(Acetonitrile-κN)(2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrinato-$\kappa^4 N$)zinc(II) acetonitrile solvate

Takahiko Kojima* and Ryosuke Harada

Department of Chemistry, Faculty of Sciences, Kyushu University, 6-10-1 Hakozaki, Higashi-Ku, Fukuoka 812-8581, Japan

Correspondence e-mail:
cosyscc@mbox.nc.kyushu-u.ac.jp

Key indicators

Single-crystal X-ray study
$T = 183$ K
Mean σ(C–C) = 0.004 Å
R factor = 0.054
wR factor = 0.165
Data-to-parameter ratio = 16.8

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

The structure of the title compound, $[\text{Zn}(\text{C}_{92}\text{H}_{60}\text{N}_4)(\text{C}_2\text{H}_3\text{N})]\cdot\text{C}_2\text{H}_3\text{N}$, shows relatively small saddle-type distortion with ruffling, compared to other dodecaphenylporphyrin complexes.
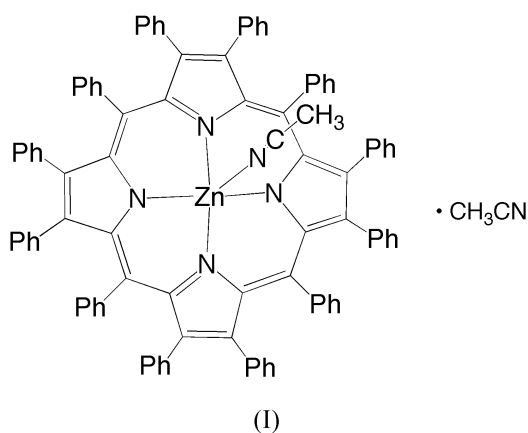
Comment

Zinc(II)–porphyrin complexes have been well studied in terms of photochemical behavior to mimic photosynthetic systems, in which a long-lived charge separation is required (Gust *et al.*, 2001, and references therein). As for the porphyrin ligands, multisubstituted porphyrins are known to exhibit severe distortion (Shelnutt *et al.*, 1998). Among those distorted porphyrins, 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenylporphyrin (H_2DPP) is known to show a large saddle-type distortion (Medforth *et al.*, 1992). In the absence of its crystal structure, the zinc(II) complex of DPP^{2-} has been reported to show a reduced lifetime of the lowest excited state, compared to a planar ZnTPP (TPP^{2-} is the 5,10,11,20-tetraphenylporphyrin dianion) (Gentemann *et al.*, 1997). In order to obtain structural information, we have determined the crystal structure of the title compound, (I).

(I)

The crystal structure of (I) is shown in Fig. 1. Selected bond lengths and angles are listed in Table 1. The geometry around the Zn^{II} center is distorted square-pyramidal and the DPP^{2-} ligand exhibits a saddle distortion with ruffling (Fig. 2). The distortion is described in terms of the deviation of each atom from the least-squares plane of the porphyrin core (in units of 0.01 Å in Fig. 3). The deviation of each atom is quite small (up to 0.60 Å) compared with those of other metal complexes of the DPP^{2-} ligand, in which deviations are over 1 Å (Retsek *et al.*, 2003; Harada *et al.*, 2004). However, the deviation is larger than those of five-coordinate Zn–TPP-type complexes (Collins & Hoard, 1970; Boblik & Walker, 1980; Li *et al.*, 1997). The Zn^{II} ion is located 0.233 (1) Å above the least-
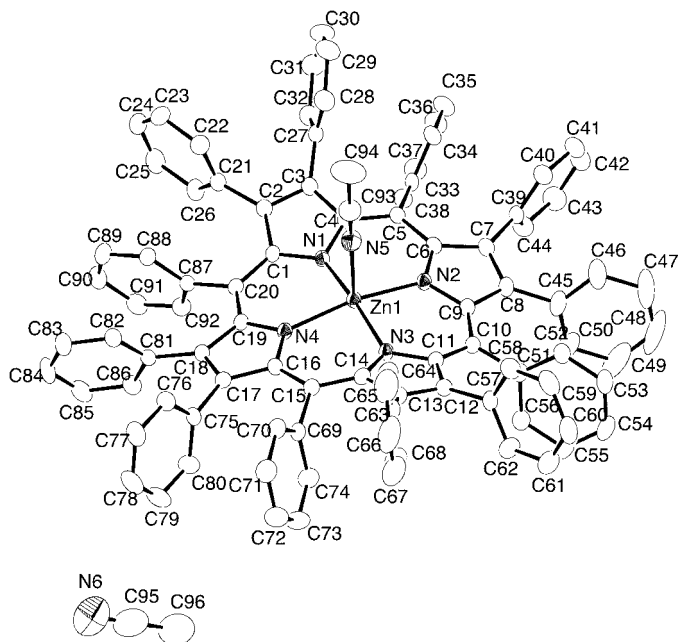
Figure 1
A view of the structure of (I), with 50% probability displacement ellipsoids. H atoms have been omitted.

