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[Tetrakis(3-chlorophenyl)porphyrinato]zinc(II)

The title compound, $[\text{Zn}(\text{C}_{44}\text{H}_{28}\text{Cl}_4\text{N}_4)]$, is a four-coordinate zinc–porphyrin complex, with 3-chlorophenyl substituents at the *meso* positions of the planar metalloporphyrin core. The molecules are located on crystallographic inversion centres, exhibiting partial orientational disorder of the aryl residues. The crystal packing is stabilized by van der Waals forces and intermolecular $\text{Cl}\cdots\text{Cl}$ interactions.

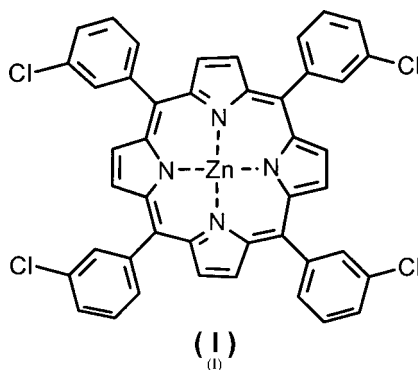
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Key indicators

Single-crystal X-ray study
 $T = 110\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$
Disorder in main residue
 R factor = 0.061
 wR factor = 0.171
Data-to-parameter ratio = 16.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

Comment

The title compound, (I), which is commercially available, serves as a starting material in the preparation of functionalized tetraarylporphyrin building blocks of lower than D_{4h} symmetry, to be then used in supramolecular syntheses of new centrosymmetric and noncentrosymmetric materials (Goldberg, 2005; Vinodu & Goldberg, 2005; George & Goldberg, 2006). Activation of a single *meta* (rather than *para*) position of the four phenyl arms presents one approach (among many others) to lowering the molecular symmetry of the porphyrin framework. A survey of the Cambridge Crystallographic Database (Version 5.27 of November 2005; Allen, 2002) reveals that porphyrin compounds with 3,5-disubstituted functionality are abundant in the literature (see, for example, Bonifazi *et al.*, 2004; Suijkerbuijk *et al.*, 2004; Sugiura *et al.*, 1999; Boyd *et al.*, 1999), which is not the case for the crystal structures of the 3-monosubstituted analogues. The present report is one of the few examples of the latter, describing the structure of (I), precisely analysed at *ca* 110 K (Fig. 1).



In this structure, the 25-atom porphyrin core, including the Zn atom, is essentially planar, the deviations of the individual atoms from its mean plane being within ± 0.044 (3) Å. The molecules are located on centres of inversion. One pair of the chlorophenyl rings reveals an orientational disorder, with relative occupancies of the two sites in each ring of 0.653 (3) and 0.347 (3). Possible minor disorder in the other two

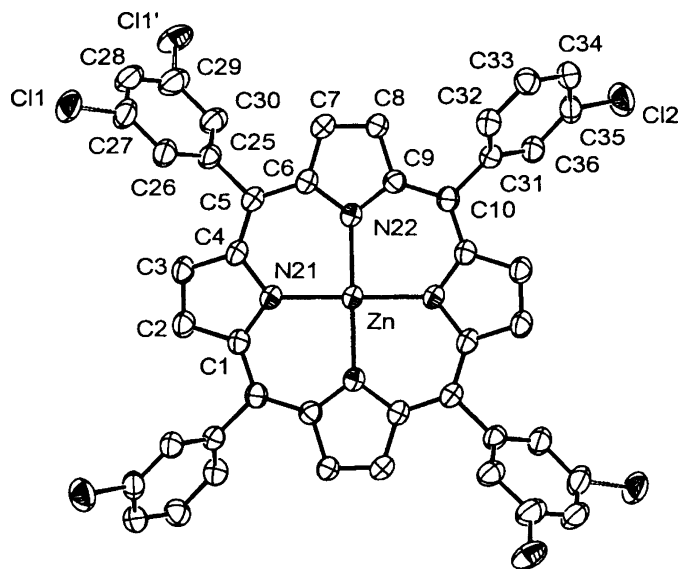


Figure 1

The molecular structure of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level at *ca* 110 K. The molecule is located on a centre of inversion at $(0, \frac{1}{2}, 0)$. Note that atom Cl1 is disordered over two positions, Cl1 and Cl1', in an approximately 2:1 ratio. H atoms have been omitted. Zn, N and Cl atoms are indicated by shaded ellipsoids.

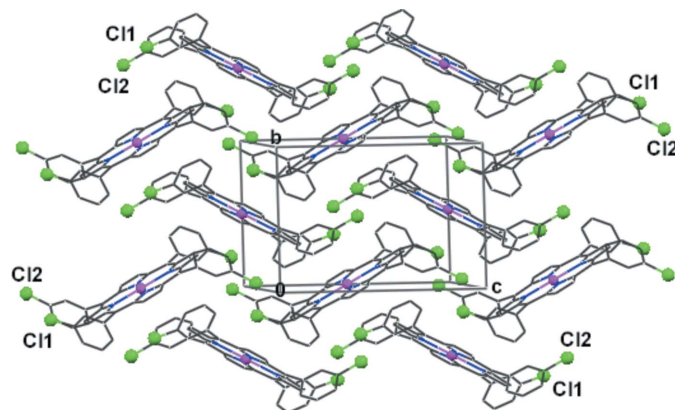


Figure 2

A perspective view of the herring-bone-type organization of the porphyrin molecules in layered zones perpendicular to the *b* axis. H atoms have been omitted. Note the flat shape of the porphyrin core macrocycle. Zn atoms are coloured purple, N atoms blue, Cl atoms green and C atoms black. Atom Cl1 is shown only in its major (65%) orientation.

chlorophenyl groups could not be well characterized and was ignored. Similar disorder was observed when the crystallographic refinement was carried out in lower symmetry space groups wherein the molecules are not constrained to be centrosymmetric (e.g. $P\bar{1}$ and $P2_1$), indicating that the observed disorder is an inherent feature of the molecular structure, as would be expected from the spatial equivalence of the upper and lower surfaces of the porphyrin framework.

