

Aqua(phthalocyaninato- κ^4N)-magnesium(II) 3-chloropyridine disolvate

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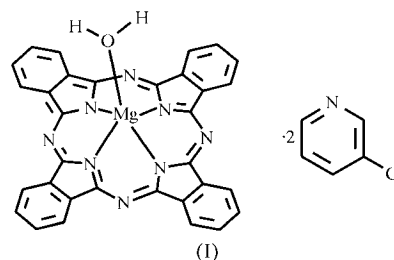
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The structure of the title compound, $[\text{Mg}(\text{C}_{32}\text{H}_{16}\text{N}_8)(\text{H}_2\text{O})] \cdot 2\text{C}_5\text{H}_4\text{ClN}$, comprises MgPcH_2O [Pc is phthalocyaninate(2-)] and 3-chloropyridine solvent molecules interacting *via* $\text{O} \cdots \text{H} \cdots \text{N}$ hydrogen bonds and π - π interactions. The central Mg atom is (4+1)-coordinated by four equatorial isoindole N atoms of the macrocycle and by the O atom of an axial water molecule. The MgPcH_2O molecule is not planar, the Mg atom being displaced by 0.496 (2) Å from the isoindole N_4 plane towards the water O atom. MgPcH_2O molecules related by a twofold screw axis interact *via* $\text{O} \cdots \text{H} \cdots \text{N}_{\text{azamethine}}$ hydrogen bonds, forming a polymeric chain along the b axis, while those related by inversion centres form π - π interacting dimers.

Comment

Our interest in magnesium phthalocyanine (Pc) and its complexes exhibiting (4+1)-coordination of the central Mg atom (Kubiak *et al.*, 1995; Janczak & Kubiak, 2001; Janczak & Idemori, 2002) arises from their similarities to chlorophyll (Clayton, 1966; Sauer *et al.*, 1968; Balischmiter & Katz, 1969; Larkum & Kühl, 2005), as they possess a similar coordination environment of the central Mg atom, as well as from their solid-state optical properties (especially the 'X-phase'). However, the origin and nature of the near-IR broad absorption are not completely understood, though a few possible explanations are found in the literature. Endo *et al.* (1999) assigned the $\text{MgPc}(\text{H}_2\text{O})_2$ composition to the 'X-phase' and suggested that the near-IR broad absorption band arises from exciton coupling effects. Janczak & Idemori (2003) studied the solid-state near-IR absorption spectra of MgPc and the triclinic modification of MgPcH_2O , suggesting that the origin of this near-IR absorption arises from the specific molecular arrangement in the crystal structures. In both structures, a similar arrangement of the structural motif is present, *i.e.* face-to-face dimers of π - π stacked molecules (Janczak & Kubiak, 2001; Janczak & Idemori, 2003). Furthermore, the monoclinic modification of MgPcH_2O does not exhibit near-IR absorption, since the molecular arrange-

ment is different from that in the active triclinic form (Mizuguchi, 2002). This hypothesis is supported by works reporting the solid-state spectra of titanyl phthalocyanine (TiOPc) and vanadyl phthalocyanine (VOpc), which analogous to MgPcH_2O appear in two crystallographic modifications, *i.e.* in monoclinic and triclinic forms (Ziolo *et al.*, 1980; Yamada *et al.*, 1996; Hiller *et al.*, 1982; Oka *et al.*, 1992). However, only the triclinic form is near-IR active (Saito *et al.*, 1993, 1994; Naleva *et al.*, 1993; Mizuguchi *et al.*, 1995). Thus, the electronic spectra vary significantly as a result of molecular interactions and, especially, of the molecular arrangement in the crystal structures. The present structure analysis has been carried out in order to study the correlation between the crystal and electronic structures in the title compound, (I).



