

The nature of supramolecular interactions in tetrakis(4-iodophenyl)porphyrin and its zinc(II) complex

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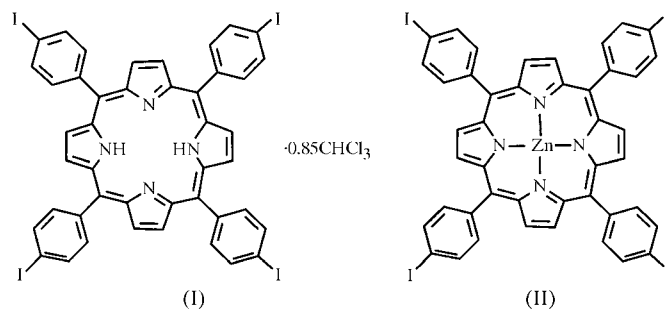
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Crystals of tetrakis(4-iodophenyl)porphyrin chloroform 0.85-solvate, $C_{44}H_{26}I_4N_4 \cdot 0.85CHCl_3$, (I), and [tetrakis(4-iodophenyl)porphyrinato]zinc(II), $[Zn(C_{44}H_{24}I_4N_4)]$, (II), reveal different modes of supramolecular organization. $I \cdots I$ attractions provide a significant contribution to the layered interporphyrin arrangement in (I), wherein all molecules have the same orientation. Weak axial coordinations of the I atoms to the Zn centres appear to have a dominant effect on the formation of two-dimensional supramolecular assemblies in (II), with a herring-bone arrangement of the metalloporphyrin species. Both molecules are located on inversion centres.

Comment

We have described previously the structural patterns and crystal inclusion chemistry of a large variety of tetra(4-halogenophenyl)porphyrin materials with F, Cl and Br atoms as the halogen substituents (Krupitsky *et al.*, 1995; Dastidar *et al.*, 1996). The observed interporphyrin architectures of the chloro and bromo derivatives were found to be affected by directional $Cl \cdots Cl$ and $Br \cdots Br$ interactions. On the other hand, the fluoro-substituted compounds exhibit intermolecular organization similar to that observed in unsubstituted tetraphenylporphyrin moieties (Byrn *et al.*, 1993). This is consistent with recent evaluations that $F \cdots F$ interactions are inferior to the other halogen \cdots halogen forces and have a negligible effect on intermolecular organization in crystalline solids (Awwadi *et al.*, 2006). It has been further shown that this trend in halogen \cdots halogen interaction strength parallels the polarizability of the electronic charge around the halogen atoms, and that $I \cdots I$ interactions are the strongest in this series and readily expressed in different crystal environments (*e.g.* Awwadi *et al.*, 2006; Bosch & Barnes, 2002). Most halogen-substituted porphyrin compounds exhibit layered molecular patterns in their respective crystal structures, the stability of which is also affected by co-operative dipolar attractions between carbon-halogen bonds of neighbouring species oriented in an antiparallel manner with respect to each

other (Krupitsky *et al.*, 1995; Dastidar *et al.*, 1996). Similarly layered structures have been observed for porphyrin derivatives with other polar substituents at the *meso* positions, such as 4-cyanophenyl (Krishna Kumar *et al.*, 1998). In the above



context, only one crystal structure of a tetra(4-iodophenyl)porphyrin compound (as an Mn^{III} -tetracyanoethenide complex) is known (Rittenberg & Miller, 1999). It was used as a building block for the construction of one-dimensional hybrid polymeric entities, sustained by charged $Mn \cdots N(\text{ligand})$ bonds. These polymers exhibit magnetic ordering, without a visible effect on the crystal packing of intermolecular interactions involving the I substituents. We report here the structures of the free-base title porphyrin, which crystallizes as the chloroform solvate, (I), and the corresponding Zn^{II} complex, (II), focusing on the intermolecular organization in their crystal structures.

