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Aqua{5,15-bis[4-(2-trimethylsilylacetylene)phenyl]-2,8,12,18-tetrakis(2-methoxycarbonylethyl)-3,7,13,17-tetramethyl-10,20-dioxoporphyrinato}zinc(II)

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The crystal structure of the title compound, [Zn($C_{62}H_{66}N_4O_{10}$-Si_2)(H_2O)], has been determined at 160 (2) K by utilization of a synchrotron X-ray source. The molecular units dimerize *via* hydrogen bonds involving the water molecules, and these dimers form π-stacks *via* interactions between the hydrophobic porphyrin faces.

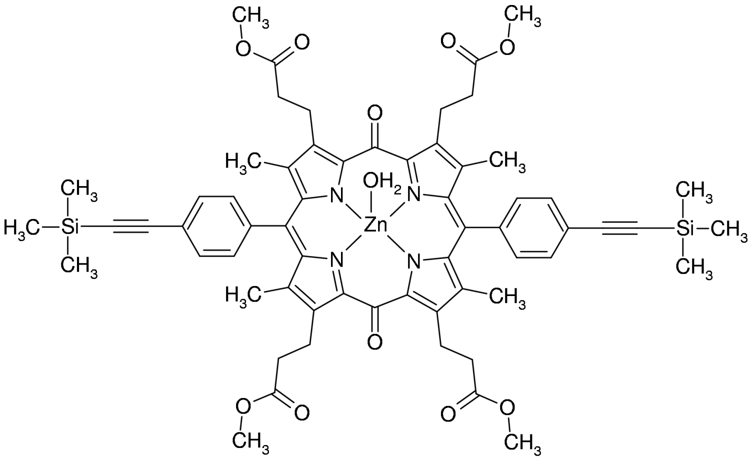
Key indicators

Single-crystal synchrotron study
T = 160 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.054
wR factor = 0.135
Data-to-parameter ratio = 16.4

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

Comment

The bright-orange monomeric dioxoporphyrin unit aqua{5,15-bis[4-(2-trimethylsilylacetylene)phenyl]-2,8,12,18-tetrakis(2-methoxycarbonylethyl)-3,7,13,17-tetramethyl-10,20-dioxoporphyrinato}zinc(II), (I), is prepared by thallium trifluoroacetate oxidation (McCallien & Sanders, 1995) of the purple porphyrinic zinc precursor (Bampos *et al.*, 1998). The presence of electron-withdrawing cross-conjugated carbonyl groups on the macrocyclic periphery gives (I) two characteristic properties in solution: lack of a diagnostic NMR diamagnetic ring current and an increased Lewis acidity of the central metal ion, leading to stronger binding of N- and O-ligands. Both these properties make (I) attractive as a building block in the templated construction of supramolecular architectures (Clyde-Watson *et al.*, 1998).



(I)

(I) crystallizes with a saddle conformation (Scheidt & Lee, 1987) characterized by alternate pyrrole-ring displacements above and below the least-squares plane through the 24 atoms of the porphyrin unit (Fig. 1). Molecules of (I) are linked into centrosymmetric dimers *via* hydrogen bonds formed by the zinc-bound water molecule with one oxo group in the 10-position of an adjacent porphyrin and one carbonyl oxygen of a 2-methoxycarbonylethyl side chain [H11*A*···O3^i =

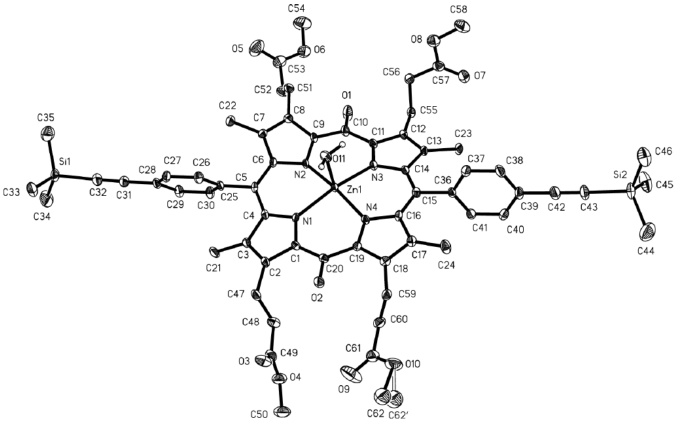


Figure 1
The molecular unit in (I) showing displacement ellipsoids at the 50% probability level (*XP*; Sheldrick, 1993).