The crystal packing of (I) can be best described as consisting of layered zones of the molecules oriented roughly parallel to the *bc* plane (Fig. 2). Within these zones, the mol-

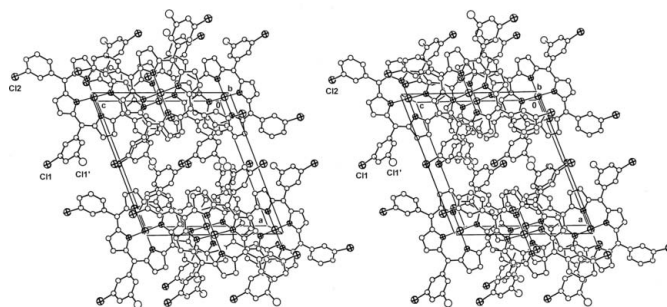


Figure 3

A stereoview of the crystal packing of (I), approximately down the *b* axis, showing two porphyrin layers displaced by *c*. H atoms have been omitted. Note that the C–Cl1 and C–Cl1' bonds line the interface between these layers.

ecules are arranged in a tight herring-bone manner, wherein the molecular surfaces of the porphyrin core of one species are approached from above and below by the chlorophenyl arms of neighbouring units, imparting to the central Zn^{II} ion a centrosymmetric axial environment. The C–Cl2 bonds are oriented within these layers, but are not involved in specific intermolecular interactions. Stacking of the layered zones along the *a* axis is illustrated in Fig. 3. The C–Cl1 and C–Cl1' bonds line the interface between the layers, being involved in close $Cl \cdots Cl$ non-bonding contacts: $Cl1 \cdots Cl1(-1-x, 1-y, -1-z) = 3.471(5) \text{ \AA}$, and $Cl1 \cdots Cl1'(x, \frac{3}{2}-y, z-\frac{1}{2}) = 3.540(5) \text{ \AA}$. These provide attractive contributions to the lattice energy, as is often observed in crystal structures of halogenated hydrocarbons (Pedireddi *et al.*, 1994; Desiraju & Parthasarathy, 1989).

In view of the general tendency of tetraphenyl metalloporphyrins to crystallize as solvates or clathrates (Byrn *et al.*, 1993), the efficient solvent- and void-free crystal packing of the title compound is rather uncommon, possibly also due to these halogen \cdots halogen attractions.

Experimental

The crystals of the title compound were obtained by dissolving the commercially available 95% pure material (MidCentury Chemicals; 11 mg) in a 4:1 chloroform–methanol (Aldrich) mixture (10 ml). The solution thus formed was filtered and left for crystallization at room temperature, yielding diffraction quality violet crystals of (I) after a few days.

Crystal data

$[Zn(C_{24}H_{24}Cl_4N_4)]$
 $M_r = 815.84$
 Monoclinic, $P2_1/c$
 $a = 14.7205(4) \text{ \AA}$
 $b = 9.4071(3) \text{ \AA}$
 $c = 13.5925(5) \text{ \AA}$
 $\beta = 110.7208(17)^\circ$
 $V = 1760.50(10) \text{ \AA}^3$
 $Z = 2$

$D_x = 1.539 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 3801 reflections
 $\theta = 2.6\text{--}27.9^\circ$
 $\mu = 1.04 \text{ mm}^{-1}$
 $T = 110(2) \text{ K}$
 Prism, violet
 $0.40 \times 0.35 \times 0.25 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer	4179 independent reflections 2961 reflections with $I > 2\sigma(I)$
φ scans	$R_{\text{int}} = 0.047$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{\text{max}} = 27.9^\circ$ $h = -19 \rightarrow 18$ $k = -12 \rightarrow 12$ $l = -17 \rightarrow 17$
$T_{\text{min}} = 0.681$, $T_{\text{max}} = 0.781$	
12967 measured reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0873P)^2 + 1.8321P]$
$R[F^2 > 2\sigma(F^2)] = 0.061$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.171$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 1.49 \text{ e } \text{\AA}^{-3}$
4179 reflections	$\Delta\rho_{\text{min}} = -0.73 \text{ e } \text{\AA}^{-3}$
251 parameters	
H-atom parameters constrained	

The H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C—H distances in the range 0.95–0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$. The final residual electron-density map contains one significant peak of $1.5 \text{ e } \text{\AA}^{-3}$ at 1.503 Å from atom C33, which can be attributed to a possible alternative position of Cl2 (Cl2'), thus indicating either partial orientational disorder (about 0.90:0.10) of this group, or the presence of minor and otherwise undetected amounts of the tetrakis(3-methylphenyl)zincporphyrin analogue in the crystal (as often the 3-chlorobenzaldehyde starting material for the porphyrin synthesis is contaminated by the *m*-tolualdehyde analog). As no acceptable structural model for either of these possibilities could be reliably refined, this residual peak has not been accounted for in the final structure.

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* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97*.

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