The asymmetric unit in (I) consists of an aqua-(phthalocyaninato)magnesium(II) and two 3-chloropyridine (A and B) molecules (Fig. 1). The geometry of the MgPcH_2O unit is not planar and the central Mg atom exhibits (4+1) geometry, coordinated equatorially by four isoindole N atoms of the Pc macrocycle and by the O atom of an axial water molecule (Table 1). This coordination environment of the central Mg atom is similar to that found in several chlorophyll derivatives (Kratky & Dunitz, 1975; Chow *et al.*, 1975; Serlin *et al.*, 1975). Owing to the interaction with the axially coordinated water O atom, the central Mg atom is significantly displaced [0.496 (2) Å] from the weighted least-squares plane defined by the four isoindole N atoms. The displacement of the Mg atom from the N_4 plane is comparable to that observed in

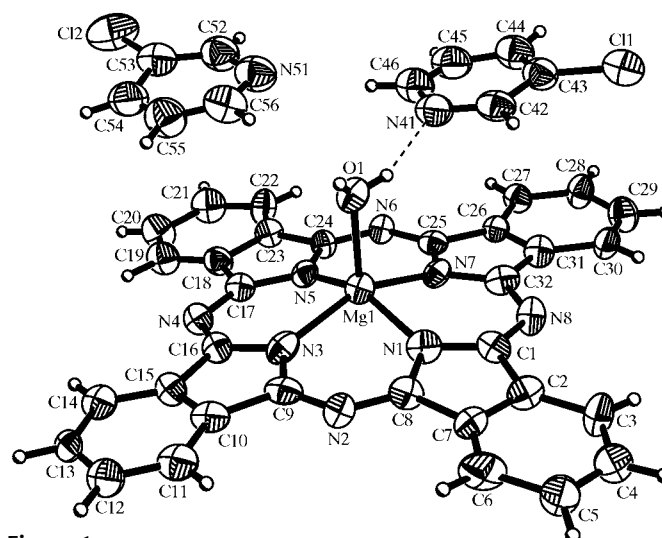


Figure 1
The asymmetric unit of (I), showing the atom labelling and displacement ellipsoids drawn at the 50% probability level.

other aqua–magnesium–phthalocyanine complexes solvated by pyridine (Fischer *et al.*, 1971; Mizuguchi & Mochizuki, 2002), diethylamine (Kinzyhalo & Janczak, 2007c), *n*-propylamine (Kinzyhalo & Janczak, 2007a) or 2-methoxyethylamine (Kinzyhalo & Janczak, 2007b), as well as in the triclinic and monoclinic modifications of MgPcH₂O (Janczak & Idemori, 2003; Mizuguchi, 2002). In all cases, the Mg atom displacement from the N₄ plane lies between 0.442 (2) and 0.502 (2) Å.

The displacement of Mg from the N₄ plane in magnesium–phthalocyaninate complexes is significantly greater (by about 0.15 Å) than that in aqua–magnesium–porphyrinate complexes (Choon *et al.*, 1986; McKee & Rodley, 1988; Yang & Jacobson, 1991; Timkovich & Tulinsky, 1969; Velazquez *et al.*, 1992; Barkigia *et al.*, 1983) and in chlorophyll derivatives (Kratky & Dunitz, 1975; Chow *et al.*, 1975; Serlin *et al.*, 1975) owing to the greater flexibility of the porphyrinate ring, as well as to the larger central hole in comparison with the Pc macro-ring. The saucer-shape geometry of MgPcH₂O in (I) results from the interaction of the positively charged central Mg atom of about +0.5 (Zerner *et al.* 1966) with the negatively charged O atom of the water molecule and is comparable to that in the gas phase obtained by molecular orbital calculations (Janczak & Idemori, 2003). However, the *ab initio* calculated axial Mg–O bond (2.142 Å) is significantly longer than that in (I) [2.029 (2) Å].

