metal-organic compounds

Why magnesium is five-coordinate in methanol(phthalocyaninato)-magnesium(II)

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The square-pyramidal Mg center in the title compound, $[Mg(C_{32}H_{16}N_8)(CH_4O)]$, is five-coordinate due to the formation of back-to-back π–π dimers that saturate the vacant apical site of the metal coordination sphere. Each complex is a member of a back-to-back and a face-to-face dimer; the latter are tethered by two strong O—H···N hydrogen bonds. The dimers form columns that likely determine the solid-state packing. The phthalocyaninate ligands are essentially planar, with a slight 'hat visor' conformation character.

Comment

For several years we have been interested in the synthesis and structures of metallophthalocyanine complexes. As a broad class of compounds, the metallophthalocyanines exhibit a wide array of optical, electronic, magnetic and chemical/photo-chemical properties that can be profoundly affected by subtle modifications to their solid-state and/or solution structures (McKeown, 1998, and references therein; Schultz et al., 1990, and references therein; Leznoff & Lever, 1989–1996, and references therein). We have recently broadened our ongoing investigations involving solvothermal (solventothermal) reactions of transition metal starting materials with 1,2-dicyanobenzene, which result in modified metallophthalocyanine derivatives, to include main group metals, in hopes that we may compare and contrast their reactivity. As part of these efforts, we carried out the reaction of 1,2-dicyanobenzene with magnesium acetate tetrahydrate and found that the title compound, (I), was produced.

(I)
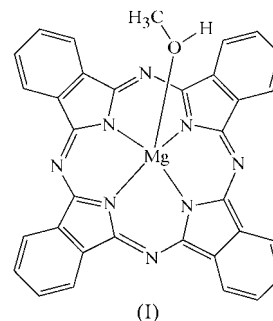
Apart from the more subtle aspects of the structure of (I) discussed later in this paper, it is interesting from a chemical standpoint that the compound possesses a (flat) unsubstituted phthalocyaninate (Pc) ligand, in contrast to the saddle-shaped alkoxy-modified Pc moieties observed in complexes that form in similar reactions involving Ni^{II} that we have reported elsewhere, even as the reaction and crystallization conditions were essentially identical (Molek et al., 2001).

Methanol(phthalocyaninato)magnesium(II) (Fig. 1) is one of the five crystallographically characterized complexes in which the magnesium center is bound to a κ^4N_4-type ligand with a delocalized π system and one or two alcohol ligands, and the first example of such a complex with a Pc ligand.
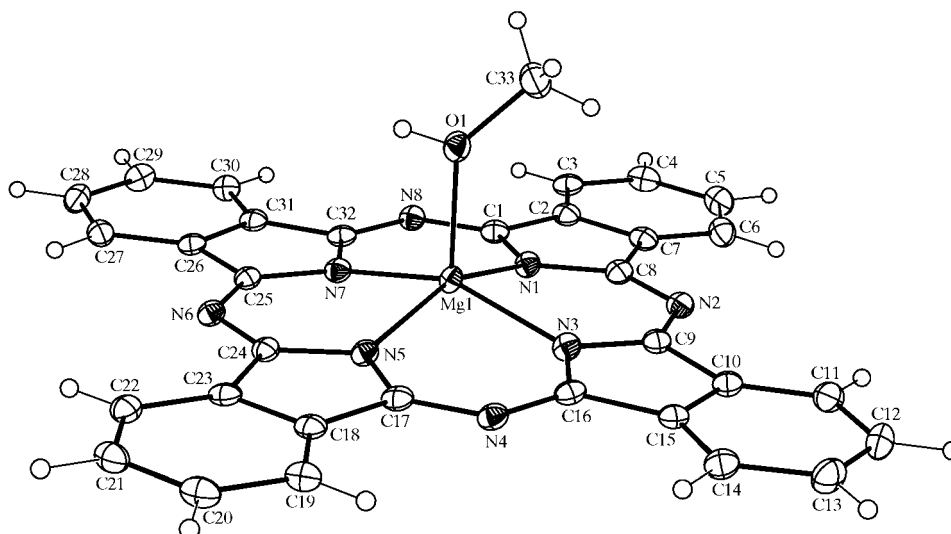

Figure 1
The molecular structure of (I), drawn with 50% probability displacement ellipsoids, showing a near-perfect square-pyramidal geometry at magnesium.

