Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Hydrogen-bonded supramolecular arrays of aqua[20-(4-carboxyphenyl)-5,10,15-triphenylporphyrinato]zinc(**II**) in crystals of its nitrobenzene disolvate

Sophia Lipstman, Sankar Muniappan and Israel Goldberg*

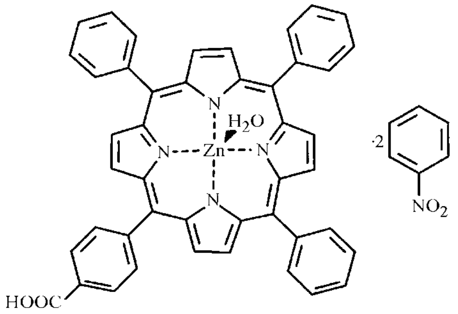
School of Chemistry, Sackler Faculty of Exact Sciences, Tel-Aviv University, Ramat-Aviv, 69978 Tel-Aviv, Israel
Correspondence e-mail: goldberg@post.tau.ac.il

Received 7 September 2006
Accepted 24 September 2006
Online 31 October 2006

Crystals of the title compound, $[Zn(C_{45}H_{28}N_4O_2)(H_2O)]\cdot 2C_6H_5NO_2$, consist of multiporphyrin supramolecular assemblies sustained by intermolecular COOH···COOH and $Zn(H_2O)$···COOH hydrogen bonds. One of the two nitrobenzene solvent molecules hydrogen bonds peripherally to these arrays.

Comment

Following our earlier studies on the designed construction of framework solids from symmetrically functionalized porphyrin building blocks of square-planar D_{4h} symmetry (Goldberg, 2005, and references therein), the supramolecular chemistry of porphyrin derivatives of reduced symmetry has also deserved considerable attention (Vinodu & Goldberg, 2003; George & Goldberg, 2006; George *et al.*, 2006). Within this context, porphyrin cores substituted with four, three or two carboxylic acid functions of complementary hydrogen-bonding capacity have been investigated (Diskin-Posner & Goldberg, 1999; Vinodu & Goldberg, 2003, 2004*a*). In most cases, the predominant propensity of these groups to associate *via* the cyclic dimeric $(COOH)_2$ hydrogen-bonding synthon has been demonstrated. In related structures based on five- or six-coordinate metalloporphyrins, wherein the core metal ion is coordinated axially to oxo- (as methanol or water) or pyridine-type ligands, hydrogen-bond formation was observed also between the lateral carboxylic acid function of one unit and the axial ligand of a neighboring porphyrin entity (George & Goldberg, 2006; Vinodu & Goldberg, 2004*b*). We report here on the self-assembly features of the title compound, (I), which bears two different substituents capable of forming O—H···O hydrogen bonds. The COOH and H_2O groups on the porphyrin can act both as H-atom donors and as acceptors, while molecules of nitrobenzene may reveal the latter functionality only. Fig. 1 shows the molecular structure of (I). The metalloporphyrin entity exhibits a slightly domed conformation typical of five-coordinate zinc–porphyrin complexes, with the central zinc ion deviating by 0.199 (1) Å from the plane of the four pyrrole N atoms towards the water ligand (*e.g.* Lipstman & Goldberg, 2006; Allen, 2002). The porphyrin core itself adopts a saddle conformation, with the pyrrole N atoms deviating alternately ±0.043 (1) Å from this plane. The bond lengths and angles in (I) (Table 1) show standard values



(I)