The electron-rich N atom of one 3-chloropyridine (3-Clpyr) molecule (*A*) accepts the O-donor atom of the water molecule and forms an O–H···N hydrogen bond (Fig. 1 and Table 2). Molecule *A* is almost parallel to the mean Pc plane [~ 6.1 (2)°]. The second 3-Clpyr molecule (*B*) is also almost parallel to the Pc plane, although it is not hydrogen bonded with the MgPcH₂O molecule; ring atom N51 is oriented towards the H46–C46 group of molecule *A*. The C···N distance between these halopyridines [the ring plane dihedral angle is 7.7 (2)°] is long [C46···N51 = 3.343 (3) Å] but important, as shown by molecular orbital calculations (Frisch *et al.*, 1998) on 3-Clpyr dimers with geometry similar to that of molecules *A* and *B* in (I). The electrostatic potential calculated for the 3-Clpyr

molecules has an opposite sign around the interacting N51···H46 atoms. The lone electron pair on atom N51 is oriented towards H46–C46 of the other 3-Clpyr molecule (*A*), and between atoms N51 and H46 the (3,–1) critical point characterizing the interaction between N51 and H46 can be localized (Bader, 1990). Molecules *A* and *B* are essentially parallel to the Pc macro-ring, inclined at 1.1 (2) and 3.8 (2)° to their closest Pc C₆ rings; however, owing to the saucer shape of the ring, the ring centroid distances are slightly longer than the van der Waals distance between the π -aromatic rings (by about 0.1 Å) but indicate significant π – π overlaps between the aromatic-ring π clouds (the ring centroid distances are 3.4–3.6 Å). As a result of the π – π interactions, the C18–C23 and C26–C31 benzene rings are less distorted from the Pc N₄ plane than the other half of the Pc macrocycle. The average deviations of the C atoms of these two C₆ aromatic rings are 0.269 and 0.143 Å, while the average deviations of the C atoms of the C2–C7 and C10–C15 rings are 0.569 and 0.324 Å, respectively.

MgPcH₂O–3-chloropyridine systems related by a twofold screw axes interact *via* O–H···N_{azamethine} hydrogen bonds, forming pseudo-one-dimensional chains along the *b* axis (Fig. 2). MgPcH₂O molecules related by inversion interact *via* π – π interactions in a back-to-back fashion [the N₄ interplanar distance is 3.392 (3) Å]. The overlap of the Pc ligands in this manner in (I) is characteristic of five-coordinate (4+1)-Mg–phthalocyaninate(2–) complexes (Fig. 3). Scheidt & Lee (1987) examined the overlap in neutral, structurally characterized, sterically unhindered metal–porphyrinate complexes and discovered that the distribution of the lateral shift of the ligands is trimodal rather than continuous. The values appear to cluster at ~ 1.5 Å for dimers with strong π – π overlap, at ~ 3.5 Å with intermediate π – π overlap and at ~ 6.5 Å with weak overlap. The Pc ligands in the dimers of (I) [with an N₄ interplanar distance of 3.392 (3) Å] represent an intermediate overlap between the ligand π systems. However, owing to the saucer shape of the Pc ligands, the mean interplanar separation between the dimer 40-atom rings (~ 3.22 Å) is nearly midway between the sum of the C-atom van der

