

## Synchrotron study of a fully protonated tetraphenyl porphyrin

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## Key indicators

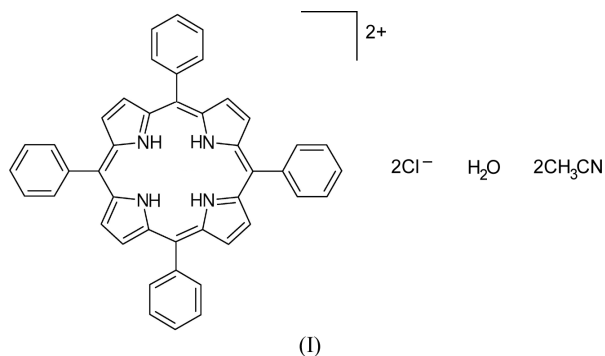
Single-crystal synchrotron study  
 $T = 150$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.052  
 $wR$  factor = 0.125  
Data-to-parameter ratio = 20.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

5,10,15,20-Tetraphenylporphyrindium dichloride acetonitrile disolvate monohydrate,  $\text{C}_{44}\text{H}_{32}\text{N}_4^{2+} \cdot 2\text{Cl}^- \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ , crystallizes in space group *Pnma*, with the porphyrin and water molecules sited on crystallographic mirror planes. The extended structure includes a one-dimensional network of hydrogen bonds between the NH groups of the porphyrin, the two  $\text{Cl}^-$  anions and the solvent water molecule.

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## Comment

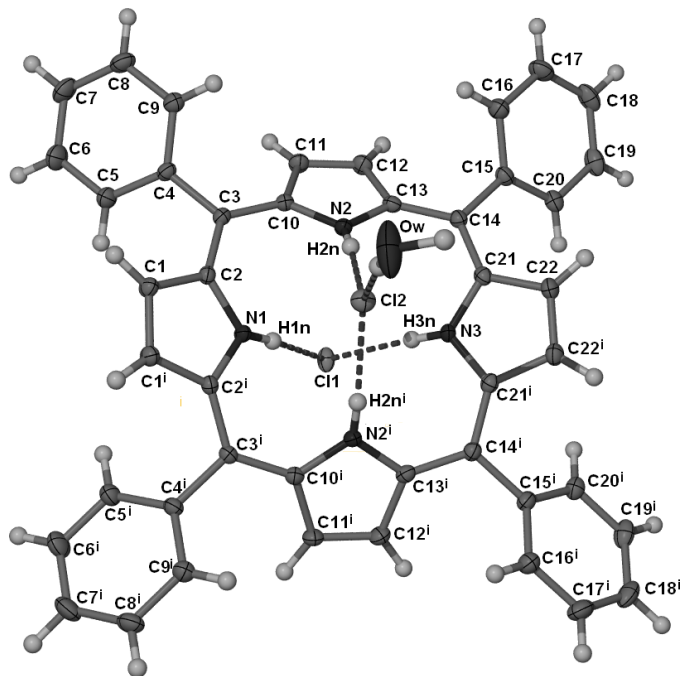
During an attempt to prepare a gold porphyrin complex from  $\text{HAuCl}_4$  and 5,10,15,20-tetraphenylporphyrin ( $\text{H}_2\text{TPP}$ ) in glacial acetic acid, the green title compound  $[\text{H}_4\text{TPP}]\text{Cl}_2 \cdot 2\text{CH}_3\text{CN} \cdot \text{H}_2\text{O}$ , (I), was isolated. Crystals of (I) grew as needles of up to *ca* 2 mm in length, but with diameters of only 5–10  $\mu\text{m}$ , necessitating the use of a synchrotron source (Station 9.8, SRS Daresbury, UK) for structure determination.



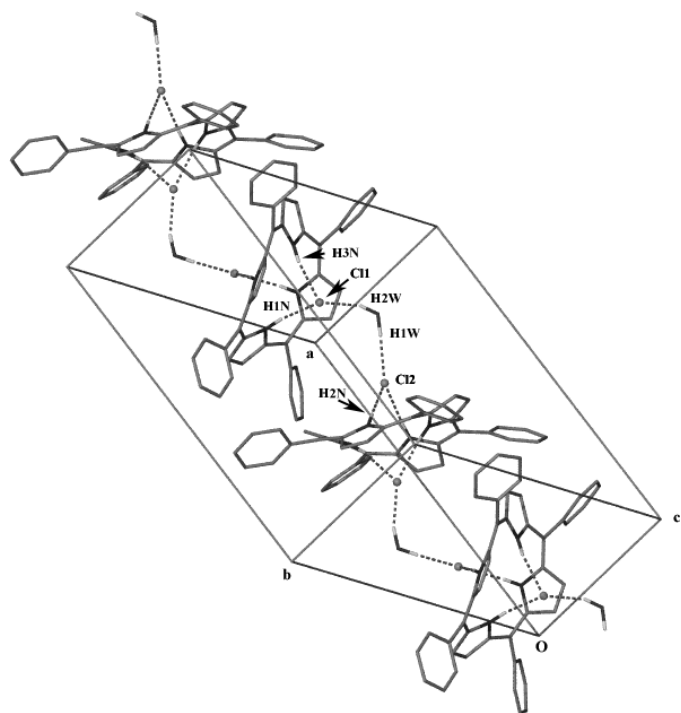
The porphyrin cation and water molecule lie on crystallographic mirror planes. The structure of (I) (Fig. 1) includes *trans* NH groups of the porphyrin moiety hydrogen-bonded to  $\text{Cl}^-$  anions on either side of the porphyrin plane. This hydrogen-bond motif is commonly adopted by diprotonated porphyrins (Cheng *et al.*, 1997), and results in a distortion of the macrocycle core from planarity towards a saddle shape. Additional hydrogen bonding between the  $\text{Cl}^-$  anions and the water molecules gives rise to a one-dimensional network, consisting of alternating  $\text{N}-\text{H} \cdots \text{Cl}$  and  $\text{O}-\text{H} \cdots \text{Cl}$  hydrogen bonds (Table 1 and Fig. 2).