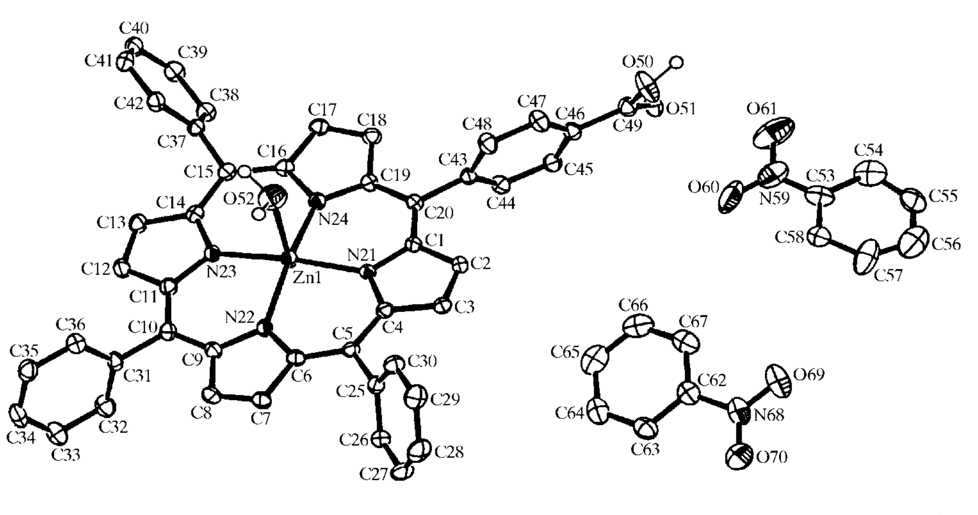


Figure 1
The molecular structure of the title compound, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level at *ca* 110 K. H atoms have been omitted, except for those involved in hydrogen bonding.

DOI: 10.1107/S0108270106038996

(Cambridge Structural Database; Version 5.27; Allen, 2002), in particular for the Zn—N(pyrrole) distances (Shmilovits *et al.*, 2004).

Fig. 2 illustrates the main hydrogen-bonding motif in (I). The porphyrin groups organize in pairs around inversion at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), with a head-to-head orientation of their carboxylic acid functions. Association within these dimers is effected by the common strong $(COOH)_2$ centrosymmetric synthon of self-complementary hydrogen bonding. It is characterized by an OH···O distance of 2.677 (3) Å. Additional weak hydrogen bonding then occurs between adjacent porphyrin dimers displaced by ±*a* with respect to the central pair. This interaction is between the axial water ligand of one species and the carboxyl C═O acceptor sites of a neighboring unit, with an OH···O distance of 2.952 (4) Å. Thus, every porphyrin molecule is involved in four hydrogen bonds, which results in the formation of one-dimensional hydrogen-bonded assemblies of interconnected porphyrin dimers (Table 2). The periphery of these chains is lined with the lipophilic phenyl substituents. In addition, however, the axial water ligands form another hydrogen bond, *via* their second H atom, to the nitro group of one of the nitrobenzene solvent molecules (containing atoms C53/O61), with an OH···O distance of 2.767 (4) Å (Table 2 and Fig. 3).

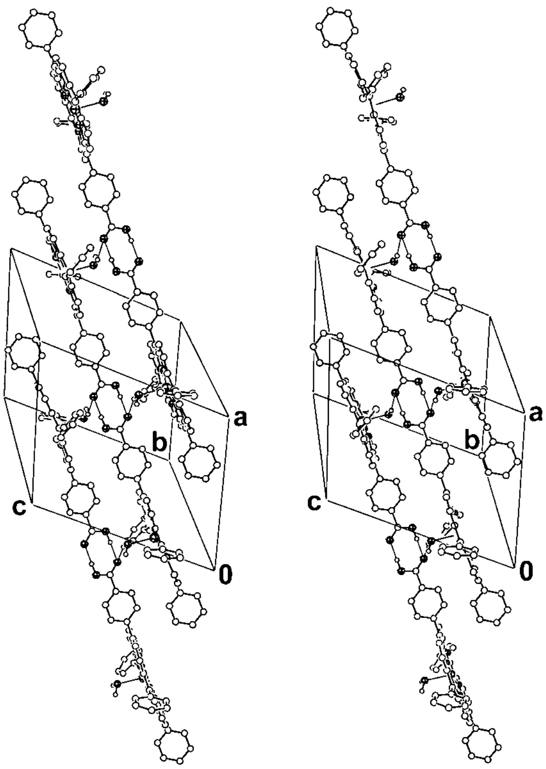


Figure 2
A stereoview of the hydrogen-bonding interaction scheme in (I). H atoms have been omitted, except for those involved in the hydrogen bonds. The Zn, N and O atoms are shown as darkened spheres. For clarity, the nitrobenzene solvent molecules have been excluded. Note the chain connectivity of the $(COOH)_2$ hydrogen-bonded porphyrin dimers [centered at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)] along the vertical direction.

