Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

(Methanol){α-5,10,15:β-20-tetrakis[2-(chloroacetamido)phenyl]porphyrin}zinc(II) chloroform solvate

David Ricard, Philippe Richard* and Bernard Boitrel

LSEO, Faculté des Sciences, 6 Bd Gabriel, 21000 Dijon, France

Correspondence e-mail: prichard@u-bourgogne.fr

Received 29 June 2001
Accepted 30 July 2001
Online 17 August 2001

The pentacoordinated Zn atom in the title compound, $[Zn(C_{52}H_{36}Cl_4N_8O_4)(CH_4O)]\cdot CHCl_3$, is displaced from the porphyrin N_4 plane towards the axial methanol ligand by 0.269 (2) Å. The average Zn—N(porphyrin) distance is 2.063 (9) Å and the axial Zn—O(MeOH) distance is 2.147 (5) Å.

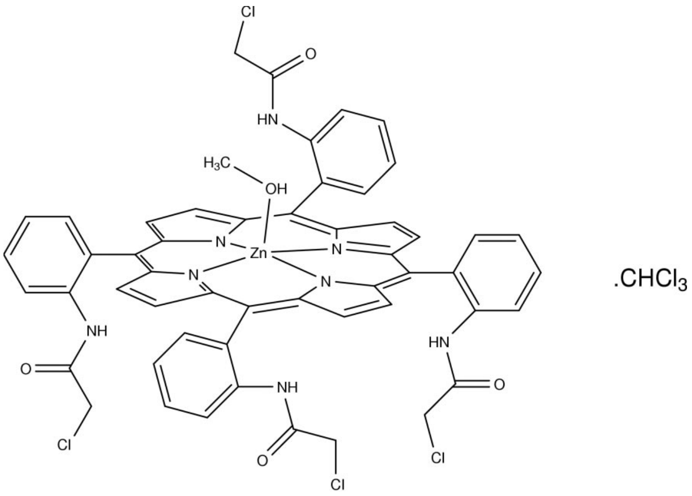
Key indicators

Single-crystal X-ray study
T = 110 K
Mean σ(C–C) = 0.008 Å
R factor = 0.069
wR factor = 0.187
Data-to-parameter ratio = 17.4

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

Comment

Porphyrins are of biological importance and therefore commonly used as building blocks in biomimetic chemistry.



(I)

Very elegant heme protein models have been synthesized to elucidate the mechanism of function of the native enzymes, such as P-450 cytochromes (Sono *et al.*, 1996), dioxygen carriers (Jameson & Ibers, 1994) or cytochrome *c* oxidase (Yoshikawa *et al.*, 2000). In the latter case, different porphyrins bearing four pickets on the same side of the porphyrin have been reported and have been shown to be powerful and versatile intermediates (Collman *et al.*, 1994). We recently observed that the spatial arrangement depends not only on the nature of the pickets, but also on the number of pickets per side of the porphyrin (Didier *et al.*, 2001). Additionally, the interactions that the pickets can establish between them *via* a hydrogen-bonding net may be of prime importance (Ricard *et al.*, 2001). We now report the structure of a zinc(II) porphyrin, (I), bearing three pickets on one side and the fourth on the other side of the porphyrin.

The porphyrin complex crystallizes with a chloroform molecule and an axially coordinated methanol molecule. The porphyrin ring adopts a nearly planar conformation. The

