Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A dimethyl sulfoxide/chloroform clathrate of (dimethyl sulfoxide)(tetraphenylporphyrinato)-zinc(II)

Mikki Vinodu 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 30 March 2004
Accepted 13 April 2004
Online 17 April 2004

The title compound, $[Zn(C_{44}H_{28}N_4)(C_2H_6OS)]\cdot 0.79C_2H_6OS\cdot 0.21CHCl_3$, crystallizes as a sulfoxide–chloroform true clathrate. The main residue, (dimethyl sulfoxide)(tetraphenylporphyrinato)zinc(II), is a five-coordinate zinc–porphyrin complex, with dimethyl sulfoxide as an axial ligand. The crystal structure is characterized by a typical layered organization of the porphyrin species, with the solvent guest molecules intercalated between the layers.

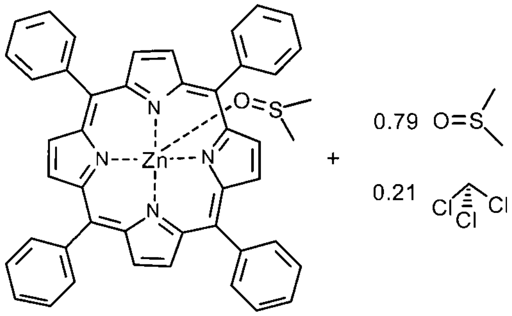
Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.003 Å
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.112
Data-to-parameter ratio = 14.8

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

Comment

Numerous four-, five- and six-coordinate complexes of metallo-tetraphenylporphyrins have been reported with a wide variety of crystallization solvents (many of these compounds forming true clathrates) and axial ligands coordinating to the metal centre (Byrn *et al.*, 1991, 1993). Zinc–porphyrin complexes with dimethyl sulfoxide are known only for the tetra(4-carboxyphenyl), tetra(4-chlorophenyl), tetra(4-amidophenyl) and tetra(3-hydroxyphenyl) porphyrin derivatives (Dastidar *et al.*, 1996; Krupitsky *et al.*, 1995*a*,*b*; Krishna Kumar *et al.*, 1998*a*). The present report provides complementary information for the five-coordinate complex of the title non-functionalized zinc–tetraphenylporphyrin, (I).



(I)

Compound (I) has been precisely analysed at *ca* 110 K (Fig. 1). In this structure, the porphyrin core is essentially planar, the central Zn ion deviating by 0.317 (1) Å from the plane of the four pyrrole N atoms towards the axial ligand.

The intermolecular organization of (I) can be best described in terms of the intercalated model, characteristic of the 'porphyrin sponges' described by Strouse and coworkers (Byrn *et al.*, 1991, 1993). It consists of corrugated sheets of tightly packed units of the domed porphyrin complex, with the solvent guest species intercalated between the inversion-related layers (Fig. 2). The zinc-coordinated dimethyl sulfoxide (DMSO) ligands are oriented towards the interlayer zones occupied by the solvent.

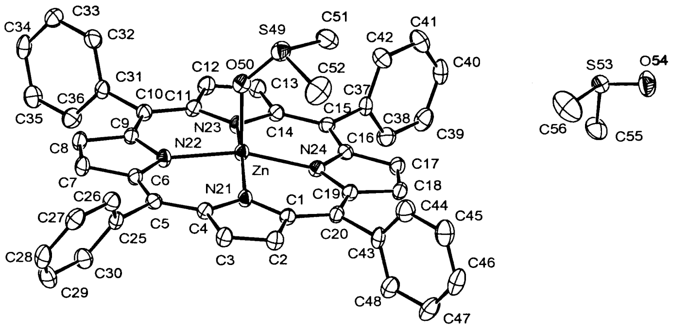


Figure 1
The molecular structure of the constituent species of (I), showing the atom-labelling scheme. H atoms have been omitted. Only the major solvent component is shown. Displacement ellipsoids are drawn at the 50% probablity level.

