

## Aqua(phthalocyaninato)magnesium

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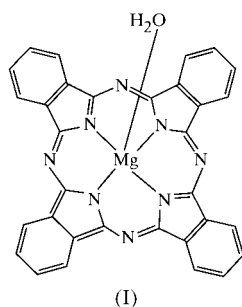
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The title compound,  $[\text{Mg}(\text{C}_{32}\text{H}_{16}\text{N}_8)(\text{H}_2\text{O})]$ , crystallizes with two  $\text{MgPc}(\text{H}_2\text{O})$  molecules (Pc is phthalocyaninate) in the asymmetric unit. The geometries of the two molecules are very similar, with the Mg atoms each 4+1-coordinated by four isoindole N atoms at the base and by the O atom of the water molecule. The Mg atoms are displaced by 0.447 (1) and 0.468 (1) Å from the basal coordination planes towards the water O atoms.  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds form dimers stacked along the  $b$  axis in a herring-bone fashion.

## Comment

Our interest in magnesium phthalocyaninate,  $\text{MgPc}$ , and its 4+1- and 4+2-coordinated complexes (Kubiak *et al.*, 1995; Janczak & Kubiak, 2001, 2002) is due to their optical properties in the solid state, especially the X-phase. The literature data related to this phase are inconsistent (Davidson, 1982; Hor & Loutfy, 1983; Krishankumer & Menon, 1997; Sakakibara *et al.*, 2001). Endo *et al.* (1999) assigned the  $\text{MgPc}(\text{H}_2\text{O})_2$  composition to the X-phase. Until now, however, there has been no evidence for the existence of this complex. Quite recently, we have determined the crystal structure of the  $\beta$ -modification of  $\text{MgPc}$  and, contrary to our expectations, the



geometry of the  $\text{MgPc}$  molecule was found to be different from that of other  $M^{\text{II}}\text{Pc}$  compounds in that it is non-planar. The Mg atom in  $\text{MgPc}$  is displaced by 0.557 (2) Å (at 120 K) from the plane defined by the four isoindole N atoms of the

$\text{Pc}^{2-}$  ring due to its interaction with an azamethine N atom of a neighbouring  $\text{MgPc}$  molecule (Janczak & Kubiak, 2001).

In the asymmetric unit of the triclinic form of aqua-(phthalocyaninato)magnesium, (I), there are two crystallographically independent  $\text{MgPc}(\text{H}_2\text{O})$  molecules (Fig. 1). The geometries of these independent molecules are very similar and neither  $\text{MgPc}$  moiety is planar (Table 1). The central Mg atom in (I) is significantly displaced [0.447 (1) Å for Mg1 and 0.468 (1) Å for Mg2] from the weighted least-squares plane defined by the four isoindole N atoms towards the water O atom. The displacement of the central Mg atom from the  $\text{Pc}^{2-}$  plane is comparable to that observed in other aqua(phthalocyaninato)magnesium complexes (Mizuguchi, 2002; Mizuguchi & Mochizuki, 2002; Fischer *et al.*, 1977). In the title crystal, the  $\text{MgPc}(\text{H}_2\text{O})$  molecules form dimers *via* intermolecular  $\text{O}-\text{H}\cdots\text{N}_{\text{azamethine}}$  hydrogen bonds. These dimers are stacked along the  $b$  axis in a herring-bone fashion. The  $\text{Pc}\cdots\text{Pc}$  distances between the benzo rings in the dimers are shorter than the distance of 3.4 Å between  $\pi$ -aromatic ring systems (Pauling, 1960) and indicate strong  $\pi$ - $\pi$  interactions between the Pc rings. The face-to-face orientation of the  $\text{MgPc}(\text{H}_2\text{O})$  molecules in the dimers is similar to the orientation of the  $\text{MgPc}$  molecules in the crystal, in which, due to intermolecular  $\text{Mg}\cdots\text{N}_{\text{azamethine}}$  interactions, the  $\text{MgPc}$  molecules also form a dimeric  $(\text{MgPc})_2$  structure (Janczak & Kubiak, 2001).

The geometry of the  $\text{MgPc}(\text{H}_2\text{O})$  molecules in the triclinic crystals is similar to that in the monoclinic modification, although the refinement parameters of the latter are relatively

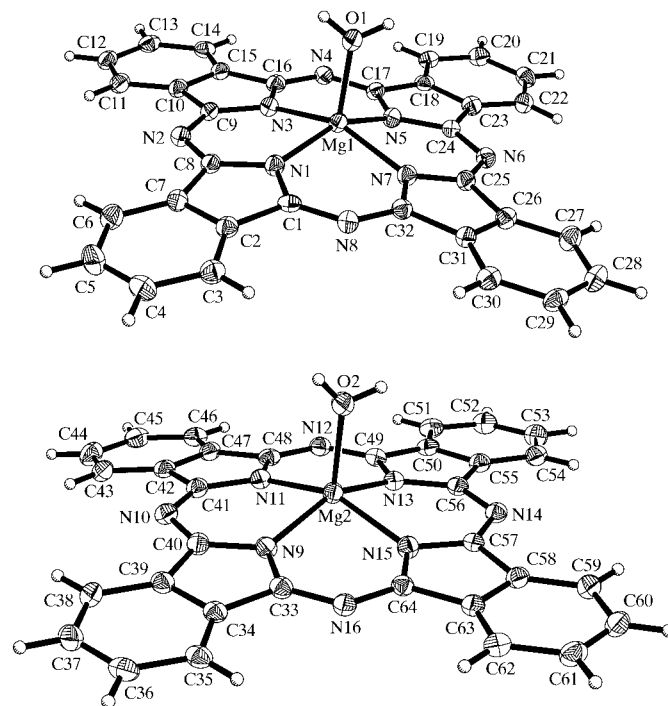


Figure 1

A view of both independent molecules in (I), shown with 50% probability displacement ellipsoids. H atoms are shown as spheres of arbitrary radii.

