Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1221). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Zinc–*meso*-tetra-*p*-tolylporphyrin and its Chlorotoluene Channel-Type Clathrate with π–π and C—H$\cdots\pi$ Interaction Modes Stabilizing the Porphyrin Host Lattice

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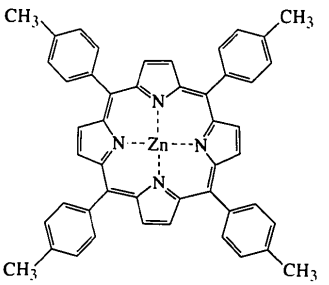
Abstract

The title compound, (*meso*-5,10,15,20-tetra-*p*-tolylporphyrinato-*N*,*N*′,*N*″,*N*‴)zinc(II), $[Zn(C_{48}H_{36}N_4)]$, displays a high tendency to form complexes and clathrates with other components from various environments, and is a useful building block for the construction of heteromolecular solids. Modes of its intermolecular assembly in the pure compound and in its clathrate with *m*-chlorotoluene, $[Zn(C_{48}H_{36}N_4)].C_7H_7Cl$, have been characterized by X-ray crystal-structure analysis. The clathrate appears to be stabilized by π–π stacking and cooperative C—H$\cdots\pi$ interactions between the tolyl substituents and contains large interporphyrin channels extending throughout the crystal.

Comment

This study is part of an ongoing investigation of the crystalline architectures afforded by functionalized tetraphenylmetalloporphyrins and of the potential utility of these materials for the development of simple chemical models of self-assembly *via* weak intermolecular forces (Goldberg, Krupitsky, Stein, Hsiou & Strouse, 1995; Krupitsky, Stein & Goldberg, 1995). The tetra-*p*-tolylporphyrin compound readily forms crystalline adducts with metal ions in different oxidation states. The crystal structures of the non-metallated tetra-*p*-tolylporphyrin (Butcher, Jameson & Storm, 1985), and of its numerous five- and six-coordinate metal complexes with various axial ligands and Cr, Fe, Mo, Os, V, Ti, Sc, Sb and Re ions in the porphyrin center, have been reported previously (October 1995 release of the Cambridge Structural Database; Allen & Kennard, 1993). The metal complexes reveal intermolecular architectures common to the tetraphenylporphyrin 'sponges' (Byrn, Curtis, Goldberg, Hsiou, Khan, Sawin, Tendick & Strouse, 1991; Byrn, Curtis, Hsiou, Khan, Sawin, Tendick, Terzis & Strouse, 1993) and consistently crystallize as solvates. It was of further interest in the present context to investigate the intermolecular organization in crystalline solids based on the four-coordinate zinc–tetra-*p*-tolylporphyrin framework.

The crystallization mode of the title compound is affected by the solvent environment, yielding a homomolecular solvent-free solid, (1), from guaiacol, and a clathrate, (2), from the more lipophilic *m*-chlorotoluene. The molecular structures of zinc–tetra-*p*-tolylporphyrin in the two crystals are depicted in Fig. 1 and they do not exhibit unusual features. In both compounds,