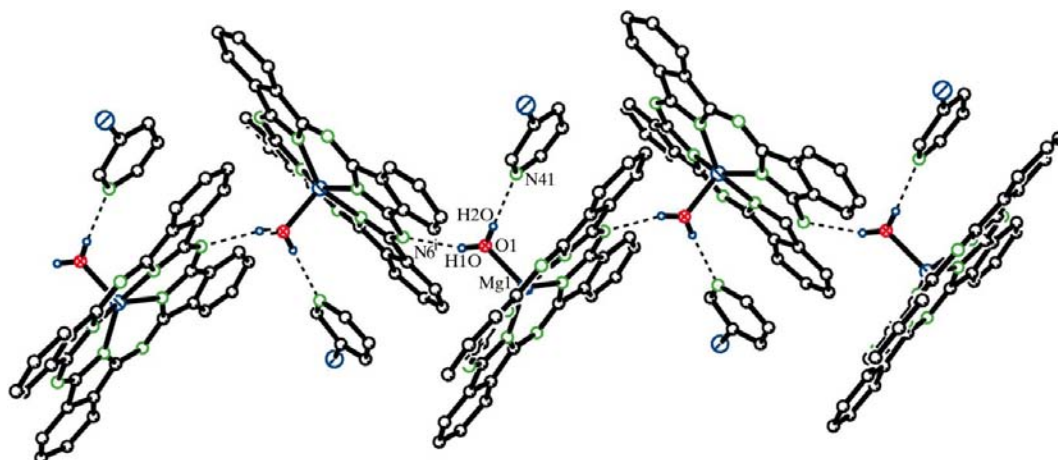


Figure 2

A view of the hydrogen-bonded polymeric structure of (I). H atoms, except those of the water ligands, have been omitted for clarity. [Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

Waals radii of the π -ring system (~ 3.4 Å) and the distance at which the steric interactions between the π -aromatic ring systems becomes predominantly repulsive (~ 3.08 Å; Pauling, 1960). Thus, a degree of π - π stabilization in (I) is evident, and the O—H...N hydrogen bonds play an important role in the molecular packing pattern. Besides these dimers, π - π interactions between the 3-chloropyridine molecules and half of the Pc macro-ring add to the energetically favourable molecular arrangement and yield a greater planarity in half of the Pc ligand (as noted above).

In (I), chains of MgPcH₂O and 3-chloropyridine molecules related by inversion centres interact *via* their π - π clouds, forming a hole at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ site and symmetrically equivalent (translationally and by twofold screw axis) positions in which the 3-chloropyridine molecules are located (Fig. 3). Since the molecular arrangement of the MgPcH₂O and 3-Clpyr molecules is different from that of the triclinic modification of MgPcH₂O (Janczak & Idemori, 2003) and MgPcH₂O·MPA (MPA is 2-methoxyethylamine; Kinzhybalo & Janczak, 2007a), both being near-IR active, the present crystal does not show near-IR broad absorption bands. Instead, it exhibits characteristic absorption bands caused by the molecular distortion. In 3-chloropyridine solution, this compound has a UV-vis spectrum that is quite similar to that of MgPcH₂O in pyridine solution (Janczak & Idemori, 2003). In the solid state, a slight broadening of the bands was observed, since upon crystallization the double degeneracy of the excited state is lifted because of the molecular distortion (approximately C_{4v} in solution and C_1 in the solid state).

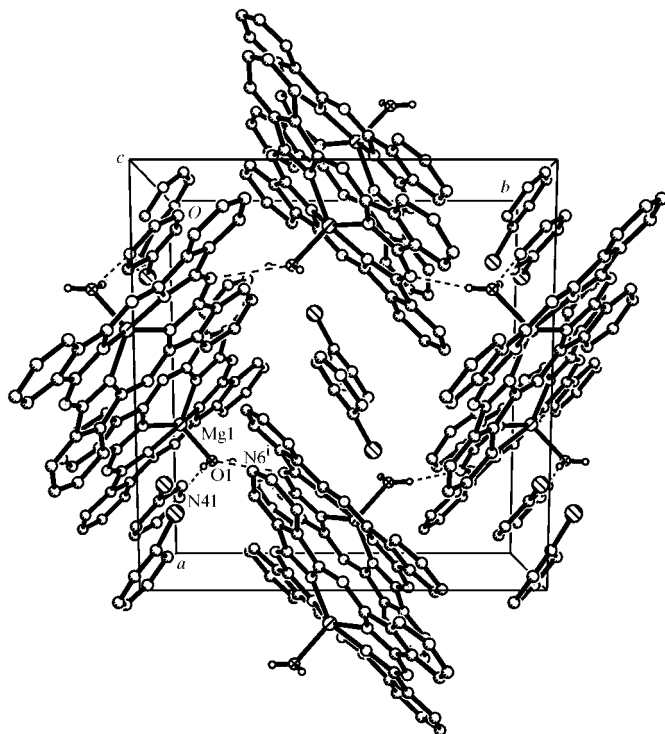


Figure 3

The molecular packing of (I), showing the π - π interactions between the MgPcH₂O molecules. H atoms, except those of the water ligands, have been omitted for clarity. [Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