squares plane consisting of atoms N1—N4 toward the aceto-nitrile ligand. The displacement of the Zn^{II} ion is smaller than that in Zn(TPP)(dimethylsulfoxide) [Vinodu & Goldberg, 2004; 0.317 (1) Å] and the complex reported by Li *et al.* (1997; 0.399 Å).

Experimental

Zn(DPP) (Ono *et al.*, 1998) (10 mg, 7.8×10^{-6} mol) was recrystallized from CHCl$_3$/CH$_3$CN (1:1 *v/v*, 5 ml) to obtain crystals of the title compound.

Crystal data

[Zn(C$_{92}$H$_{60}$N$_4$)(C$_2$H$_3$N)]·C$_2$H$_3$N	$Z = 2$
$M_r = 1369.00$	$D_x = 1.304$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo Kα radiation
$a = 11.4472$ (7) Å	Cell parameters from 8989
$b = 18.136$ (2) Å	reflections
$c = 19.063$ (2) Å	$\theta = 3.1$–27.5°
$\alpha = 117.072$ (3)°	$\mu = 0.41$ mm^{-1}
$\beta = 96.767$ (2)°	$T = 183.1$ K
$\gamma = 91.495$ (3)°	Block, green
$V = 3485.3$ (5) Å^3	$0.75 \times 0.18 \times 0.09$ mm

Data collection

Rigaku/MSC Mercury CCD diffractometer	15 607 independent reflections
ω scans	11 469 reflections with $F^2 > 2\sigma(F^2)$
Absorption correction: numerical	$R_{int} = 0.046$
(*CrystalClear*; Rigaku, 2000)	$\theta_{max} = 27.5°$
$T_{min} = 0.966$, $T_{max} = 0.990$	$h = -14 \rightarrow 10$
27 953 measured reflections	$k = -21 \rightarrow 23$
	$l = -24 \rightarrow 24$

Refinement

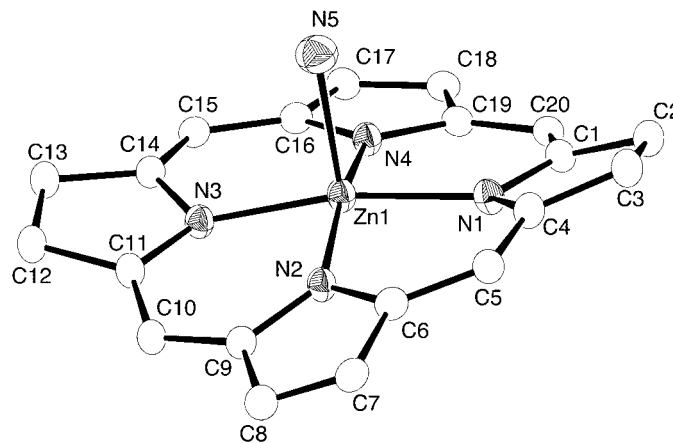|	
Refinement on F^2	H-atom parameters not refined
$R[F^2 > 2\sigma(F^2)] = 0.054$	$w = 1/[\sigma^2(F_o^2) + (0.092[\max(F_o^2,0)$
$wR(F^2) = 0.165$	$+ 2F_c^2]/3)^2]$
$S = 1.00$	$(\Delta/\sigma)_{max} = 0.001$
15 590 reflections	$\Delta\rho_{max} = 0.89$ e Å^{-3}
928 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}

Figure 2
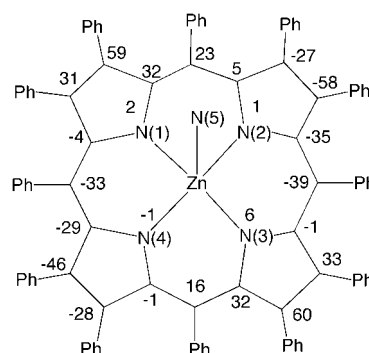The structure of the porphyrin core of (I).