(1) above
(2) (1).C_7H_7Cl

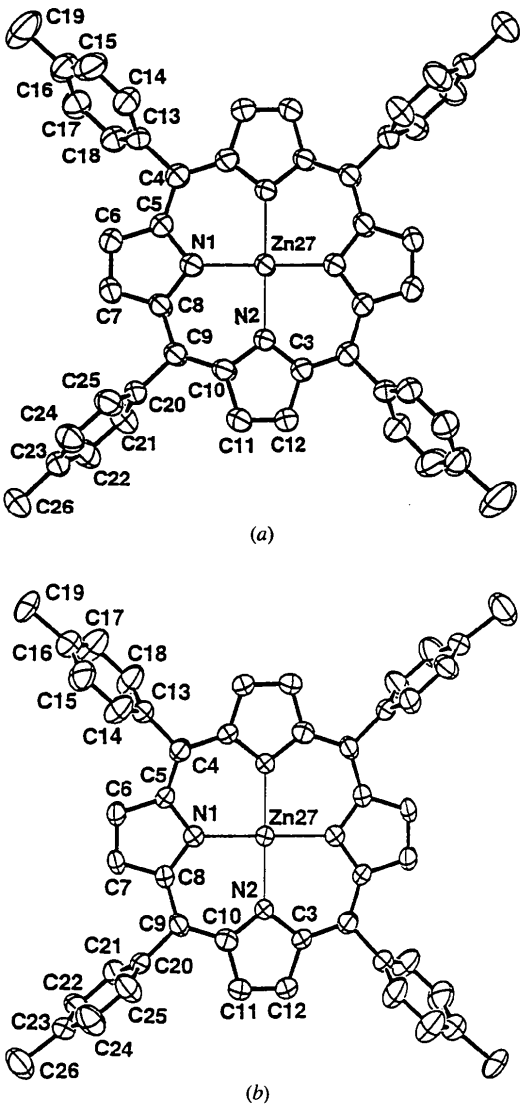


Fig. 1. The molecular structures of zinc–tetra-*p*-tolylporphyrin in (*a*) the pure compound (1) and (*b*) the clathrate (2), showing 50% probability displacement ellipsoids and the labeling of the non-H atoms. H atoms have been omitted for clarity.

the porphyrin core is essentially planar, with the four-coordinate zinc ion fitting into its center at 2.029 (3)–2.046 (3) Å from the surrounding pyrrole N atoms and the four aryl substituents oriented nearly at right angles to it.

The crystal structure of (1) (Fig. 2) is isomorphous with that of the non-metallated tetra-*p*-tolylporphyrin derivative (Butcher, Jameson & Storm, 1985). Molecules centered at $z = 0$ and $z = \frac{1}{2}$, related to each other by the glide symmetry, are aligned perpendicular to the [110] and [1$\bar{1}$0] directions, respectively. The centrosymmetric environment around the metalloporphyrin fragment (the center of every metallomacrocycle is equally approached from above and below by the tolyl substituents of neighboring species) contributes to the preservation of its planarity. In the observed structure, the methyl C atoms of the tolyl groups approach the central porphyrin core from both sides [Zn···C26($x + \frac{1}{2}$, $\frac{1}{2} - y$, $z + \frac{1}{2}$) 3.648 (5) Å], with one of the methyl H atoms pointing at, and about 2.5 Å distant from, the porphyrin ring. The observed motif of intermolecular interaction is in agreement with previous evaluations of energetically-preferred arrangements in porphyrins and other aromatic compounds (Klebe & Diederich, 1993; Hunter & Sanders, 1990).

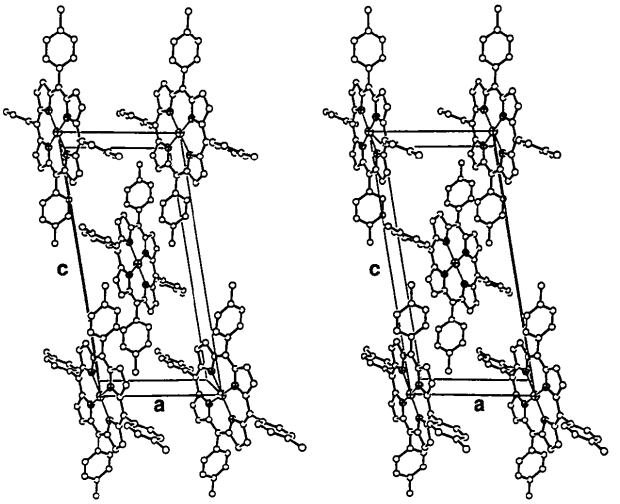


Fig. 2. Stereoview down the *b* axis of the crystal packing of compound (1). Five molecular units are shown in order to illustrate the interporphyrin organization. The Zn and N atoms are indicated by crossed circles.

A unique molecular organization characterizes the porphyrin host lattice of the clathrate, (2). The porphyrin units are clustered in layered zones centered at $x = \frac{1}{4}$ and $x = \frac{3}{4}$. Aryl–aryl π–π stacking-interaction modes occur between parallel shifted aromatic rings of porphyrin units displaced along the *c* axis of the unit cell (Fig. 3). The interplanar distance between these partly overlapping rings (labeled C20–C26) is 3.22 (1) Å, indicating a significant interaction. Cohesion of the porphyrin layers

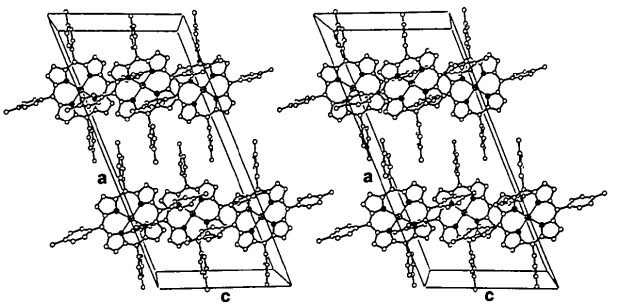
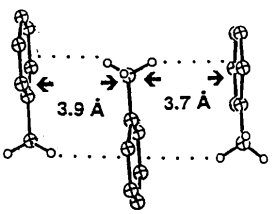