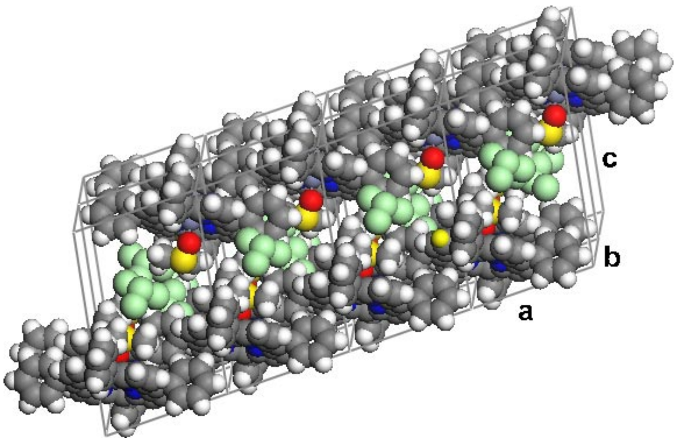


Figure 2
A space-filling illustration of the crystal structure of (I), showing solvent enclathration between layers of the five-coordinate metalloporphyrin molecules. The solvent is represented by the tetrahedral cluster of green spheres. Colour code for the host species: C grey, H white, S yellow, O red, Zn purple and N blue.

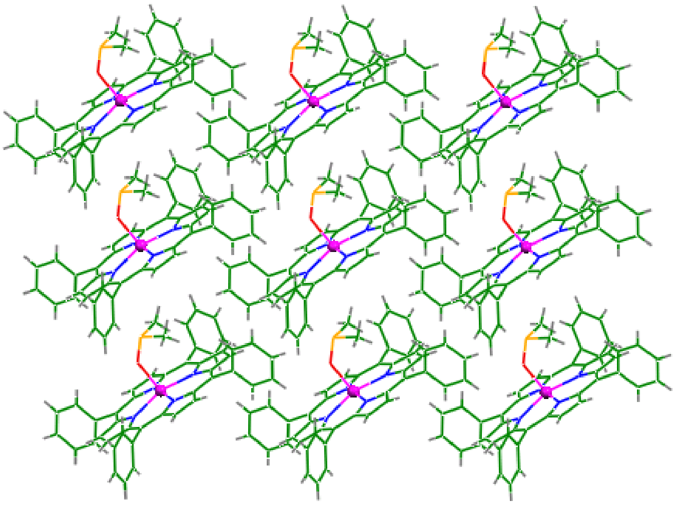


Figure 3
A perspective view of the corrugated sheet of the metalloporphyrin complex units, which is composed of molecules related by lattice translations. The Zn atoms are represented by small spheres. Colour code: C green, H grey, N blue, Zn pink, S yellow and O red.

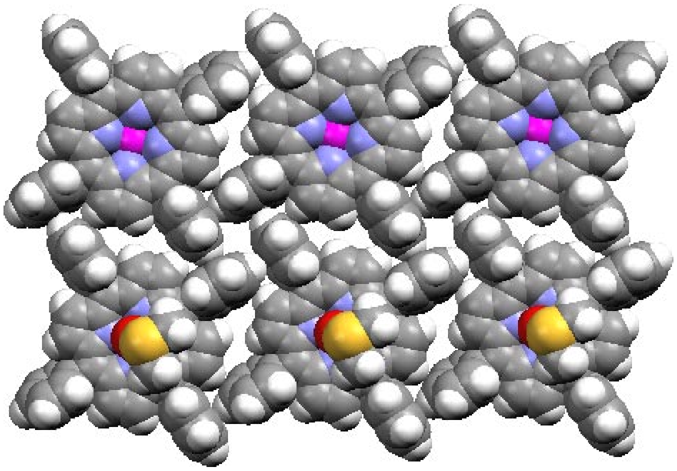


Figure 4
A space-filling illustration of tightly packed porphyrin species related by translation along the *ab* diagonal and by the inversion $(-1 - x, 1 - y, -z)$, exhibiting edge-to-face attractions between the phenyl substituents of adjacent entities (see text). Colour code: C grey, H white, S yellow, O red, Zn pink and N light blue.

Intralayer arrangements of porphyrin moieties exhibit fundamental modes of porphyrin–porphyrin interaction, which involve offset stacking in one direction and edge-to-face (T-shape) dispersive attractions in another direction (Fig. 3; Byrn *et al.*, 1991, 1993; Krishna Kumar *et al.*, 1998*b*). In the latter context, the centroids *Cg*1, *Cg*2 and *Cg*3, of the phenyl rings C37–C42, C43–C48 and C31–C36, respectively, are involved in weak intermolecular C—H$\cdots\pi$ interactions with the *para* H atoms of the aryl rings of adjacent porphyrin molecules (Desiraju & Steiner, 1999), as presented in Table 1 and Fig. 4. The perpendicular displacements of these H atoms from the mean planes of the corresponding phenyl rings with which they interact are 2.397 (2), 2.682 (2) and 2.697 (3) Å, respectively.