Thermogravimetric analysis shows three characteristic steps, the first at *ca* 400 K, the second at *ca* 440 K and the third at *ca* 478 K, and these correspond exactly to the successive weight loss of one 3-Clpyr molecule (14.51%), the second 3-Clpyr molecule and the water molecule (3.25%). The third step correlates well with the loss of water in the MgPcH₂O complex (Janczak & Idemori, 2003). Finally, above 478 K, the sample transforms into the β -modification of MgPc (Kubiak *et al.*, 1995).

Experimental

Violet crystals of (I) were obtained by recrystallization of MgPc crystals obtained as described elsewhere (Janczak & Kubiak, 2001) in 3-chloropyridine. MgPc (about 1 g) was added to 20 ml of 3-Clpyr. The suspension was degassed and sealed in a glass ampoule. The ampoule was heated at 433 K over a period of 15 h. Crystals of (I) were formed during the cooling process (at about 363–368 K). The presence of water in these crystals results from the high affinity of water to MgPc (Janczak & Idemori, 2003).

Crystal data

[Mg(C ₃₂ H ₁₆ N ₈)(H ₂ O)]·2C ₅ H ₄ ClN	$V = 3683.3$ (11) Å ³
$M_r = 781.94$	$Z = 4$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 14.981$ (3) Å	$\mu = 0.24$ mm ⁻¹
$b = 13.956$ (2) Å	$T = 295$ (2) K
$c = 18.309$ (3) Å	$0.38 \times 0.27 \times 0.24$ mm
$\beta = 105.80$ (1)°	

Data collection

Kuma KM-4 CCD area-detector diffractometer	39524 measured reflections
Absorption correction: analytical [face-indexed (SHELXTL; Sheldrick, 1990)]	8890 independent reflections
$T_{\min} = 0.929, T_{\max} = 0.947$	5340 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.063$	511 parameters
$wR(F^2) = 0.111$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.17$ e Å ⁻³
8890 reflections	$\Delta\rho_{\text{min}} = -0.16$ e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Mg1—O1	2.029 (2)	Mg1—N5	2.044 (2)
Mg1—N1	2.039 (2)	Mg1—N7	2.030 (2)
Mg1—N3	2.024 (2)		
O1—Mg1—N1	106.09 (8)	N1—Mg1—N5	152.49 (8)
O1—Mg1—N3	107.94 (7)	N1—Mg1—N7	87.50 (9)
O1—Mg1—N5	101.35 (8)	N3—Mg1—N5	86.86 (8)
O1—Mg1—N7	100.88 (8)	N3—Mg1—N7	151.10 (8)
N1—Mg1—N3	86.64 (9)	N5—Mg1—N7	85.40 (8)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1O...N41	0.82	1.99	2.758 (3)	156
O1—H2O...N6 ⁱ	0.82	2.09	2.880 (2)	163
C46—H46...N51	0.93	2.43	3.344 (8)	167

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

H atoms bonded to C atoms were positioned geometrically and treated as riding, with $U_{\text{iso}}(\text{H})$ values of $1.2U_{\text{eq}}(\text{C})$. H atoms of the coordinated water molecule were located in difference Fourier syntheses and in the final refinement cycles were constrained to O–H distances of 0.82 Å, with $U_{\text{iso}}(\text{H})$ values equal to $1.5U_{\text{eq}}(\text{O})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3098). Services for accessing these data are described at the back of the journal.

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