The only other structurally characterized complex with five-coordinate magnesium is 2-propanol(tetraphenylporphinato)magnesium, (II) (Byrn *et al.*, 1993), which crystallizes as a 2-propanol clathrate. Unfortunately, the position of the hydroxy H atom of the ligated propanol is chemically unreasonable, as reported to the Cambridge Structural Database (CSD; Version 5.26, updated May 2005; Allen, 2002) and confirmed by the authors; hence, in the following discussion, we will ignore this error. The Mg—O and Mg—N bond lengths in (I) [2.0331 (14) Å and average 2.0336 (17) Å, respectively] are appreciably shorter than the corresponding distances in (II) [2.076 Å and average 2.087 (5) Å, respectively], but all values are in the typical range. In the three relevant octahedral Mg complexes with κ^4N_4 ligands and two identical alcohols in

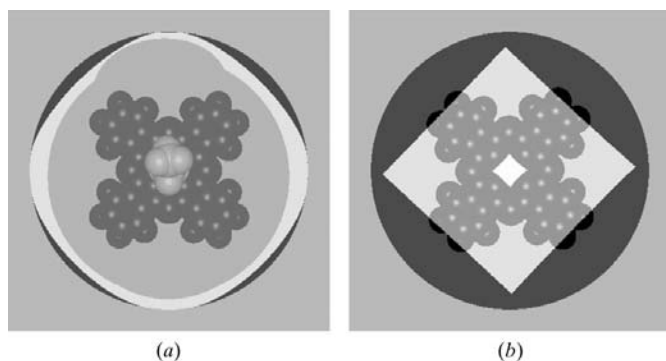the apical positions, *viz.* dimethanol(tetraphenylporphinato)-magnesium(II), (III), dimethanol(tetraphenylporphinato)-magnesium(II) acetone solvate, (IV) (both by McKee & Rodley, 1988), and bis(2-methoxyethanol-κO)(phthalocyaninato)magnesium(II), (V) (Matsumoto *et al.*, 2000), all Mg—O distances are substantially longer at 2.220, 2.187 and 2.245 Å, respectively. The Mg—N distances would be expected to be shorter since the Mg atom resides in the plane of the four ligating N atoms, but the shortening is not observed in the cases of (III) (2.069 Å) and (IV) (2.075 Å). However, in the case of the Pc ligand in (V), the two symmetry-independent Mg—N distances average 2.002 (14) Å.

There are many examples of radical and non-radical five-coordinate Mg complexes with large porphinate-like κ^4N_4 ligands, but in most cases the ligand in the apical position is water and we will not discuss compounds with aqua ligands here. The non-radical compounds include Mg(Pc)(Ph$_3$P=O), Mg(Pc)(Ph$_3$P=O)·CH$_2$Cl$_2$, Mg(Pc)(Ph$_3$P=O)·pyridine, Mg-(Pc)(Ph$_3$P=O)·tetrahydrofuran (all four by Huckstadt *et al.*, 2000), *cis*-[2,3,7,8-tetrakis(*N,N*-dimethylamino)-12,13:17,18-dibenzoporphyrazinato-κ^4N,N',N'',N'''](dimethyl sulfoxide-κO)magnesium(II), and [2,3-bis(*N,N*-dimethylamino)nor-phthalocyaninate-κ^4N,N',N'',N'''](dimethyl sulfoxide-κO) magnesium(II) (both by Montalban *et al.*, 2000). In all of these structures, the metal center is essentially square pyramidal, with Mg—O and Mg—N distances comparable to those in (I).

Several aspects of the solid-state geometry of (I) are noteworthy. One aspect is the absence of a second alcohol molecule in the sixth coordination position about the Mg center, the second is the mutual arrangement of molecules of (I) in the crystal structure, and the third is the conformation of the Pc ring.

The Mg center in (I) is square pyramidal with a very slightly distorted C_{4v} symmetry (Fig. 1). The Mg—N distances differ by less than 0.0037 Å, the Mg—O vector forms an 89.5 (2)° angle to the plane defined by atoms N1, N3, N5 and N7, and the Mg atom is displaced from this plane toward the O atom by 0.4369 (10) Å. Four equatorial coordination sites about the central metal are occupied by the Pc ligand, which shields

Figure 2
(*a*) The projection of (I) viewed from the side of the methanol ligand. The solid angles corresponding to each ligand are represented by the shadows cast by the ligands on to a sphere with a 12 Å radius from an imaginary light bulb placed at the Mg center. The light-gray shadow is for the methanol ligand and dark shadows belong to the Pc moiety. (*b*) The projection of (I) viewed from the opposite side. The white space indicates room about the Mg atom available for an incoming ligand. (These diagrams are combined into an animated feature in the online version of the journal.)
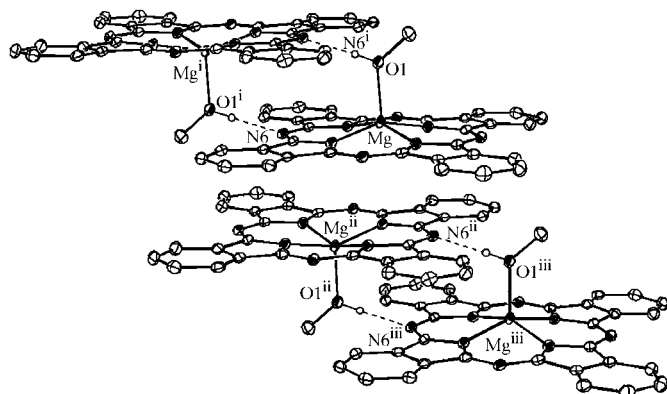