The structure of compound (I) (Fig. 1) can be best described as composed of open layers of the porphyrin species (located in the crystal on centres of inversion), which occlude molecules of the chloroform solvent in the interporphyrin void

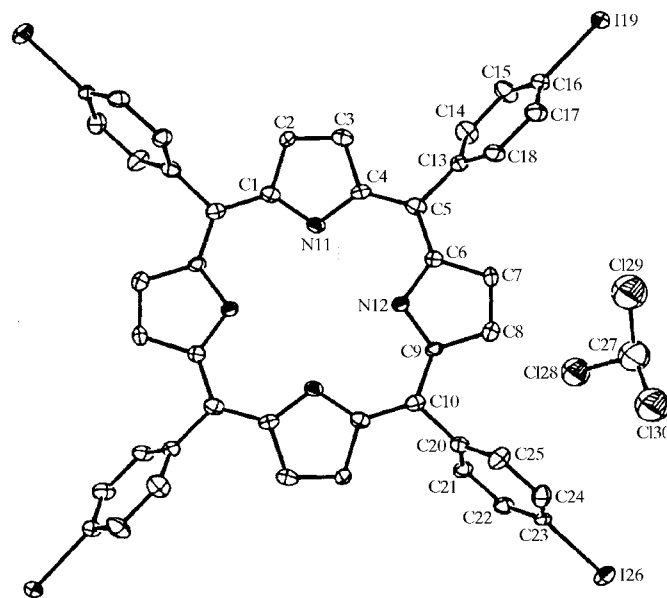


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. The porphyrin molecule resides on a centre of inversion and the asymmetric unit consists of only one half of the molecule; unlabelled atoms are related to labelled atoms by the symmetry operator $(1 - x, -y, 2 - z)$. H atoms have been omitted.

space. Fig. 2 illustrates the main intermolecular interactions that stabilize this layered arrangement. There are linear porphyrin arrays wherein every molecule is connected on both sides to two neighbouring species by four $I \cdots I$ attractive contacts of $I19 \cdots I26(2 - x, -y, 1 - z) = 3.8808(5) \text{ \AA}$. The chains thus formed are further linked to each other by dipolar forces between iodophenyl groups oriented in opposite directions, as well as by $I \cdots \pi$ interactions, with a distance of 3.6 \AA for the I atom from the plane of a nearby iodophenyl ring. This is consistent with earlier observations on the preferred intermolecular organization of halogen- and cyano-substituted tetraarylporphyrins, as well as on the attractive nature of halogen \cdots halogen attractions (Krupitsky *et al.*, 1995; Dastidar *et al.*, 1996; Awwadi *et al.*, 2006; Bosch & Barnes, 2002; Krishna Kumar *et al.*, 1998). These layers stack in the

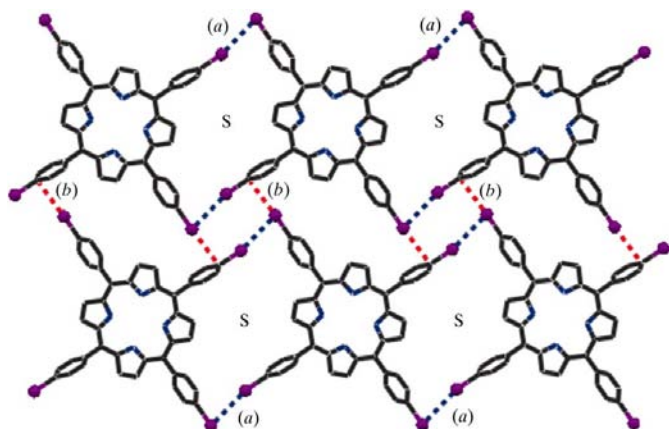


Figure 2

Stick illustration of the layered intermolecular organization of the porphyrin molecules in (I). I atoms are denoted by small spheres. Dashed lines indicate the $I \cdots I$ [labelled (a)] and $I \cdots \pi$ [labelled (b)] attractive interactions. S represents the approximate location of the chloroform solvent trapped in a disordered manner within the interporphyrin voids.