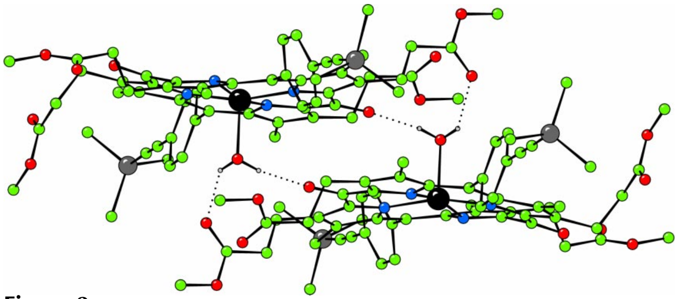


Figure 2
The molecules of (I) linked into dimers *via* hydrogen bonds. All H atoms not involved in hydrogen bonding have been omitted for clarity (*CAMERON*; Watkin *et al.*, 1996).

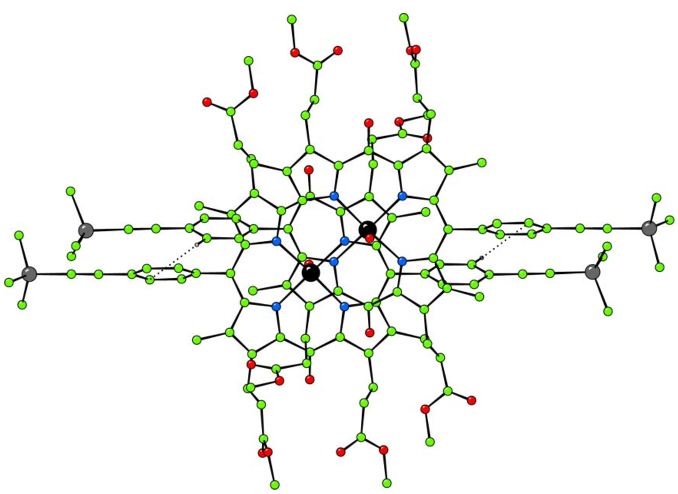


Figure 3
View along the stacking direction (approximately along [$\bar{1}$10]) showing adjacent π-stacked molecules of (I). The C—H$\cdots\pi$ interaction is indicated by a dotted line. All other H atoms have been omitted for clarity (*CAMERON*; Watkin *et al.*, 1996).

2.13 (3) Å, O11—H11*A*$\cdots$O3^{i} = 144 (4)°; H11*B*$\cdots$O2^{i} = 1.92 (2) Å, O11—H11*B*$\cdots$O2^{i} = 168 (4)°; symmetry code: (i) $-1 - x, -y, -z$] (Fig. 2). The hydrogen-bond arrangement is reminiscent of that observed in the dihydrates of ethyl chlorophyllide *a* and *b*, in which magnesium-bound water molecules hydrogen bond to oxo groups of neighbouring chlorophyllide units and also *via* a second water molecule to

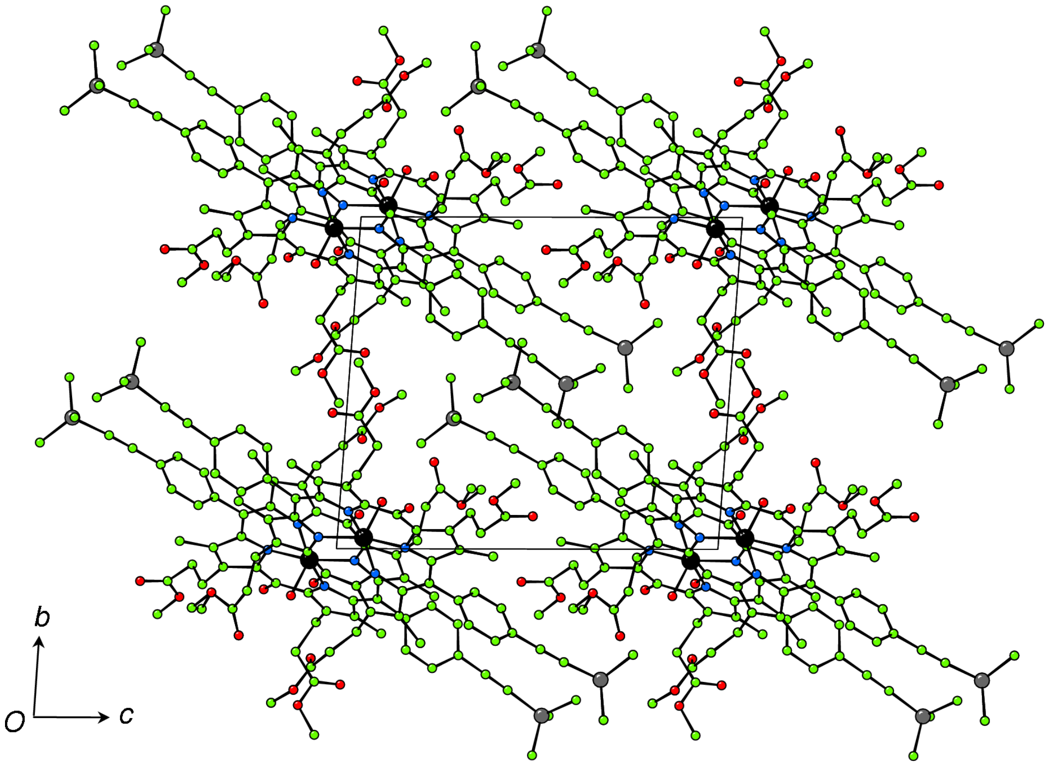


Figure 4
Projection on to the (100) plane showing interdigitation of adjacent stacks. H atoms are omitted for clarity (*CAMERON*; Watkin *et al.*, 1996).