Figure 3
The cofacial and back-to-back stacking of the centrosymmetrically related molecules results in the formation of columns in the crystal structure. All H atoms, except the hydroxy H atoms participating in hydrogen-bonding interactions, have been omitted for clarity. [Symmetry codes: (i) −*x*, −*y* + 1, −*z* + 1; (ii) −*x*, −*y* + 1, −*z*; (iii) *x*, *y*, *z* − 1.]
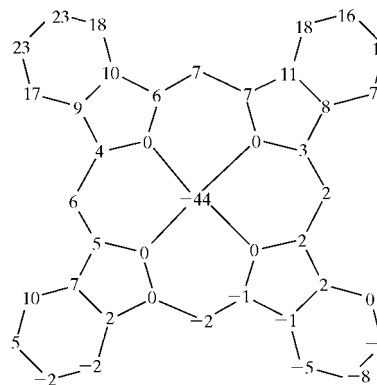

Figure 4
Perpendicular atomic displacements (in 0.01 Å units) in (I) from the least-squares plane defined by the four coordinating N atoms.

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65.07 (2)% of the Mg coordination sphere (*Solid-G*; Guzei & Wendt, 2004). The MeOH ligand shields an additional 16.80 (2)% and thus there is room [18.14 (2)%] to accommodate an additional ligand (Fig. 2). Our density functional theory computations at the pbe1pbe/6-31+G* level of theory (*GAUSSIAN03*; Frisch *et al.*, 2004) on a simplified Mg complex (VI) (see scheme below) indicate that a reaction between (VI) and MeOH is favored by -16.78 kcal mol^{-1}, while coordinating the second methanol is favored by a considerably smaller -3.25 kcal mol^{-1}. Apparently, there are two ways of saturating the magnesium coordination sphere, *viz.* (i) introduction of another ligand with a solid angle less than 0.8π (or shielding percentage of $\sim$20%), and (ii) mutual back-to-back arrangement of molecules of (I) in the lattice in order to compensate for the small 'sixth ligand' coordination energy by forming favorable van der Waals interactions between the π systems of the Pc ligands (see below). A review of relevant structures reported to the CSD reveals that in the magnesium complexes with a large κ^4N_4 ligand, five-coordinate complexes outnumber six-coordinate systems in an approximate 2:1 ratio. This may be an indication that expansive van der Waals contacts between large planar ligands are more favorable than saturating the metal coordination sphere with a lone ligand.

(VI)
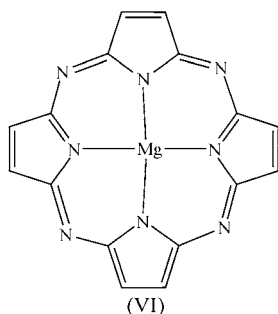
The overlap of the Pc ligands in the back-to-back π–π dimers of (I) is a characteristic of this structure type (Fig. 3). Scheidt & Lee (1987) examined the overlap in all neutral structurally characterized sterically unhindered metal–porphinate complexes and discovered that the distribution of the lateral shift of the ligands is trimodal rather than continuous. The values seemed to cluster at $\sim$1.5 Å for dimers with strong overlap, at $\sim$3.5 Å with intermediate overlap and at $\sim$6.5 Å with weak overlap. The Pc ligands in the π–π dimers of (I) are laterally offset by 1.612 (2) Å, which according to the above classification represents a strong overlap between the ligand π systems. The mean interplanar separation between the dimer 40-atom rings, 3.33 (4) Å, is approximately halfway between the sum of the C-atom van der Waals radii (3.650 Å) and the distance at which the steric interaction becomes predominantly repulsive (3.078 Å). Thus, a degree of π–π stabilization in (I) is evident and plays a role in the molecular packing pattern.

