

Aqua(phthalocyaninato)magnesium
n-propylamine disolvate

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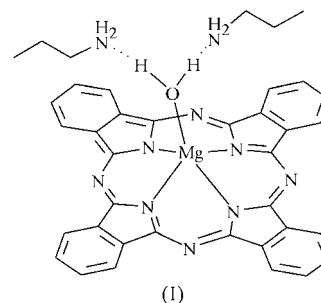
The crystals of the title compound, $[\text{Mg}(\text{C}_{32}\text{H}_{16}\text{N}_8)(\text{H}_2\text{O})] \cdot 2\text{C}_3\text{H}_9\text{N}$, are built up from $\text{MgPc}(\text{H}_2\text{O})$ [Pc is phthalocyaninate(2-)] and *n*-propylamine molecules that interact via $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds. The $\text{MgPc}(\text{H}_2\text{O})$ molecule is non-planar. The central Mg atom is coordinated by the four equatorial isoindole N atoms of the Pc ring system and by the O atom of an axial water molecule. The Mg atom is displaced by 0.509 (1) Å from the N_4 plane towards the water O atom. $\text{MgPc}(\text{H}_2\text{O}) \cdot 2(\textit{n}\text{-propylamine})$ molecules related by the inversion centre are linked by $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds to form a dimeric aggregate.

Comment

Our interest in magnesium phthalocyanine and its complexes exhibiting (4+1)-coordination (Kubiak *et al.*, 1995; Janczak & Kubiak, 2001; Janczak & Idemori, 2002) is due both to their similarities to chlorophyll (Clayton, 1966), since they possess a coordination environment of the central Mg atom analogous to that in chlorophyll, and to their optical properties in the solid state, especially the 'X-phase'. However, the origin and nature of the near-IR broad absorption are not completely clear, though several possible explanations can be found in the literature. Endo *et al.* (1999) suggested that the near-IR broad absorption band arises from the exciton coupling effects and assigned the composition $\text{MgPc}(\text{H}_2\text{O})_2$ [Pc is phthalocyaninate(2-)] to the 'X-phase'.

Janczak & Idemori (2003) studied the solid-state near-IR absorption spectra of MgPc and the triclinic modification of MgPcH_2O , and suggested that this near-IR absorption arises from the specific molecular arrangement in the crystals. In both near-IR active crystals, a similar arrangement of the structural motif can be found, *i.e.* face-to-face dimers of π - π stacked molecules (Janczak & Kubiak, 2001; Janczak & Idemori, 2003). Furthermore, the monoclinic modification of $\text{MgPc}(\text{H}_2\text{O})$ does not show the near-IR absorption, since the molecular arrangement is quite different from that in the active triclinic form of $\text{MgPc}(\text{H}_2\text{O})$ (Mizuguchi, 2002). Thus, the electronic spectra vary significantly as a result of the

molecular interactions and, especially, because of the molecular arrangement in the crystals. Therefore, 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 of (I) consists of one aqua(phthalocyaninato)magnesium and two *n*-propylamine molecules (Fig. 1) linked *via* $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds. The $\text{MgPc}(\text{H}_2\text{O})$ unit is not planar. The central Mg atom exhibits (4+1)-coordination by four equatorial isoindole N atoms of the Pc system and by an axial water molecule (Table 1). This coordination of Mg 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 O atom of the water molecule, the central Mg atom is significantly displaced [0.509 (1) 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 other aqua-magnesium-phthalocyanine complexes solvated by pyridine (Fischer *et al.*, 1971; Mizuguchi & Mochizuki, 2002) or diethylamine (Kinzhybalo & Janczak, 2007a), as well as in the triclinic and monoclinic modifications of $\text{MgPc}(\text{H}_2\text{O})$ (Janczak & Idemori, 2003; Mizuguchi, 2002).

In all cases, the displacement of the Mg atom from the N_4 plane ranges from 0.442 (2) to 0.496 (2) Å. The displacement of the Mg atom from the N_4 plane is significantly smaller (by about 0.15 Å) in the aqua-magnesium-porphyrinate complexes (Choon *et al.* 1986; McKee & Rodley, 1988; Yang &