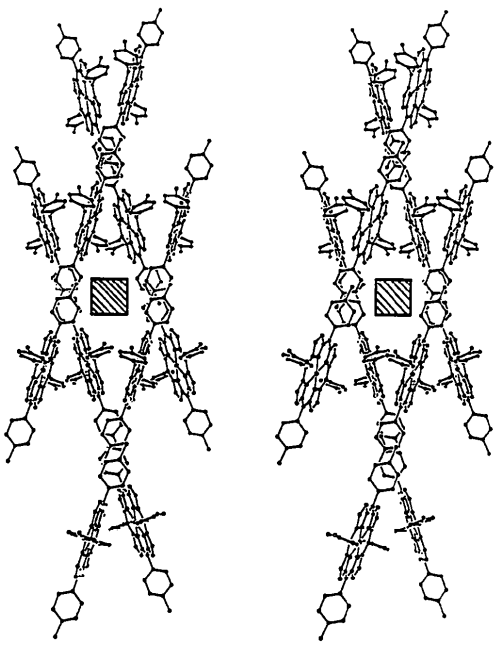
Fig. 3. Stereoview down the *b* axis of the interporphyrin organization in the clathrate structure (2), showing the aryl–aryl stacking interactions along **c**.

along the *a* axis of the crystal appears to be effected by a stacked arrangement of the C13–C19 tolyl rings directed at the interface between these layers. The major interaction along the stacks is not of the π–π type. Rather, the methyl group of one ring is sandwiched between the phenyl fragments of neighboring species along the stack and its C—H dipoles are oriented toward the negatively charged surface of the latter [Fig. 4(*a*)]. The attractive nature of such cooperative C—H$\cdots\pi$ contacts and their possible utility as design elements in molecular recognition have been extensively discussed in several recent publications (Cochran, Parrott, Whitlock & Whitlock, 1992; Steiner, Starikov, Amado & Teixeira-Dias, 1995). Formation of a hollow architecture (as opposed to the condensed one in the previous example), with interporphyrin channels extending throughout the crystal parallel to the *c* axis [Fig. 4(*b*)], manifests the dominant effect of such interactions in the present structure. The channels center at $x = 0$ and $y = 0$ and symmetry equivalent sites, and are about 5.5–6 Å wide (this distance is between the tolyl residues across the channel after subtracting their van der Waals volume). They are occupied by highly disordered molecules of the solvent which could not be reliably located within the otherwise relatively precise structure of the host lattice.

Quantitative assessment of the relative stability of the different interporphyrin architectures awaits a suitable evaluation by theoretical and computational methods.



(*a*)



(*b*)

Fig. 4. (*a*) The stacking geometry of the C13–C19 tolyl residues along the *c* axis, depicting the interplanar distances and possible C—H$\cdots\pi$ contacts along the stack (dotted lines). (*b*) Perspective view of the porphyrin host lattice of (2) down the channel axis (*c* axis of the crystal) and parallel to the planes of the porphyrin entities. The van der Waals width of the interporphyrin channels is close to 6 Å, allowing inclusion of sizeable guest components. The cross-section of the central channel is marked by a hatched square.

Experimental

Starting materials were purchased from Midcentury Chemicals, Posen, Illinois (porphyrin) and Fluka (*o*-chlorotoluene and *m*-chlorotoluene). Detailed experimental procedures have been reported previously (Goldberg, Krupitsky, Stein, Hsiou & Strouse, 1995). Crystals of the clathrate were prepared by slow recrystallization of the tetra-*p*-tolylporphyrin host from an analytically pure *m*-chlorotoluene solvent. A similar crystallization procedure from analytically pure *o*-chlorotoluene yielded tiny dark crystals [cell dimensions: $a = 32.341\,(6)$, $b = 9.600\,(1)$, $c = 15.001\,(5)$ Å and $\beta = 111.89\,(2)°$], indicating formation of a clathrate structure isomorphous with (2) from this solvent.

