

[5,10,15,20-Tetrakis(2-thienyl)- porphyrinato]zinc(II)

Bhavana Purushothaman,^a Babu Varghese^b and Puttaiah Bhyrappa^{a*}

^aDepartment of Chemistry, Indian Institute of Technology – Madras, Chennai 600 036, India, and ^bRegional Sophisticated Instrumentation Centre, Indian Institute of Technology – Madras, Chennai 600 036, India

Correspondence e-mail: bhyrappa@acer.iitm.ernet.in

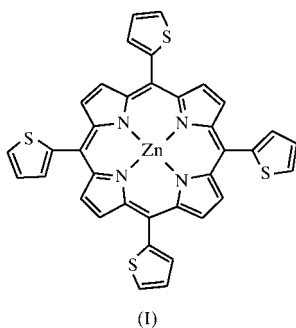
Received 3 May 2000

Accepted 23 November 2000

In the title complex, $[\text{Zn}(\text{C}_{36}\text{H}_{20}\text{N}_4\text{S}_4)]$, the Zn^{II} ion occupies a special position on an inversion centre with four-coordinate geometry. The porphyrin ring shows a wave-like conformation, with the closest interporphyrin plane separation being 3.60 (6) Å. The two disordered thienyl groups are inclined with respect to the porphyrin plane at angles of 70 (4) and 67 (2)°.

Comment

meso-Tetrathienylporphyrins are of growing interest, owing to their unique energy transfer (Vollmer *et al.*, 1998) and electrochemical (Ono *et al.*, 1998) properties. Oligomeric (Shimidzu *et al.*, 1995) and polymeric (Maruyama *et al.*, 1998) thienylporphyrin films show interesting physicochemical properties. We present here the crystal structure of [*meso*-tetrakis(2-thienyl)porphyrinato]zinc(II), (I).



The molecular structure of (I) is shown in Fig. 1. The Zn^{II} ion is free of axial ligands and there are no solvate molecules in the crystal lattice. The closest Zn^{II} to a thienyl S of an adjacent molecule is at a distance of 5.245 (3) Å. The observed bond lengths of the 24-atom core of (I) are similar to those of the four-coordinate complex [*meso*-5,10,15,20-tetraphenylporphyrinato]zinc(II), (II) (Scheidt & Lee, 1987).

Selected dihedral angles and bond lengths for (I) and (II) (Scheidt *et al.*, 1986) are given in Table 1. The comparison is made to illustrate the effect of the thienyl groups on the

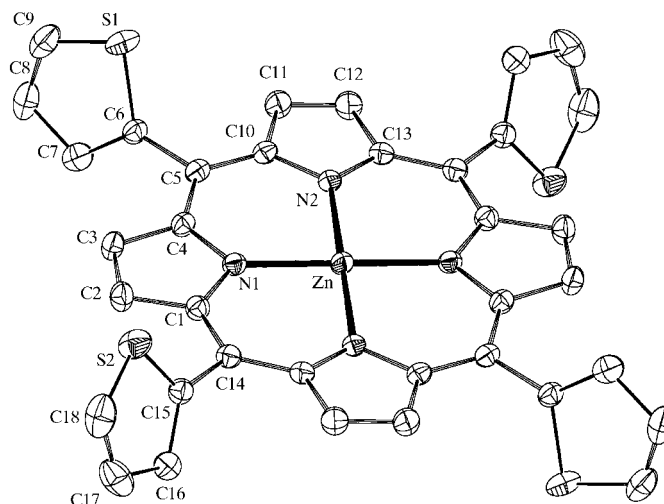


Figure 1

The molecular structure (ORTEP; Johnson, 1965) of (I), with the atom-numbering scheme and 50% probability displacement ellipsoids. Only one of the two orientations of each of the disordered 2-thienyl rings is shown. H atoms have been omitted for clarity.

stereochemical features of the porphyrin ring system. Notably, the central Zn to the *meso* carbon distance is shorter in (I) than in (II), indicative of a contraction of the porphyrin core. This is further reflected in the contraction of the Zn–N bond lengths (Table 1).