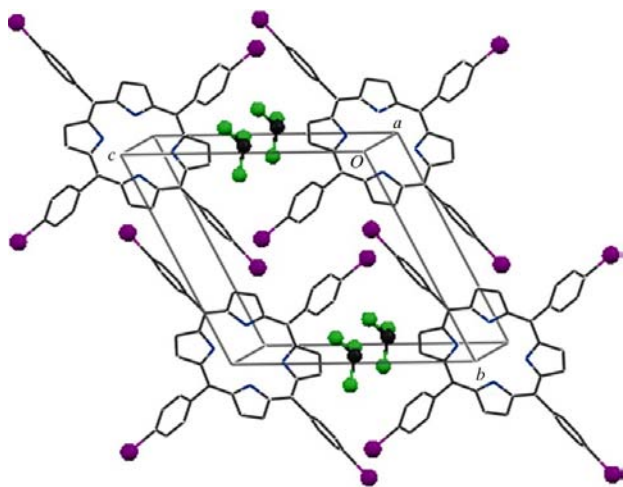


Figure 3

The crystal structure of (I), viewed approximately down the a axis. The I atoms of the porphyrin molecules and the atoms of the chloroform solvent molecules (only one of its orientations is shown at each site) are depicted by small spheres. The four porphyrin molecules belong to four different porphyrin layers of the type illustrated in Fig. 2.

crystal structure in a partly overlapping manner, and the overall packing arrangement reveals solvent-occupied canals that propagate through the crystal structure parallel to the a axis (Fig. 3).

Compound (II) crystallizes in an unsolvated form (Fig. 4), with the porphyrin units located on centres of inversion at $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, \frac{1}{2})$. The Zn–porphyrin molecules are arranged in a herring-bone manner to allow weak ligation of the metal centre to the I sites of two other species approaching from above and below. The corresponding interaction distances, $Zn \cdots I19(\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$ and $Zn \cdots I19(x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2})$, are $3.4747(3) \text{ \AA}$. As Zn–I bonds are generally much shorter (within 2.5 – 2.7 \AA ; Cambridge Structural Database, Version 5.27; Allen, 2002), these contacts represent rather weak interactions. Evidently, each porphyrin molecule is associated through such ligation to four other molecules, by attracting to its Zn metal centre the I-ligating sites of two adjacent moieties, while its own I19 and I19($1 - x, -y, -z$) sites link to the Zn centres of two additional porphyrins (Fig. 5). In this case, the $I \cdots I$ intermolecular interactions play a less significant role, as the shortest $I \cdots I$ intermolecular distances, $I19 \cdots I26(x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} + z)$ and $I19 \cdots I26(\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z)$, are within the range 4.24 – 4.25 \AA , considerably longer than the sum of the van der Waals radii (about 4.0 \AA ; Rowland & Taylor, 1996). However, the $I \cdots \pi$ interactions of about 3.6 \AA between adjacent molecules are preserved (Fig. 5). A similar four-point connection model of the metal–ligand linkages, resulting in the formation of two-dimensional coordination polymers, has been observed in other structures of zinc or manganese

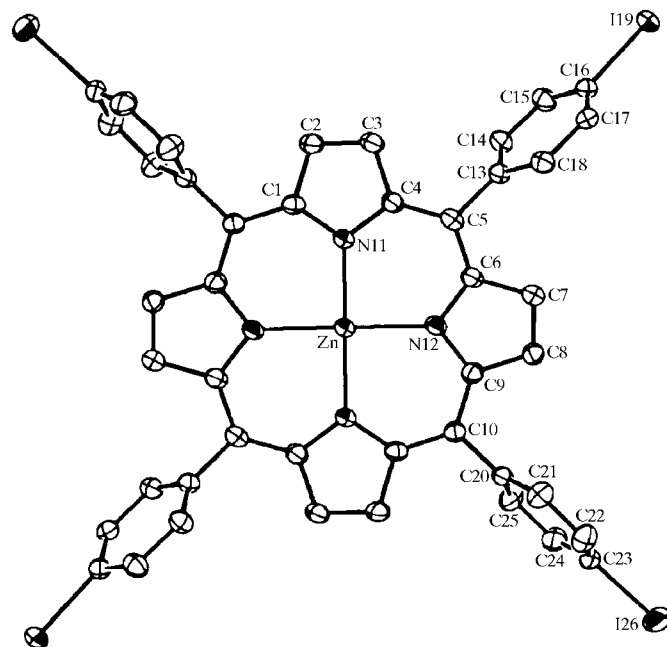


Figure 4

The molecular structure of (II), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at ca 110 K . The metalloporphyrin molecule resides on a centre of inversion and the asymmetric unit consists of only one half of the molecule; unlabelled atoms are related to labelled atoms by the symmetry operator $(1 - x, -y, -z)$. H atoms have been omitted.