The guest solvent intercalated in the crystal structure of (I) consists of a 79%:21% molar mixture of DMSO and chloroform, as determined by a best fit of the proposed structural model to the experimental diffraction data. The two similarly shaped guest species are randomly distributed over the solvent-occupied sites in the crystal structure. These are localized between the axial DMSO ligands which protrude into the interlayer zone. The covalent parameters of the molecular structure of (I) and the coordination around Zn are unexceptional.

Experimental

Crystals of the title compound were obtained as a by-product by dissolving zinc tetraphenylporphyrin in a mixture of dimethylsulfoxide and chloroform, in the presence of various pyridylporphyrins, in an attempt to formulate new composite materials with mixed porphyrin content.

Crystal data

$[\mathrm{Zn}(\mathrm{C_{44}H_{28}N_4})(\mathrm{C_2H_6OS})]\cdot 0.79\mathrm{C_2H_6OS}\cdot 0.21\mathrm{CHCl_3}$
$M_r = 842.99$
Triclinic, $P\overline{1}$
$a = 10.9118\ (3)$ Å
$b = 11.0998\ (2)$ Å
$c = 17.4255\ (4)$ Å
$\alpha = 87.9607\ (9)°$
$\beta = 81.5984\ (9)°$
$\gamma = 75.2901\ (10)°$
$V = 2019.60\ (8)$ Å^3
$Z = 2$
$D_x = 1.387$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6359 reflections
$\theta = 2.2$–$27.0°$
$\mu = 0.79$ mm^{-1}
$T = 110\ (2)$ K
Rod, red
0.30 × 0.15 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer
1° φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.798$, $T_{\max} = 0.891$
16 161 measured reflections
8203 independent reflections
6359 reflections with $I > 2\sigma(I)$
$R_{\mathrm{int}} = 0.032$
$\theta_{\max} = 27.0°$
$h = -12 \rightarrow 13$
$k = -13 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.112$
$S = 1.02$
8203 reflections
555 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0562P)^2 + 0.8349P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.094$
$\Delta\rho_{\max} = 0.59$ e Å^{-3}
$\Delta\rho_{\min} = -0.59$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

*Cg*1, *Cg*2 and *Cg*3 are the centroids of the phenyl rings C37–C42, C43–C48 and C31–C36, respectively

D—H···A	D—H	H···A	D···A	D—H···A
C34—H34···$Cg1^{\mathrm{i}}$	0.95	2.66	3.582 (3)	163
C28—H28···$Cg2^{\mathrm{ii}}$	0.95	2.78	3.705 (3)	165
C40—H40···$Cg3^{\mathrm{iii}}$	0.95	2.77	3.702 (3)	167

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

The H atoms were located in idealized positions, with C—H distances in the range 0.95–1.00 Å, and were refined using a riding model, with $U_{\mathrm{iso}} = 1.2U_{\mathrm{eq}}$ of the parent atom.

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

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Blessing, B. (1995). *Acta Cryst.* A**51**, 33–38.

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). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Byrn, M. P., Curtis, C. J., Goldberg, I., Hsiou, Y., Khan, S. I., Sawin, P. A., Tendick, S. K. & Strouse, C. E. (1991). *J. Am. Chem. Soc.* **113**, 6549–6557.

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.

Dastidar, P., Stein, Z., Goldberg, I. & Strouse, C. E. (1996). *Supramol. Chem.* **7**, 257–270.

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond*. Oxford University Press.

Krishna Kumar, R., Balasubramanian, S. & Goldberg, I. (1998*a*). *Chem. Commun.* pp. 1435–1436.

Krishna Kumar, R., Balasubramanian, S. & Goldberg, I. (1998*b*). *Inorg. Chem.* **37**, 541–552.

Krupitsky, H., Stein, Z. & Goldberg, I. (1995*a*). *J. Incl. Phenom.* **20**, 211–232.

Krupitsky, H., Stein, Z. & Goldberg, I. (1995*b*). *Z. Kristallogr.* **210**, 665–668.

Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.

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.

Sheldrick. G. M. (1997). *SHELXL*97. University of Göttingen, Germany.