large ( $R = 10.6\%$  and  $wR = 20.9\%$ ; Mizuguchi, 2002). The difference between these two crystallographic modifications of  $\text{MgPc}(\text{H}_2\text{O})$  can be found only in the arrangements of the molecules in the crystals. In the triclinic crystals, the complex molecules form face-to-face hydrogen-bonded dimers (Table 2), in contrast with the monoclinic crystals, in which the  $\text{MgPc}(\text{H}_2\text{O})$  molecules form a hydrogen-bonded polymeric structure (Mizuguchi, 2002). The differences in the arrangement of  $\text{MgPc}(\text{H}_2\text{O})$  molecules between these two crystallographic modifications result in differences in the solid-state optical properties, the study of which is now in progress (Janczak & Idemori, 2002).

## Experimental

Crystals of the title compound were obtained from a solution in cyanobenzene–water, as described elsewhere (Janczak & Idemori, 2002).

### Crystal data

$[\text{Mg}(\text{C}_{32}\text{H}_{16}\text{N}_8)(\text{H}_2\text{O})]$	$D_m = 1.47 \text{ Mg m}^{-3}$
$M_r = 554.86$	$D_m$ measured by flotation in a mixture of chloroform and bromoform
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 12.955(2) \text{ \AA}$	Cell parameters from 4680 reflections
$b = 13.293(3) \text{ \AA}$	$\theta = 3\text{--}27^\circ$
$c = 16.202(3) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$\alpha = 65.03(2)^\circ$	$T = 200(2) \text{ K}$
$\beta = 81.91(2)^\circ$	Parallelepiped, violet
$\gamma = 83.73(2)^\circ$	$0.25 \times 0.22 \times 0.16 \text{ mm}$
$V = 2500.3(9) \text{ \AA}^3$	
$Z = 4$	
$D_x = 1.474 \text{ Mg m}^{-3}$	

### Data collection

Nonius KappaCCD area-detector diffractometer	11 221 independent reflections
$\omega$ scans	8172 reflections with $I > 2\sigma(I)$
Absorption correction: analytical face-indexed (SHELXTL; Sheldrick, 1990b)	$R_{\text{int}} = 0.040$
$T_{\text{min}} = 0.966$ , $T_{\text{max}} = 0.982$	$\theta_{\text{max}} = 27.4^\circ$
47 310 measured reflections	$h = -16 \rightarrow 16$
	$k = -17 \rightarrow 16$
	$l = -20 \rightarrow 20$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0301P)^2 + 0.8806P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.099$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
11 221 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
769 parameters	
H atoms treated by a mixture of independent and constrained refinement	

The water H atoms were refined, while the H atoms of the benzene rings of the  $\text{Pc}^{2-}$  system were treated as riding.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *COLLECT*; data reduction: *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990a); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXL97*.

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Mg1—O1	2.029 (2)	Mg2—O2	2.048 (2)
Mg1—N1	2.039 (2)	Mg2—N9	2.055 (2)
Mg1—N5	2.049 (2)	Mg2—N13	2.055 (2)
Mg1—N3	2.053 (2)	Mg2—N11	2.048 (2)
Mg1—N7	2.055 (2)	Mg2—N15	2.056 (2)
O1—Mg1—N1	102.00 (6)	O2—Mg2—N9	105.07 (6)
O1—Mg1—N5	103.58 (6)	O2—Mg2—N13	101.63 (6)
N1—Mg1—N5	154.41 (6)	N13—Mg2—N9	153.24 (6)
O1—Mg1—N3	104.09 (6)	O2—Mg2—N11	104.53 (6)
N1—Mg1—N3	86.85 (6)	N11—Mg2—N9	86.06 (6)
N5—Mg1—N3	87.80 (6)	N11—Mg2—N13	88.85 (6)
O1—Mg1—N7	100.71 (6)	O2—Mg2—N15	101.42 (6)
N1—Mg1—N7	88.78 (6)	N9—Mg2—N15	88.22 (6)
N5—Mg1—N7	85.66 (6)	N13—Mg2—N15	84.94 (6)
N3—Mg1—N7	155.18 (6)	N11—Mg2—N15	154.03 (6)

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
O1—H1O1 $\cdots$ N6 <sup>i</sup>	0.84 (2)	2.02 (2)	2.837 (3)	164 (2)
O2—H2O2 $\cdots$ N14 <sup>ii</sup>	0.82 (2)	1.97 (2)	2.776 (3)	166 (2)

Symmetry codes: (i)  $1 - x, -y, 1 - z$ ; (ii)  $1 - x, -y, -z$ .

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1580). Services for accessing these data are described at the back of the journal.

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