Compound (1)

Crystal data

[$Zn(C_{48}H_{36}N_4)$]
$M_r = 734.22$
Monoclinic
$P2_1/n$
$a = 9.942\,(2)$ Å
$b = 9.245\,(2)$ Å
$c = 20.982\,(4)$ Å
$\beta = 99.12\,(2)°$
$V = 1904.2\,(7)$ Å^3
$Z = 2$
$D_x = 1.281$ Mg m^{-3}
$D_m = 1.27$ Mg m^{-3}
D_m measured by flotation

Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 25 reflections
$\theta = 7.2$–$10.5°$
$\mu = 0.684$ mm^{-1}
$T = 297\,(2)$ K
Prism
0.40 × 0.20 × 0.20 mm
Dark

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3157 measured reflections
2999 independent reflections
2490 observed reflections [$I > 2\sigma(I)$]

$R_{int} = 0.0551$
$\theta_{max} = 24.99°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 10$
$l = 0 \rightarrow 24$
3 standard reflections
frequency: 90 min
intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0473$
$wR(F^2) = 0.1461$
$S = 1.012$

$(\Delta/\sigma)_{max} = 0.005$
$\Delta\rho_{max} = 0.45$ e Å^{-3}
$\Delta\rho_{min} = -0.55$ e Å^{-3}
Extinction correction: none

2999 reflections
241 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
N1	−0.0955 (3)	0.1761 (3)	−0.04368 (13)	0.0432 (6)
N2	0.0452 (3)	−0.0703 (3)	−0.08656 (12)	0.0442 (6)
C3	0.1122 (3)	−0.1960 (3)	−0.0980 (2)	0.0457 (8)
C4	−0.1643 (3)	0.2979 (3)	0.0513 (2)	0.0451 (8)
C5	−0.1574 (3)	0.2855 (4)	−0.0152 (2)	0.0447 (8)
C6	−0.2176 (4)	0.3862 (4)	−0.0636 (2)	0.0551 (9)
C7	−0.1927 (4)	0.3366 (4)	−0.1211 (2)	0.0556 (9)
C8	−0.1162 (3)	0.2053 (4)	−0.10904 (15)	0.0451 (8)
C9	−0.0670 (3)	0.1225 (4)	−0.1567 (2)	0.0450 (8)
C10	0.0073 (4)	−0.0046 (3)	−0.1462 (2)	0.0458 (8)
C11	0.0553 (4)	−0.0906 (4)	−0.1950 (2)	0.0576 (10)
C12	0.1180 (4)	−0.2080 (4)	−0.1659 (2)	0.0578 (9)
C13	−0.2325 (3)	0.4309 (4)	0.0720 (2)	0.0452 (8)
C14	−0.3537 (4)	0.4209 (4)	0.0965 (2)	0.0611 (10)
C15	−0.4152 (4)	0.5426 (6)	0.1165 (2)	0.0730 (12)
C16	−0.3605 (4)	0.6777 (5)	0.1119 (2)	0.0652 (11)
C17	−0.2394 (4)	0.6888 (4)	0.0879 (2)	0.0601 (10)
C18	−0.1757 (4)	0.5660 (4)	0.0687 (2)	0.0543 (9)
C19	−0.4279 (6)	0.8145 (6)	0.1331 (3)	0.112 (2)
C20	−0.0965 (4)	0.1791 (3)	−0.2243 (2)	0.0466 (8)
C21	−0.0032 (4)	0.2655 (4)	−0.2486 (2)	0.0634 (10)
C22	−0.0308 (5)	0.3207 (4)	−0.3108 (2)	0.0674 (11)
C23	−0.1519 (4)	0.2896 (4)	−0.3506 (2)	0.0566 (10)
C24	−0.2443 (4)	0.2056 (4)	−0.3267 (2)	0.0629 (10)
C25	−0.2188 (4)	0.1494 (4)	−0.2642 (2)	0.0591 (10)
C26	−0.1796 (5)	0.3472 (5)	−0.4192 (2)	0.0809 (14)
Zn27	0	0	0	0.0409 (2)

Compound (2)

Crystal data

$[Zn(C_{48}H_{36}N_4)].C_7H_7Cl$
$M_r = 860.80$
Monoclinic
$C2/c$
$a = 32.468$ (9) Å
$b = 9.5320$ (10) Å
$c = 15.048$ (2) Å
$\beta = 112.03$ (2)°
$V = 4317.1$ (15) Å³
$Z = 4$
$D_x = 1.324$ Mg m^{-3}
$D_m = 1.30$ Mg m^{-3}
D_m measured by flotation
Mo $K\alpha$ radiation
$\lambda = 0.71070$ Å
Cell parameters from 25 reflections
$\theta = 5.9$–$11.8°$
$\mu = 0.674$ mm^{-1}
$T = 297$ (2) K
Needle
0.50 × 0.20 × 0.20 mm
Dark