While the formation of back-to-back dimers explains the five-coordinate nature of the Mg center, bonding in the face-to-face dimers deserves separate scrutiny. Centrosymmetrically related molecules of (I) form strongly bonded face-to-face dimers in which molecules are held together by two identical hydrogen-bonding interactions between the hydroxyl group and an 'outer' N atom of the Pc ring (Table 1). The 6.030 (2) Å offset between the participating molecules allows for energetically favorable molecular arrangement. Because of the significant lateral displacement, only half of the Pc ligand including atoms C17–C32 overlaps with the other Pc ligand, but the π systems are in very close proximity [3.32 (4) Å]. Thus, each molecule of (I) is a member of a strongly hydrogen-bonded cofacial dimer and a π–π back-to-back dimer that form columns in the crystal structure (Fig. 3). The mutual arrangement of the dimers is likely to govern the solid-state packing pattern rather than *vice versa*. It is also possible that there are weaker hydrogen-bonding interactions of the C—H$\cdots\pi$ type between dimer columns related by a crystallographic *c*-glide plane, but our examination shows that they must be very weak and it is not clear how much they affect the crystal structure of (I).

A useful way of describing the conformation of the Pc ligand is by looking at the signs of the net r.m.s. displacements of the four quadrants of the ligand (*e.g.* Ph rings) from the plane of the four ligating N atoms. To each quadrant either a '+' or a '−' is assigned. A dome or concave conformation is characterized by a '+ + + +' combination of the four signs (C_{4v} symmetry), a '+ + − −' sequence yields a wave conformation (C_{2h}), a '+ − + −' arrangement is a saddle conformation (D_{2d}), and a '+ + + −' series is a 'hat visor' conformation (C_s). Of course, the planar Pc ligand complies with the D_{4h} symmetry and in chemical praxis numerous examples of deviations from the idealized geometries are expected. Huckstadt *et al.* (2000) studied the conformation of the Pc ring in several aforementioned Mg complexes and concluded that the ring has a 'concave' (+ + + + in our classification) conformation when the ring overlap within back-to-back π–π dimers in monoclinic systems is weak, and a 'waving' (+ + − −) conformation when the overlap is good in triclinic systems. The r.m.s. deviation of atoms from the 40-atom π system in (I) is 0.036 Å, and thus the ruffling of the system is slight. On the other hand, the analysis of atomic displacements from the plane defined by atoms N1, N3, N5 and N7 indicates that the ligand conformation in (I) is closer to the 'hat visor' (+ + + −) symmetry (Fig. 4). The crystal system of (I) is monoclinic and the ligand overlap is strong, which makes us conclude that the crystal system is inconsequential for ligand conformation. Additionally, the 'hat visor' geometry of the Pc moiety in (I) with good overlap contrasts with the findings of Huckstadt *et al.* (2000). Perhaps the scarcity of five-coordinate Mg complexes with Pc ligands does not currently allow for reliable generalizations in this area.

Experimental

All reagents were obtained from commercial sources and used as received. Magnesium acetate tetrahydrate (47.1 mg, 0.220 mmol) and 1,2-dicyanobenzene (99.2 mg, 0.774 mmol) were combined with methanol (4 ml) in a PTFE-lined (PTFE is polytetrafluoroethylene) autoclave and heated at 343 K for one week. Thin purple needles of (I) were observed upon opening the autoclave.

Crystal data

$[Mg(C_{32}H_{16}N_8)(CH_4O)]$
$M_r = 568.88$
Monoclinic, $P2_1/c$
$a = 13.1896 (10)$ Å
$b = 24.3104 (18)$ Å
$c = 8.0185 (6)$ Å
$\beta = 100.103 (2)°$
$V = 2531.2 (3)$ Å^3
$Z = 4$

$D_x = 1.493$ Mg m^{-3}
Mo- $K\alpha$ radiation
Cell parameters from 5952
reflections
$\theta = 1.8–26.4°$
$\mu = 0.12$ mm^{-1}
$T = 100 (2)$ K
Needle, purple
$0.46 \times 0.27 \times 0.20$ mm

Data collection

Bruker SMART 1000 CCD area-
detector diffractometer
ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 2003)
$T_{min} = 0.948$, $T_{max} = 0.977$
20390 measured reflections

5168 independent reflections
3871 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 26.4°$
$h = -16 \rightarrow 16$
$k = -30 \rightarrow 30$
$l = -10 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.120$
$S = 1.01$
5168 reflections
392 parameters
H atoms treated by a mixture of
independent and constrained
refinement

$w = 1/[\sigma^2(F_o^2) + (0.0688P)^2 + 0.9057P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.25$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1$\cdots$N6^i	0.83 (2)	1.87 (2)	2.698 (2)	177 (2)

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

All H atoms bound to C atoms were placed in idealized positions and refined as riding, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic C atoms, and C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms. Atom H1 attached to atom O1 was refined with $U_{iso}(H) = 1.5U_{eq}(O)$; the O1—H1 distance was allowed to refine (see Table 1).

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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