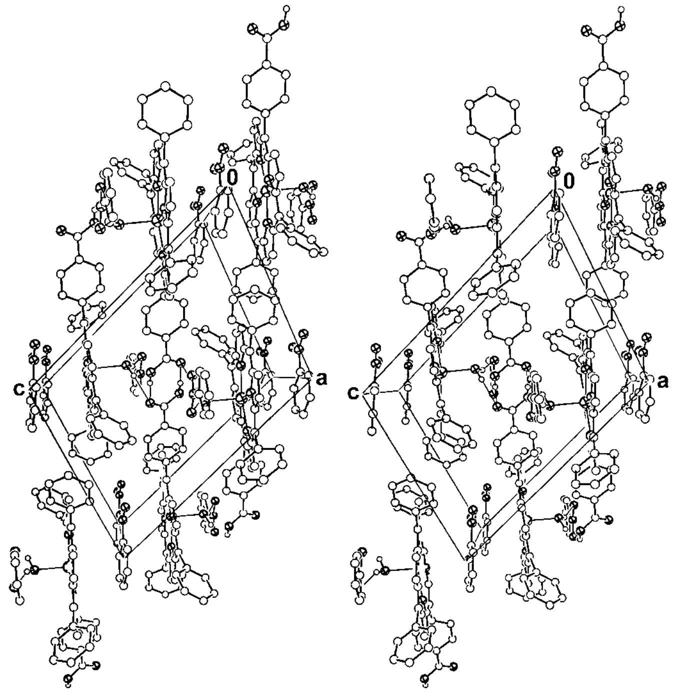


Figure 3
A stereoview of the crystal packing down the *b* axis. Half of the nitrobenzene solvent species are hydrogen bonded to the axial water ligands of (I), while the other half reside in interporphyrin channel voids centered at (0, *y*, 0). The Zn, N and O atoms are shown as darkened spheres.

Fig. 3 shows that the remaining molecules of nitrobenzene (containing atoms C62/O70) reside in channel voids centered at (0, *y*, 0), which are created between the hydrogen-bonded arrays. This imparts to this structure the characteristics of a channel clathrate (Byrn *et al.*, 1993). There are no specific interactions (other than dispersion) between these solvent species and the surrounding porphyrin units.

Experimental

The free-base porphyrin molecule was synthesized by a standard literature procedure (Adler *et al.*, 1970). Condensation of a 3:1 mixture of benzaldehyde and 4-(methoxycarbonyl)benzaldehyde with distilled pyrrole in hot propionic acid, followed by separation on a silica-gel column, led to the isolation of 5,10,15-triphenyl-20-[4-(methoxycarbonyl)phenyl]porphyrin. The latter was then converted to the corresponding carboxyphenyl porphyrin by alkaline hydrolysis, and subsequently metalated with zinc. The final as well as the intermediate products were fully characterized by ^{1}H NMR, UV–vis and MS spectral techniques. Crystallization of the title porphyrin was carried out by evaporation of a nitrobenzene solution in air.