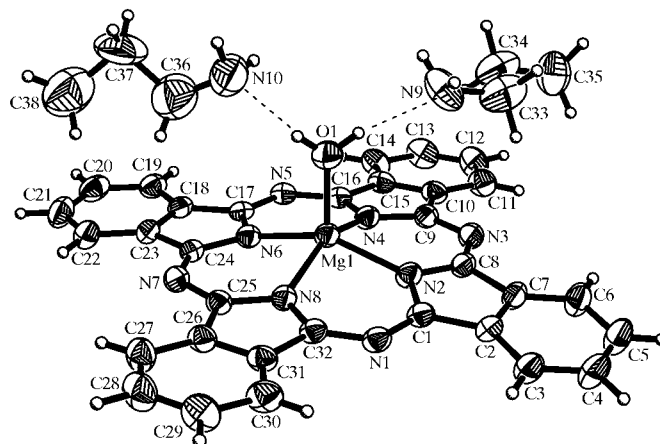


Figure 1
The structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

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 system and to the larger central hole in relation to the Pc macrocycle. The geometry of the MgPc(H₂O) molecule in (I) is comparable to that in the gas phase obtained from molecular orbital calculations (Janczak & Idemori, 2003). However, the *ab initio* calculated axial Mg—O bond is significantly longer (2.142 Å) than that found in this crystal [1.9712 (15) Å]. The shortening of this bond is probably due to the interaction with the two *n*-

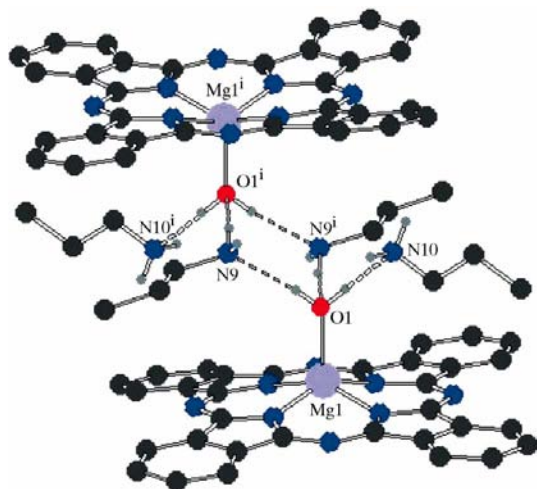


Figure 2
The hydrogen-bonded dimeric structure of (I). All H atoms attached to C atoms have been omitted for clarity. [Symmetry code: (i) $-x + 1, -y + 1, -z$.]

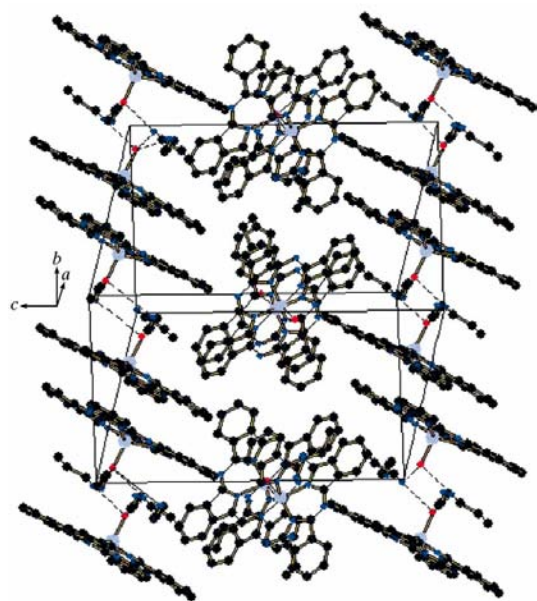


Figure 3
The molecular packing of (I) in the unit cell, showing the back-to-back π - π interaction between the dimeric [MgPc(H₂O)·2(*n*-propylamine)]₂ aggregates. H atoms attached to C atoms have been omitted for clarity.

propylamine molecules and to intermolecular interactions present in the crystal.

The electron-rich N atoms of the *n*-propylamine molecules each accept an O—H···N hydrogen bond from the water molecule (Fig. 1 and Table 2). Two MgPc(H₂O)·2(*n*-propylamine) units related by inversion interact *via* two additional N—H···O hydrogen bonds, forming a dimeric structure. In the dimer, one of the two *n*-propylamine molecules acts as a bridge (as a donor and as an acceptor) between two MgPc(H₂O) molecules, while the other *n*-propylamine molecule is involved as an acceptor in a single hydrogen bond (see Fig. 2). However, the orientation of the former *n*-propylamine molecule in relation to the Pc ring brings one of the H atoms of the amine group close to the C2—C7(1 - *x*, -*y*, -*z*) ring. This orientation results in an N—H··· π interaction with the benzene ring (Table 2), but this interaction is rather weak and therefore plays an insignificant role in the molecular arrangement.

In the crystal structure of (I), the dimeric aggregates, [MgPc(H₂O)·2(*n*-propylamine)]₂, are stacked along the [110] direction in a herring-bone fashion, forming layers that are parallel to the (001) crystallographic plane. The dimeric aggregates are arranged in the stack in a back-to-back fashion, with a distance of 3.386 (3) Å between the Pc macrocycles (Fig. 3). This value indicates a strong π - π interaction between the π -clouds of the Pc rings, since this value is comparable to the typical distance of 3.4 Å between aromatic ring systems involved in such interactions (Pauling, 1960). Since the molecular arrangement of MgPc(H₂O)·2(*n*-propylamine) is different from that of the triclinic modification of MgPc(H₂O) (Janczak & Idemori, 2003) and MgPc(H₂O)·MPA (where MPA is 2-methoxyethylamine; Kinzhybalo & Janczak, 2007*b*), which are both near-IR active, the present crystal does not show a near-IR broad absorption band. Instead, it exhibits characteristic absorption bands caused by the molecular distortion. In *n*-propylamine solution this compound has a UV-vis spectrum quite similar to that of MgPc(H₂O) in 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 as a result of the molecular distortion (approximately *C*_{4*v*} in solution and *C*₁ in the solid state).