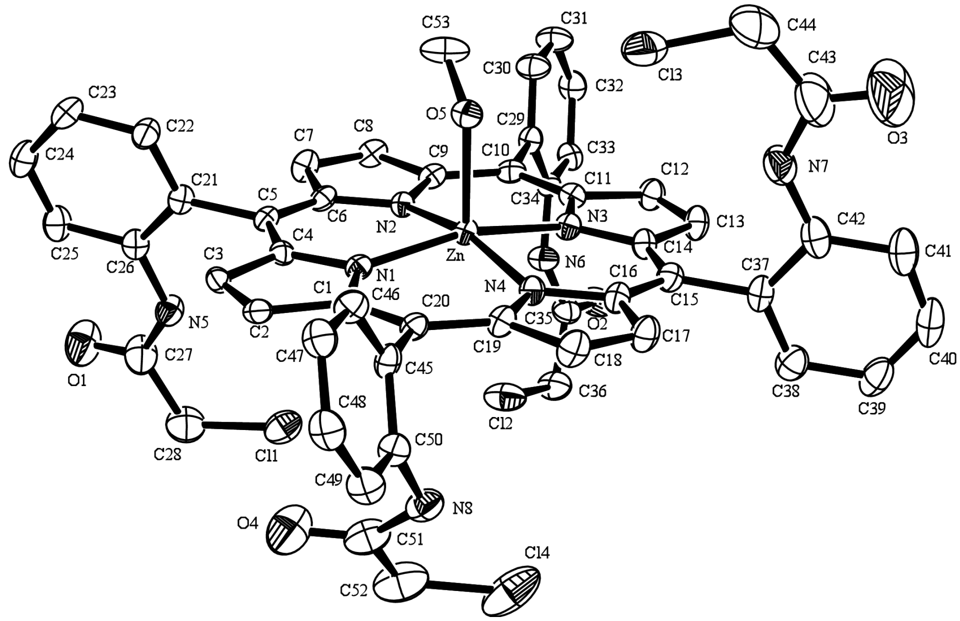


Figure 1

View of (I) with 50% probability displacement ellipsoids. The H atoms and the chloroform solvate molecule have been omitted for clarity.

coordination geometry is square pyramidal and the Zn atom is displaced from the N_4 least-squares plane by 0.269 (2) Å towards the axial methanol O atom. The mean Zn—N(porphyrin) distance is 2.063 (9) Å and the Zn—O(methanol) distance is 2.147 (5) Å [the average Zn—O(methanol) value found for 13 analogous methanol zinc porphyrins is 2.20 (4) Å].

No intramolecular hydrogen bonds are observed in the crystal. The O5—HO5$\cdots$O2^{i} hydrogen bond [O5$\cdots$O2^{i} 2.726 (11), HO5$\cdots$O2^{i} 1.82 Å and O5–HO5$\cdots$O2^{i} 171.8°; symmetry code: (i) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$] links the molecules of the complex into infinite chains along the [101] direction.

Experimental

The free base used for the preparation of the title compound was synthesized according to a previously reported procedure (Collman *et al.*, 1997). A 150 ml three-necked round-bottomed flask equipped with a stirrer bar was charged with the $\alpha\alpha\alpha\beta$-atropisomer of 5,10,15,20-tetrakis(2-aminophenyl)porphyrin (TAPP; 337 mg, 0.5 mmol), dry THF (30 ml) and six equivalents of Et_3N, then cooled in an ice bath, at which time, five equivalents of chloroacetyl chloride in 30 ml of dry THF were injected dropwise. The solution was stirred for 3 h, after which the THF was removed *in vacuo*. The α-5,10,15:β-20-[tetrakis(2-chloroacetamido)phenyl]porphyrin was purified by flash chromatography on a silica column and eluted with 3% methanol in CH_2Cl_2; the yield was 73%.The title compound, (I), was obtained by zinc insertion according to the usual method which consists of refluxing a chloroform solution of the free-base porphyrin with a saturated solution of zinc acetate in methanol (Smith, 1975). Crystals suitable for X-ray data collection were obtained by slow (over a three-month period) diffusion of MeOH into a $CHCl_3$ solution of compound (I) at room temperature.

