shown. Note the honeycomb architecture of the metalloporphyrin framework, and the channel voids that perforate the porphyrin framework along this axis. The pyridyl functions, which outline the channels walls, point alternately up and down the channels. In the crystal structure, they are hydrogen bonded to the included acetic acid solvent molecule (omitted for clarity). Color code: C gray, N blue, Zn pink, H white.

mixture of acetic acid and water, and MnTPyP with water and with a mixture of ethanol and water (Lin, 1999). These five crystal structures are isomorphous, and reveal identical modes of the interporphyrin self-assembly and similar 'porosity' features. During our continuing search for new porphyrin-based zeolite analogs (Goldberg, 2005) another crystal structure of this type was obtained, namely the title compound, (I), a clathrate of ZnTPyP with acetic acid.

The molecular structure of (I) at *ca* 110 K is illustrated in Fig. 1. The interporphyrin self-assembly is propagated by zinc-to-pyridyl ligations. Every metalloporphyrin monomer utilizes two *trans*-related pyridyl arms to associate with the metal center of two adjacent porphyrins along one axis, while its zinc ion links to two pyridyl functions of other units approaching from both sides of the molecular framework along a roughly perpendicular axis (Fig. 2). Propagation of this inter-pophyrin binding throughout the crystal structure yields a unique honeycomb organization of the porphyrin units (Figs. 2 and 3). The crystal structure thus consists of a single-framework coordination polymer of ZnTPyP (Krupitsky *et al.*, 1994), which is perforated by channel voids around the threefold symmetry axes. The van der Waals diameter of these voids is about 6 Å, large enough to entrap various small molecular guests. The channel walls are lined with pyridyl functions, which do not coordinate to the metal centers (Fig. 3). Instead, they are solvated by the acetic acid solvent that occupies the channels, forming N22(pyridyl)$\cdots$HAc hydrogen bonds at 2.790 (8) Å. Incomplete occupancy (refined as 0.8) and partial disorder characterize the acetic acid species in this structure. This seem to have little effect on the structural integrity of the open supramolecular porphyrin organization, as the latter is preserved even at high temperatures in the absence of crystallization solvent (Lin, 1999). The occurrence of the unique honeycomb polymeric organization with six-coordinate zinc ions in the porphyrin core, (though zinc ions usually reveal weak propensity for octahedral coordination), further attests to the thermodynamic stability of the observed multi-porphyrin architecture.

Experimental

Tetra(4-pyridyl)porphyrin (MidCentury Chemicals) was mixed thoroughly with zinc diperchlorate hexahydrate (Aldrich) in a 1:1 ratio. The resulting mixture was dissolved in glacial acetic acid, with a few drops of methanol and dimethyl formamide to enhance solubility. The solution was set aside for crystallization at room temperature, yielding red–violet crystals suitable for X-ray diffraction analysis.

Crystal data

$[Zn(C_{40}H_{24}N_8)]\cdot 1.6C_2H_4O_2$
$M_r = 778.79$
Trigonal, $R\overline{3}$
$a = 33.0359$ (2) Å
$c = 9.0191$ (3) Å
$V = 8524.4$ (3) Å^3
$Z = 9$
$D_x = 1.365$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8992 reflections
$\theta = 2.1$–$27.9°$
$\mu = 0.70$ mm^{-1}
$T = 110$ (2) K
Prism, red–violet
$0.25 \times 0.20 \times 0.20$ mm

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: none
21174 measured reflections
4514 independent reflections
3055 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\rm max} = 27.9°$
$h = -36 \rightarrow 36$
$k = -43 \rightarrow 43$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.165$
$S = 1.03$
4514 reflections
261 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0988P)^2 + 2.8002P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 1.38$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.47$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Zn—N12	2.063 (2)	Zn—N11	2.074 (2)
Zn—N12	2.063 (2)	Zn—N22$^{\rm i}$	2.336 (2)
Zn—N11	2.074 (2)	Zn—N22$^{\rm ii}$	2.336 (2)

Symmetry codes: (i) $-x+y+\frac{1}{3}, -x+\frac{2}{3}, z-\frac{1}{3}$; (ii) $x-y, x, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O28—H28···N16$^{\rm iii}$	1.01	1.78	2.790 (8)	179

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

H atoms bound to C atoms were placed in idealized positions and refined as riding on their carrier atoms, with C—H distances of 0.95–0.98 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(C) and $1.5U_{\rm eq}$(C$_{\rm methyl}$). H atoms bound to the acetic acid O atom were placed in a calculated position and refined with $U_{\rm iso} = 0.10$ Å^2. The residual electron-density map shows two relatively high peaks of 1.38 e Å^{-3} at (0,0,0) and 0.91 e Å^{-3} at (0.0117,0.0364,−0.0310) (with shortest distances from one of the methyl protons of the surrounding solvent molecules of 2.43 and 2.03 Å, respectively), which may reflect presence of traces of disordered water on or around centers of inversion and between the acetic acid species. All the remaining peaks and troughs are below 0.65 e Å^{-3}.

Data collection: *COLLECT* (Nonius , 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *DIRDIF96* (Beurskens *et al.*, 1996); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *MERCURY* (Bruno *et al.*, 2002) and *DS ViewerPro* (Accelrys, 2002); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Israel Science Foundation (grant No. 254/04).

References

Accelrys (2002). *DS ViewerPro*. Version 5.0. Accelrys Inc., San Diego, CA, USA.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda S., Gould, R. O., Smits, J. M. M. & Smukalla, C. (1996). *DIRDIF96*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Goldberg, I. (2005). *Chem. Commun.* pp. 1243–1254.

Krupitsky, H., Stein, Z., Goldberg, I. & Strouse, C. E. (1994). *J. Incl. Phenom.* **18**, 177–192.

Lin, K.-J. (1999). *Angew. Chem. Int. Ed.* **38**, 2730–2732.

Nonius (1999). *COLLECT*. Nonius BV, Delft, Holland.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pan, L., Kelly, S., Huang, X. & Li, J. (2002). *Chem. Commun.* pp. 2334–2335.

Sheldrick. G. M. (1997). *SHELXL97*. University of Göttingen, Germany.