The thermogravimetric analysis shows two characteristic steps, the first at about 368 K and the second at about 478 K. These steps correspond exactly to the weight loss of both *n*-propylamine molecules (17.57%) and the water molecule (2.67%). The second step at 478 K correlates well with the loss of water in the MgPc(H₂O) complex (Janczak & Idemori, 2003). Finally, above 278 K, the sample transforms into the β -modification of MgPc (Kubiak *et al.*, 1995).

Experimental

Violet crystals of the title compound were obtained by recrystallization of MgPc crystals obtained as described elsewhere (Janczak & Kubiak, 2001) from *n*-propylamine. MgPc (about 1 g) was added to *n*-propylamine (20 ml). The suspension was degassed and sealed into a glass ampoule. The ampoule was heated at 423 K for 10–12 h.

During the cooling process, the title crystals were formed (from a hot solution, at about 353–363 K). The presence of water in the crystals is governed by the high affinity of MgPc for water (Janczak & Idemori, 2003).

Crystal data

[Mg(C₃₂H₁₆N₈)(H₂O)]·2C₃H₉N
M_r = 673.08
 Monoclinic, *C*2/*c*
a = 23.227 (5) Å
b = 14.526 (3) Å
c = 20.765 (4) Å
 β = 94.99 (2)°
V = 6979 (2) Å³
Z = 8
D_x = 1.281 Mg m⁻³
D_m = 1.28 Mg m⁻³
D_m measured by floatation
 Mo *K*α radiation
 μ = 0.10 mm⁻¹
T = 295 (2) K
 Parallelepiped, violet
 0.50 × 0.24 × 0.14 mm

Data collection

Kuma KM-4 diffractometer with a CCD area-detector
 ω scans
 Absorption correction: analytical, face-indexed (SHELXTL; Sheldrick, 1991)
T_{min} = 0.949, *T_{max}* = 0.984
 38071 measured reflections
 8356 independent reflections
 4307 reflections with *I* > 2σ(*I*)
R_{int} = 0.034
 θ_{\max} = 28.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.048
wR (*F*²) = 0.107
S = 1.01
 8356 reflections
 457 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0342P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.002$
 $\Delta\rho_{\max} = 0.32 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.26 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Mg1—O1	1.9712 (15)	Mg1—N4	2.0446 (17)
Mg1—N6	2.0316 (17)	Mg1—N8	2.0471 (16)
Mg1—N2	2.0327 (18)		
O1—Mg1—N6	105.74 (7)	N2—Mg1—N4	86.38 (7)
O1—Mg1—N2	102.72 (7)	O1—Mg1—N8	103.84 (7)
N6—Mg1—N2	151.54 (7)	N6—Mg1—N8	86.15 (7)
O1—Mg1—N4	105.55 (7)	N2—Mg1—N8	86.64 (7)
N6—Mg1—N4	86.53 (7)	N4—Mg1—N8	150.61 (7)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1—H2O···N9	0.80	2.05	2.841 (3)	170
O1—H1O···N10	0.80	1.99	2.689 (4)	147
N9—H92···O1 ⁱ	0.90	2.26	3.092 (3)	153
N10—H10B···Cg ⁱ	0.87	2.76	3.478 (4)	141

Symmetry code: (i) $-x + 1, -y + 1, -z$.

C-bound H atoms were placed in geometric positions, with C—H distances of 0.93–0.97 Å, and treated as riding, with *U_{iso}*(H) values of

1.2*U_{eq}*(C) (for aromatic) and 1.5*U_{eq}*(C) (for *n*-propylamine CH₂ and CH₃ H atoms). The H atoms of the coordinated water molecule and amine groups were located in difference Fourier syntheses, but were constrained in the final refinement, with O—H distances of 0.80 Å and N—H distances of 0.86–0.90 Å, and with *U_{iso}*(H) values of 1.2*U_{eq}*(O) and 1.5*U_{eq}*(N). Refinement of the occupancy factors for the two independent propylamine units gave values of 0.998 (4) and 0.996 (4); thereafter, these occupancies were fixed at unity.

Data collection: *KM-4 CCD Software* (Kuma, 2004); cell refinement: *KM-4 CCD Software*; data reduction: *KM-4 CCD Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL97*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3085). Services for accessing these data are described at the back of the journal.

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