Acta Cryst. (2001). E**57**, m454–m456 Andrew D. Bond *et al.* • [Zn($C_{62}H_{66}N_4O_{10}Si_2$)($H_2O$)] **m455**

the carbonyl oxygen of a methyl ester side chain, forming one-dimensional polymers (Chow *et al.*, 1975; Serlin *et al.*, 1975). The omission of the second water molecule in (I) allows both interactions to form between the same molecular units, giving rise to the observed dimers.

Dimers are π-stacked *via* interactions between hydrophobic porphyrin faces, with the stacking direction approximately perpendicular to ($\overline{1}10$). Least-squares planes through adjacent porphyrin units in the stacks are coplanar with a separation of *ca* 3.8 Å, and a Zn1$\cdots$Zn1$^{\rm ii}$ distance of 5.719 (1) Å [symmetry code: (ii) $-2-x$, $-y$, $-z$] (Fig. 3). In adjacent molecules, phenyl groups of the 4-(2-trimethylsilylacetylene)phenyl substituents are twisted with respect to each other by an angle of *ca* 33°, adopting a geometry indicative of an edge-to-face C—H$\cdots\pi$ interaction [H30$\cdots$(centroid C36–C41)$^{\rm ii}$ = 3.45 Å, C30—H30$\cdots$centroid = 163°] (Desiraju & Steiner, 1999). This interaction may contribute towards the stability of the π-stacks. The 4-(2-trimethylsilylacetylene)phenyl substituents in adjacent stacks are interdigitated, maximizing dispersion interactions between stacks (Fig. 4).

Experimental

Crystals of (I) were grown from a solution in dichloromethane, layered with methanol.

Crystal data

[Zn($C_{62}H_{66}N_4O_{10}Si_2$)($H_2O$)]
M_r = 1166.75
Triclinic, $P\overline{1}$
a = 12.570 (2) Å
b = 14.285 (3) Å
c = 17.502 (4) Å
α = 85.082 (10)°
β = 69.225 (12)°
γ = 87.07 (2)°
V = 2926.9 (11) Å^3
Z = 2

D_x = 1.324 Mg m^{-3}
Synchrotron radiation
λ = 0.6879 Å
Cell parameters from 17 561 reflections
θ = 3.4–27.1°
μ = 0.52 mm^{-1}
T = 160 (2) K
Plate, red
0.07 × 0.06 × 0.02 mm

Data collection

Bruker SMART CCD diffractometer
Thin-slice ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\rm min}$ = 0.964, $T_{\rm max}$ = 0.990
17 561 measured reflections

12 222 independent reflections
8256 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.066
$\theta_{\rm max}$ = 27.1°
$h = -15 \rightarrow 16$
$k = -18 \rightarrow 17$
$l = -18 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.135
S = 0.92
12 222 reflections
743 parameters

H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0676P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.023
$\Delta\rho_{\rm max}$ = 1.19 e Å^{-3}
$\Delta\rho_{\rm min}$ = −1.10 e Å^{-3}

H atoms attached to C atoms were placed geometrically and refined using a riding model with an isotropic displacement parameter fixed at 1.2$U_{\rm eq}$ for the carbon to which they are attached (1.5$U_{\rm eq}$ for methyl groups). H11*A* and H11*B*, associated with the water molecule, were located in a difference Fourier map and refined with an isotropic displacement parameter and the O11—H distance restrained to be 0.84 (1) Å. The terminal methyl group of one 2-methoxycarbonylethyl side chain was found to be disordered and was modelled as two equally occupied sites (C62 and C62′), each refined with an isotropic displacement parameter. The O10—C62 and O10—C62′ bond distances were restrained to be identical, with an s.u. of 0.02 Å.

Data collection: *SMART* (Siemens, 1994); cell refinement: *LSCELL* (Clegg, 1995); data reduction: *SAINT* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL*97.

The title structure is the one of the first from Cambridge to be collected at Station 9.8, Daresbury SRS, and marks the beginning of an extremely fruitful collaboration. We thank the EPSRC for financial assistance.

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m456 Andrew D. Bond *et al.* • [Zn($C_{62}H_{66}N_4O_{10}Si_2$)($H_2O$)] *Acta Cryst.* (2001). E**57**, m454–m456