Figure 3
The deviation of each atom from the least-squares plane of 24 atoms of the porphyrin core (in units of 0.01 Å).

Table 1
Selected geometric parameters (Å, °).

Zn1—N1	2.030 (2)	Zn1—N4	2.095 (2)
Zn1—N2	2.106 (2)	Zn1—N5	2.204 (2)
Zn1—N3	2.032 (2)		
N1—Zn1—N2	89.43 (8)	N2—Zn1—N4	166.19 (7)
N1—Zn1—N3	167.95 (8)	N2—Zn1—N5	96.18 (8)
N1—Zn1—N4	89.39 (8)	N3—Zn1—N4	89.34 (8)
N1—Zn1—N5	94.76 (8)	N3—Zn1—N5	97.28 (8)
N2—Zn1—N3	88.95 (8)	N4—Zn1—N5	97.63 (8)

H atoms were position geometrically (C—H = 0.96 Å and were included but not refined. 17 reflections were omitted in the course of the least-squares refinement of the setting $I > -10\sigma(I)$.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); program(s) used to solve structure: *PATTY* in *DIRDIF*94 (Beurskens *et al.*, 1994); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1999); *TEXSAN* (Molecular Structure Corporation & Rigaku, 2000); software used to prepare material for publication: *TEXSAN* (Molecular Structure Corporation, 1999).

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R. & Smits, J. M. M. (1994). *The DIRDIF94 Program System*. Technical Report. Crystallography Laboratory, University of Nijmegen, The Netherlands.

Boblik, M. A. & Walker, F. A. (1980). *Inorg. Chem.* **19**, 3383–3390.

Collins, D. M. & Hoard, J. L. (1970). *J. Am. Chem. Soc.* **92**, 3761–3771.

Gentemann, S., Nelson, N. Y., Jaquinod, L., Nurco, D. J., Leung, S. H., Medforth, C. J., Smith, K. M., Fajer, J. & Holten, D. (1997). *J. Phys. Chem. B*, **101**, 1247–1254.

Gust, D., Moore, T. A. & Moore, A. L. (2001). *Acc. Chem. Res.* **34**, 40–48.

Harada, R., Matsuda, Y., Okawa, H. & Kojima, T. (2004). *Angew. Chem. Int. Ed.* **43**, 1825–1828.

Li, M., Xu, Z., You, X., Huang, X., Zheng, X. & Wang, H. (1997). *Inorg. Chim. Acta*, **261**, 211–215.

Medforth, C. J., Senge, M. O., Smith, K. M., Sparks, L. D. & Shelnutt, J. A. (1992). *J. Am. Chem. Soc.* **114**, 9859–9869.

Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 9009 New Trails Drive, The Woodlands, TX 77381–5209, USA.

Molecular Structure Corporation & Rigaku (2000). *TEXSAN*. Version 1.11. MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA, and Rigaku Corporation, Tokyo, Japan.

Ono, N., Miyazawa, H., Ueta, T., Ogawa, T. & Tani, H. (1998). *J. Chem. Soc. Perkin Trans.* 1, pp. 1595–1601.

Shelnutt, J. A., Song, X.-Z., Ma, J.-G., Jia, S.-L., Jentzen, W. & Medforth, C. J. (1998). *Chem. Soc. Rev.* **27**, 31–41.

Retsek, J. L., Drain, C. M., Kirmaier, C., Nurco, D. J., Medforth, C. J., Smith, K. M., Sazanovich, I. V., Chirvony, V. S., Fajer, J. & Holten, D. (2003). *J. Am. Chem. Soc.* **125**, 9787–9800.

Rigaku (2000). *CrystalClear*. Version 3. Rigaku Corporation, Tokyo, Japan.

Vinodu, M. & Goldberg, I. (2004). *Acta Cryst.* E**60**, m579–m581.