metalloporphyrins functionalized with methoxycarbonylphenyl and carboxyphenyl groups (Muniappan *et al.*, 2006; Shmilovits *et al.*, 2004; George *et al.*, 2006). The latter examples involve much shorter Zn–O and Mn–O coordinations, within the range 2.2–2.5 Å, but the same unique pattern of supramolecular multiporphyrin assembly. In all structures, these two-dimensional arrays have corrugated surfaces and their stacking along the normal direction is stabilized by dispersion forces (Fig. 6). The latter correlations may support the notion that, although the axial Zn···I contacts in (II) are rather long at nearly 3.5 Å, due to the large size and high polarizability of the I atoms they may still have a sufficiently attractive nature to induce a supramolecular organization, which was previously observed in true coordination polymers (Muniappan *et al.*, 2006; Shmilovits *et al.*, 2004; George *et al.*, 2006).

In summary, the free-base title porphyrin, (I), and its zinc complex, (II), reveal two different interaction schemes and crystal packing modes. The layered intermolecular organization in (I) is affected primarily by I···I, I··· π and dipolar

(between antiparallel C–I dipoles) attractions, in addition to typical stacking of flat aromatic surfaces and dispersion forces. The presence of the metal centre in (II) induces the formation of pseudo-coordination polymers of the porphyrin entities, in which the tetracoordinate Zn ion forms weakly attractive contacts along the axial directions with the I sites of two neighbouring species, while donating two of its own I sites to the Zn centres of two further porphyrin units. Optimization of these interactions requires a herring-bone arrangement of the square-planar molecules.

Experimental

The free-base and zinc-metallated tetrakis(4-iodophenyl)porphyrin derivatives were synthesized from commercially available reagents, *viz.* 4-iodobenzaldehyde and pyrrole, according to standard procedures of porphyrin synthesis (Lindsey *et al.*, 1987). They were fully characterized by ^1H NMR, UV–Vis and MS techniques. For the free base, (I): ^1H NMR (CDCl_3): δ 8.80 (s, 8H), 8.07 (d, 8H, $J = 8.2$ Hz), 7.89 (d, 8H, $J = 8.3$ Hz), -2.92 (s, 2H); UV–Vis (in CHCl_3 , λ_{max} , nm): 421, 516, 551, 591, 646; FAB mass spectrum (m/z) for $\text{C}_{44}\text{H}_{26}\text{I}_4\text{N}_4$: found 1118, calculated 1118.34. For the Zn–porphyrin, (II): ^1H NMR (CDCl_3): δ 8.90 (s, 8H), 8.06 (d, 8H, $J = 8.2$ Hz), 7.89 (d, 8H, $J = 8.2$ Hz); UV–Vis (in CHCl_3 , λ_{max} , nm): 421, 548, 588; FAB mass spectrum (m/z) for $\text{C}_{44}\text{H}_{24}\text{I}_4\text{N}_4\text{Zn}$: found 1182, calculated 1181.70. Compound (I) was crystallized by slow evaporation of a solution in chloroform, while compound (II) was crystallized from a 4:1 mixture of chloroform and methanol.

Compound (I)

Crystal data

$\text{C}_{44}\text{H}_{26}\text{I}_4\text{N}_4 \cdot 0.85\text{CHCl}_3$
 $M_r = 1219.99$
 Triclinic, $P\bar{1}$
 $a = 6.5360$ (2) Å
 $b = 13.4507$ (3) Å
 $c = 13.8558$ (4) Å
 $\alpha = 117.1350$ (10)°
 $\beta = 100.6121$ (10)°

$\gamma = 92.7217$ (19)°
 $V = 1053.40$ (5) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 3.16$ mm⁻¹
 $T = 110$ (2) K
 $0.30 \times 0.10 \times 0.05$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\text{min}} = 0.451$, $T_{\text{max}} = 0.858$

11891 measured reflections
 5033 independent reflections
 3760 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$
 $wR(F^2) = 0.134$
 $S = 1.05$
 5033 reflections

252 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 2.51$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.63$ e Å⁻³

Compound (II)

Crystal data

$[\text{Zn}(\text{C}_{44}\text{H}_{24}\text{I}_4\text{N}_4)]$
 $M_r = 1181.64$
 Monoclinic, $P2_1/n$
 $a = 10.2165$ (3) Å
 $b = 9.2289$ (3) Å
 $c = 20.5252$ (5) Å
 $\beta = 97.914$ (2)°