Crystal data

$[Zn(C_{52}H_{36}Cl_4N_8O_4)(CH_4O)]\cdot CHCl_3$
$M_r = 1195.47$
Monoclinic, $P2_1/n$
$a = 13.078$ (6) Å
$b = 17.899$ (7) Å
$c = 22.79$ (9) Å
$\beta = 105.009$ (2)°
$V = 5153$ (21) Å^3
$Z = 4$

$D_x = 1.541$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19 872 reflections
$\theta = 1.0$–27.5°
$\mu = 0.90$ mm^{-1}
$T = 110$ (2) K
Prism, red
0.25 × 0.25 × 0.25 mm

Data collection

KappaCCD diffractometer
φ scans ($\kappa = 0$) + additional ω scans
19 872 measured reflections
11 775 independent reflections
7802 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.033$
$\theta_{\rm max} = 27.5°$
$h = -16 \rightarrow 16$
$k = -16 \rightarrow 23$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.187$
$S = 1.04$
11775 reflections
676 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0845P)^2 + 10.6403P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 1.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.62$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Zn—N1	2.051 (5)	Zn—N4	2.067 (4)
Zn—N2	2.072 (3)	Zn—O5	2.147 (5)
Zn—N3	2.062 (7)		
N1—Zn—N2	89.48 (13)	N4—Zn—N2	165.12 (13)
N1—Zn—N3	164.92 (13)	N1—Zn—O5	95.6 (3)
N1—Zn—N4	88.84 (14)	N3—Zn—O5	99.5 (3)
N3—Zn—N2	88.68 (13)	N4—Zn—O5	98.35 (13)
N3—Zn—N4	89.11 (14)	N2—Zn—O5	96.52 (12)

Acta Cryst. (2001). E**57**, m404–m406 David Ricard *et al.* • $[Zn(C_{52}H_{36}Cl_4N_8O_4)(CH_4O)]\cdot CHCl_3$ **m405**

H atoms were inserted at calculated positions or found in the difference electron-density map (for those of the methanol molecule and those of the amide groups) and treated in the riding model approximation with isotropic displacement parameters set to 1.2 times those of the parent atoms. The highest residual electron-density peak was located near the Cl6 atom of the chloroform solvent molecule.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL*97 and *WinGX* (Farrugia, 1999).

Financial support from the CNRS and the Région de Bourgogne is gratefully acknowledged. DR is indebted to the MENRT for his grant.

References

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

Collman, J. P., Boitrel, B., Fu, L., Galanter, J., Straumanis, A. & Rapta, M. (1997). *J. Org. Chem.* **62**, 2308–2309.

Collman, J. P., Zhang, X., Herrmann, P. C., Uffelman, E. S., Boitrel, B., Straumanis, A. & Brauman, J. I. (1994). *J. Am. Chem. Soc.* **116**, 2681–2682.

Didier, A., Michaudet, L., Ricard, D., Baveux-Chambenoît, V., Richard, P. & Boitrel, B. (2001). *Eur. J. Org. Chem.* **10**, 1917–1926.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Jameson, G. B. & Ibers, J. A. (1994). In *Bioinorganic Chemistry*, edited by I. Bertini, H. B. Gray, S. J. Lippard & J. S. Valentine, pp. 167–251. Mill Valley, California: University Science Books.

Nonius (1997). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.

Ricard, D., L'Her, M., Richard, P. & Boitrel, B. (2001). *Chem. Eur. J.* In the press.

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

Smith, K. M. (1975). In *Porphyrins and Metalloporphyrins*. Amsterdam: Elsevier Scientific Publishing Compagny.

Sono, M., Roach, M. P., Coulter, E. D. & Dawson, J. H. (1996). *Chem. Rev.* **96**, 2841–2887.

Yoshikawa, S., Shinzawa Itoh, K. & Tsukihara, T. (2000). *J. Inorg. Biochem.* **82**, 1–7.

m406 David Ricard *et al.* • $[Zn(C_{52}H_{36}Cl_4N_8O_4)(CH_4O)]\cdot CHCl_3$ *Acta Cryst.* (2001). E**57**, m404–m406