## Experimental

The experimental procedure of Fleischer & Laszlo (1969) was utilized for the preparation of  $[\text{Au}^{\text{III}}\text{TPP}][\text{AuCl}_4]$ . During reflux, a green precipitate was formed, which was isolated. The powder was dissolved in acetonitrile and toluene was allowed to diffuse slowly into the solution. Long thin green needles of (I) formed after approximately 2 d.



**Figure 1**  
The components of (I), showing displacement ellipsoids at the 50% probability level. H atoms are shown as small spheres of arbitrary radii. The solvent acetonitrile molecules have been omitted for clarity. Dashed lines indicate hydrogen bonds. [Symmetry code: (i)  $\frac{1}{2} + x, y, \frac{1}{2} - z$ .]



**Figure 2**  
The hydrogen-bonding network in (I) (dashed lines). The solvent acetonitrile molecules and H atoms not involved in hydrogen bonding have been omitted for clarity.

#### Crystal data

$C_{44}H_{32}N_4^{2+} \cdot 2Cl^- \cdot 2C_2H_3N \cdot H_2O$   
 $M_r = 787.76$   
 Orthorhombic,  $Pnma$   
 $a = 18.975$  (4) Å  
 $b = 25.920$  (5) Å  
 $c = 8.228$  (2) Å  
 $V = 4046.8$  (15) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.293$  Mg m<sup>-3</sup>

Synchrotron radiation  
 $\lambda = 0.6900$  Å  
 Cell parameters from 5893 reflections  
 $\theta = 5.2$ – $58.6^\circ$   
 $\mu = 0.21$  mm<sup>-1</sup>  
 $T = 150$  (2) K  
 Needle, green  
 $0.08 \times 0.02 \times 0.01$  mm

#### Data collection

Bruker SMART CCD area-detector diffractometer  
 Thin slice  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)  
 $T_{min} = 0.984, T_{max} = 0.998$   
 13 131 measured reflections

5658 independent reflections  
 4241 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.039$   
 $\theta_{max} = 29.4^\circ$   
 $h = -26 \rightarrow 16$   
 $k = -22 \rightarrow 36$   
 $l = -11 \rightarrow 11$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.052$   
 $wR(F^2) = 0.125$   
 $S = 1.02$   
 5658 reflections  
 283 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0488P)^2 + 2.6837P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.41$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.40$  e Å<sup>-3</sup>

H atoms treated by a mixture of independent and constrained refinement

**Table 1**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1N \cdots Cl1$	0.88 (1)	2.18 (1)	3.052 (2)	170 (3)
$N2-H2N \cdots Cl2$	0.88 (1)	2.33 (1)	3.2095 (15)	176 (2)
$N3-H3N \cdots Cl1$	0.88 (1)	2.29 (1)	3.154 (2)	170 (3)
$O1W-H1W \cdots Cl2$	0.91 (1)	2.45 (1)	3.355 (3)	180 (3)
$O1W-H2W \cdots Cl1^i$	0.91 (1)	2.28 (1)	3.185 (2)	177 (3)

Symmetry code: (i)  $\frac{1}{2} + x, y, \frac{1}{2} - z$ .

The listed transmission factors are not real, since they include corrections for beam decay and possibly crystal decay (the two cannot be distinguished). The values listed in the CIF are those calculated by *SHELXL97* (Sheldrick, 1997). H atoms bonded to N atoms were located in difference Fourier maps and refined with isotropic displacement parameters, with N–H distances restrained to 0.90 (1) Å. Atoms H1W and H2W, bonded to atom O1W, were also located, and were refined with O–H and H···H distances restrained to ensure a chemically reasonable geometry, and with  $U_{iso}(H) = 1.2U_{eq}(O)$ . H atoms bonded to C atoms were placed geometrically and were refined using a riding model, with C–H distances of 0.95–0.98 Å, and with  $U_{iso}(H) = 1.2U_{eq}(C)$  for the C atoms of the porphyrin and  $U_{iso}(H) = 1.5U_{eq}(C)$  for the methyl group of the acetonitrile molecule. The CH<sub>3</sub> group of the acetonitrile molecule was allowed to rotate about its local threefold axis (AFIX 137).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1996); software used to prepare material for publication: *SHELXL97*.

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