Crystal data

$[Zn(C_{45}H_{28}N_4O_2)(H_2O)]\cdot 2C_6H_5NO_2$
$M_r = 986.32$
Triclinic, $P\bar{1}$
$a = 12.3796\ (2)$ Å
$b = 13.4467\ (2)$ Å
$c = 15.5757\ (3)$ Å
$\alpha = 78.1094\ (5)^\circ$
$\beta = 69.5983\ (6)^\circ$
$\gamma = 68.0862\ (6)^\circ$
$V = 2245.96\ (7)$ Å^3
$Z = 2$
$D_x = 1.458$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.61$ mm^{-1}
$T = 110\ (2)$ K
Plate, pink
0.40 × 0.20 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
1° φ and ω scans
28770 measured reflections
10851 independent reflections
7911 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\rm max} = 28.2°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.182$
$S = 1.03$
10851 reflections
642 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.1008P)^2 + 2.0583P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 1.68$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.85$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—N21	2.051 (2)	Zn1—N22	2.067 (2)
Zn1—N23	2.058 (2)	Zn1—O52	2.219 (3)
Zn1—N24	2.061 (2)		
N21—Zn1—N23	171.21 (9)	N24—Zn1—N22	166.50 (10)
N21—Zn1—N24	90.53 (9)	N21—Zn1—O52	94.14 (10)
N23—Zn1—N24	89.08 (9)	N23—Zn1—O52	94.63 (10)
N21—Zn1—N22	88.87 (9)	N24—Zn1—O52	89.03 (10)
N23—Zn1—N22	89.47 (9)	N22—Zn1—O52	104.46 (10)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O50—H50···O51$^{\rm i}$	0.96	1.72	2.677 (3)	174
O52—H52*A*···O51$^{\rm ii}$	0.97	2.04	2.952 (4)	156
O52—H52*B*···O60	0.96	1.86	2.767 (4)	156

Symmetry codes: (i) $-x + 3, -y + 1, -z + 1$; (ii) $x - 1, y, z$.

H atoms were located in calculated positions, and were constrained to ride on their parent atoms, with C—H distances of 0.95 Å, O—H distances of 0.96–0.97 Å, and $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C) and $1.5U_{\rm eq}$(O). Least certain are the positional parameters of the water ligand H atoms, as its actual orientation could not be reliably determined. The corresponding H52*A* and H52*B* atoms were positioned approximately along the relatively short contacts O52···O51-($x - 1, y, z$) and O52···O60, which are within the range of probable hydrogen-bonding interactions (Table 2), although no appropriate peaks could be found in the final difference Fourier electron-density maps. The final maps contained three relatively high peaks within 1.0–1.7 e Å^{-3} in the vicinity of the C53/O61 nitrobenzene solvent molecule, which appears to be partially disordered. This disorder and the appearance of the above-mentioned peaks could not be accounted for reliably by discrete atoms.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

This research was supported in part by The Israel Science Foundation (grant No. 254/04).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3019). Services for accessing these data are described at the back of the journal.

References

Adler, A. D., Longo, F. R., Kampas, F. & Kim, J. (1970). *J. Inorg. Nucl. Chem.* **32**, 2443–2445.
Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Byrn, M. P., Curtis, C. J., Hsiou, Y., Khan, S. I., Sawin, P. A., Tendick, S. K., Terzis, A. & Strouse, C. E. (1993). *J. Am. Chem. Soc.* **115**, 9480–9497.
Diskin-Posner, Y. & Goldberg, I. (1999). *Chem. Commun.* pp. 1961–1962.
George, S. & Goldberg, I. (2006). *Cryst. Growth Des.* **6**, 755–762.
George, S., Lipstman, S., Muniappan, S. & Goldberg, I. (2006). *CrystEngComm*, **8**, 417–424.
Goldberg, I. (2005). *Chem. Commun.* pp. 1243–1254.
Lipstman, S. & Goldberg, I. (2006). *Acta Cryst.* E**62**, m158–m160.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, pp. 307–326, edited by C. W. Carter Jr & R. M. Sweet. New York: Academic Press.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Shmilovits, M., Vinodu, M. & Goldberg, I. (2004). *Cryst. Growth Des.* **4**, 633–638.
Vinodu, M. & Goldberg, I. (2003). *CrystEngComm*, **5**, 204–207.
Vinodu, M. & Goldberg, I. (2004*a*). *CrystEngComm*, **6**, 215–220.
Vinodu, M. & Goldberg, I. (2004*b*). *New J. Chem.* **28**, 1250–1254.