$V = 1916.83$ (10) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 3.90$ mm⁻¹
 $T = 110$ (2) K
 $0.20 \times 0.20 \times 0.15$ mm

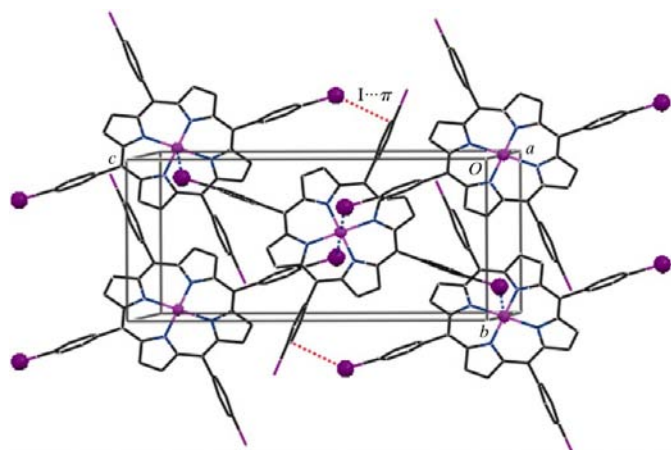


Figure 5
 Stick illustration of the interporphyrin 'coordination polymerization' via the Zn···I linkages (short dashed lines) in (II). I and Zn atoms are indicated by small spheres. Possible I··· π interactions, at an average distance of 3.6 Å, are also marked (long dashed lines at the top and bottom centre).

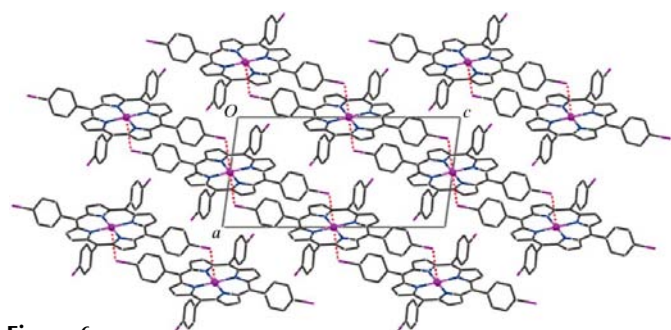


Figure 6
 The crystal structure of (II), projected down the b axis and showing the van der Waals stacking of the inter-coordinated porphyrin layers (shown edge-on). Zn atoms are indicated by small spheres and Zn···I contacts by dashed lines.

Data collection

Nonius KappaCCD area-detector diffractometer	15857 measured reflections
Absorption correction: multi-scan (Blessing, 1995)	4620 independent reflections
$T_{\min} = 0.509$, $T_{\max} = 0.592$ (expected range = 0.479–0.557)	3397 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$	241 parameters
$wR(F^2) = 0.119$	H-atom parameters constrained
$S = 1.07$	$\Delta\rho_{\text{max}} = 1.38 \text{ e } \text{\AA}^{-3}$
4620 reflections	$\Delta\rho_{\text{min}} = -1.63 \text{ e } \text{\AA}^{-3}$

The H atoms were located in calculated positions and were constrained to ride on their parent atoms, with C–H = 0.95–1.00 Å and N–H = 0.88 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$. The inner pyrrole H atoms in (I) are disordered between the four N-atom sites. In (I), the porphyrin molecule resides on an inversion centre at $(\frac{1}{2}, 0, 1)$, while the chloroform solvent [refined with a total occupancy of 0.852 (5)] is located near to and disordered about an inversion centre at $(1, 0, \frac{1}{2})$. Three significant residual electron-density peaks within the range 2.0–2.5 e Å⁻³ found near this site could not be accounted for. They may indicate that the chloroform species reveals an additional orientational and positional disorder, but this could not be resolved. While the Zn–porphyrin core in (II) is perfectly planar, the conformation of the macrocyclic ring in (I) is slightly ruffled to relieve the H···H repulsion between the inner pyrrole H atoms. All bond lengths and angles in (I) and (II) are within normal ranges (Cambridge Structural Database, Version 5.27; Allen, 2002).

For both compounds, data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3127). Services for accessing these data are described at the back of the journal.

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