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
3065 measured reflections
3018 independent reflections
1936 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0361$
$\theta_{max} = 24.98°$
$h = -37 \rightarrow 34$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 17$
3 standard reflections
frequency: 90 min
intensity decay: 7%

Refinement

Refinement on F^2
$R(F) = 0.0975$
$wR(F^2) = 0.2834$
$S = 1.405$
3018 reflections
241 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.54$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
N1	0.1943 (2)	0.2798 (7)	0.3808 (5)	0.040 (2)
N2	0.2824 (2)	0.1717 (8)	0.4180 (5)	0.039 (2)
C3	0.3266 (3)	0.1315 (9)	0.4490 (6)	0.037 (2)
C4	0.1439 (3)	0.3710 (9)	0.4548 (6)	0.041 (2)
C5	0.1540 (3)	0.3288 (10)	0.3769 (6)	0.039 (2)
C6	0.1233 (3)	0.3286 (11)	0.2790 (6)	0.049 (2)
C7	0.1449 (3)	0.2770 (11)	0.2253 (6)	0.052 (3)
C8	0.1896 (3)	0.2457 (11)	0.2888 (6)	0.043 (2)
C9	0.2225 (3)	0.1903 (9)	0.2586 (6)	0.039 (2)
C10	0.2664 (3)	0.1583 (9)	0.3201 (6)	0.041 (2)
C11	0.3003 (3)	0.1106 (10)	0.2879 (7)	0.047 (2)
C12	0.3377 (3)	0.0950 (11)	0.3688 (6)	0.049 (3)
C13	0.0981 (3)	0.4275 (11)	0.4352 (6)	0.044 (2)
C14	0.0610 (4)	0.3409 (12)	0.4033 (8)	0.063 (3)
C15	0.0186 (4)	0.3952 (14)	0.3794 (8)	0.072 (4)
C16	0.0118 (4)	0.5339 (14)	0.3868 (8)	0.064 (3)
C17	0.0485 (4)	0.6227 (12)	0.4193 (9)	0.075 (4)
C18	0.0920 (4)	0.5679 (12)	0.4433 (8)	0.068 (3)
C19	−0.0345 (4)	0.6021 (16)	0.3600 (9)	0.093 (5)
C20	0.2095 (3)	0.1658 (9)	0.1533 (6)	0.039 (2)
C21	0.2126 (3)	0.2750 (11)	0.0951 (7)	0.051 (3)
C22	0.1978 (3)	0.2524 (13)	−0.0038 (6)	0.056 (3)
C23	0.1799 (3)	0.1289 (11)	−0.0435 (6)	0.050 (3)
C24	0.1782 (4)	0.0214 (12)	0.0153 (7)	0.069 (4)
C25	0.1926 (4)	0.0385 (11)	0.1122 (7)	0.063 (3)
C26	0.1627 (5)	0.1123 (13)	−0.1536 (7)	0.083 (4)
Zn27	1/4	1/4	1/2	0.0403 (5)

The *m*-chlorotoluene guest is heavily disordered in the interporphyrin channels at 0,0,*z* (near $z = 0$ and $\frac{1}{2}$). The final difference Fourier map showed eight relatively high residual peaks of 0.65–1.54 e Å^{-3} in these channels, but no recognizable fragments of the solvent could be identified. When these peaks were included as atoms with partial occupancy (corresponding to a 1:1 porphyrin–chlorotoluene ratio as suggested by density measurements) and isotropic *U*, the refinement calculations converged at *R*(all data) = 0.115, *R*(obs) = 0.071, *wR*(all data) = 0.197, *S* = 0.966, $\Delta\rho_{max} = 0.42$ and $\Delta\rho_{min} = -0.26$ e Å^{-3}. The H atoms were introduced in calculated positions, the geometrically idealized methyl groups being staggered with respect to adjacent C—C bonds of the phenyl rings. In the refinement calculations, the methyl groups were treated as rigid groups; their H atoms were allowed to ride on their C atoms and were assigned an isotropic *U* value.

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CADINT*, locally developed software; program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick,

1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93, *PARST* (Nardelli, 1983).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: MU1248). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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