The deviations of the atoms from the mean plane passing through the 24-atom porphyrin core are shown in Fig. 2. The porphyrin plane of (I) displays a wave-like conformation (Senge, 1999), with an interplanar porphyrin separation of 3.60 (6) Å, indicative of minimal interporphyrin interactions. The porphyrin molecules pack in a slipped-stack orientation.

It can be seen from Table 1 that the dihedral angles in (I) are greater than those found in (II). The thienyl groups in (I) are inclined with respect to the porphyrin plane at angles which differ by 3°. This is similar to (II), in which the difference between the two angles is 2.8°. The third C and the S

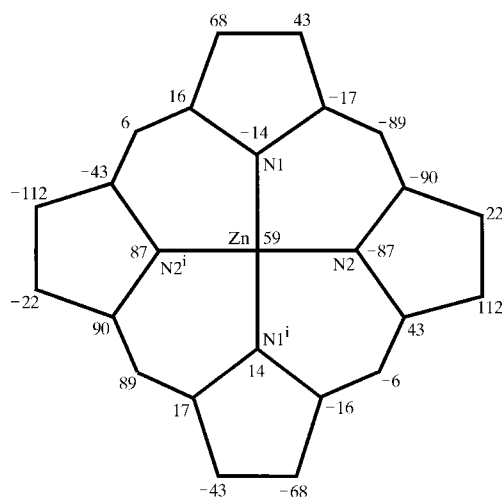


Figure 2

The perpendicular deviation of atoms (in units of 0.001 Å) from the mean plane of the 24-atom porphyrin core. Only the Zn^{II} ion and the N atoms are labelled [symmetry code: (i) 1 - x, 1 - y, -z].

atoms of the thienyl groups of (I) show disorder. In this structure, the Zn^{II} ion is free of five- or six-coordination, possibly due to steric hindrance by the 2-thienyl groups.

Experimental

5,10,15,20-Tetrakis(2-thienyl)porphyrin was synthesized using the procedure of Adler *et al.* (1967) and recrystallized from CHCl₃/CH₃OH (1:1 v/v). Metallation of the porphyrin was carried out using zinc(II) acetate dihydrate as the metal carrier (Adler *et al.*, 1970). The compound was purified by column chromatography using CHCl₃ as eluant and the yield of (I) was almost quantitative. Single crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a chloroform solution over a period of 4 d. Spectroscopic analysis, ¹H NMR (CDCl₃, p.p.m.): 9.15 (s, 8H, pyrrole-H), 7.90 (dd, 4H, thienyl-3H), 7.85 (dd, 4H, thienyl-4H), 7.50 (dd, 4H, thienyl-5H); elemental analysis calculated for C₃₆H₂₀N₄S₄Zn: H 3.15, C 61.40, N 7.96%; found: H 3.01, C 61.12, N 8.01%; FAB mass spectrum (*m/z*), calculated for C₃₆H₂₀N₄S₄Zn: 702.2; found: 702.8.

Crystal data

[Zn(C ₃₆ H ₂₀ N ₄ S ₄)]	<i>D</i> _x = 1.590 Mg m ⁻³
<i>M</i> _r = 702.17	Mo <i>K</i> α radiation
Monoclinic, <i>P</i> 2 ₁ / <i>c</i>	Cell parameters from 25 reflections
<i>a</i> = 6.6009 (11) Å	<i>θ</i> = 10–15°
<i>b</i> = 10.9678 (17) Å	<i>μ</i> = 1.158 mm ⁻¹
<i>c</i> = 20.278 (5) Å	<i>T</i> = 293 (2) K
<i>β</i> = 92.704 (16)°	Plate, black
<i>V</i> = 1466.4 (5) Å ³	0.2 × 0.2 × 0.1 mm
<i>Z</i> = 2	

Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> _{int} = 0.037
<i>ω</i> /2 <i>θ</i> scans	<i>θ</i> _{max} = 25.6°
Absorption correction: <i>ψ</i> scan (North <i>et al.</i> , 1968)	<i>h</i> = 0 → 7
<i>T</i> _{min} = 0.75, <i>T</i> _{max} = 0.86	<i>k</i> = 0 → 13
2879 measured reflections	<i>l</i> = -24 → 24
2637 independent reflections	2 standard reflections
2163 reflections with <i>I</i> > 2σ(<i>I</i>)	frequency: 60 min
	intensity decay: none

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0438 <i>P</i>) ² + 2.6353 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.040	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.121	(Δ/σ) _{max} = 0.005
<i>S</i> = 1.151	Δρ _{max} = 0.44 e Å ⁻³
2637 reflections	Δρ _{min} = -0.40 e Å ⁻³
239 parameters	
H-atom parameters constrained	

The thienyl groups exhibit twofold rotational disorder about the C5–C6 and C14–C15 bonds, which was noticed at the structure-solution stage itself. The occupancies of the two components refined to unequal values in both cases [0.615 (5) and 0.386 (5) for S1/S1', and 0.719 (6) and 0.281 (6) for S2/S2']. Except for the disordered thienyl groups, H atoms were fixed geometrically and were treated as riding on their parent atoms, with C–H distances of 0.93 Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990);

Table 1

Selected geometric parameters for (I) and (II).

	(I)	(II)†
Distances (Å)		
Zn–N1	1.998 (3)	2.045 (2)
Zn–N2	2.043 (3)	2.029 (2)
Zn ^{II} to <i>meso</i> carbon (Å)		
Zn–C5	3.395 (4)	3.443 (2)
Zn–C14 ⁱ	3.427 (5)	3.451 (2)
Dihedral angles (°)		
Core–Plane1‡	70 (4)	60.6
Core–Plane2‡	67 (2)	63.4
Plane1–Plane2	84 (3)	78.0

† The data for (II) are taken from Scheidt *et al.* (1986). ‡ For (I), Plane1 is the thienyl group attached to C5 and C5', and Plane2 is the thienyl group attached to C14 and C14'; for (II), Plane1 and Plane2 are the phenyl groups attached to the *meso*-C atoms *C*_a and *C*_b, respectively [symmetry code: (i) 1 – *x*, 1 – *y*, –*z*].

program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (Johnson, 1965) software used to prepare material for publication: *SHELXL97*.

This work was supported financially by DST (SP/S1/F09/98) and CSIR [01(1550)/98/EMR-II], India.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: VJ1107). Services for accessing these data are described at the back of the journal.

References

- Adler, A. D., Longo, F. R., Goldmacher, J., Assour, J. & Korsakoff, L. (1967). *J. Org. Chem.* **32**, 476–477.
- Adler, A. D., Longo, F. R., Kampas, F. & Kim, J. (1970). *J. Inorg. Nucl. Chem.* **32**, 2443–2445.
- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Maruyama, H., Segawa, H., Sotoda, S., Sato, T., Kosai, N., Sagisaka, S., Shimidzu, T. & Tanaka, K. (1998). *Synth. Met.* **96**, 141–149.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Ono, N., Miyagawa, H., Ueta, T., Ogawa, T. & Tani, H. (1998). *J. Chem. Soc. Perkin Trans. 1*, pp. 1595–1601.
- Scheidt, W. R. & Lee, Y. J. (1987). *Struct. Bonding (Berlin)*, **64**, 1–70.
- Scheidt, W. R., Mondal, J. U., Eigenbrot, C. W., Adler, A., Radonovich, L. J. & Hoard, J. L. (1986). *Inorg. Chem.* **25**, 795–799.
- Senge, M. O. (1999). *The Porphyrin Handbook*, Vol. 1, edited by K. M. Kadish, K. M. Smith & R. Guilard, pp. 1–250. New York: Academic Press.
- Sheldrick, W. R. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Shimidzu, T., Segawa, H., Wu, F. & Nakayama, N. (1995). *J. Photochem. Photobiol. A*, **92**, 121–127.
- Vollmer, M. S., Wurthner, F., Effenberger, F., Emele, P., Meyer, D. U., Stumpf, T., Port, H. & Wolf, H. C. (1998). *Chem. Eur. J.* **4**, 260–269.