Crystal structure of diaqua[5,10,15,20-tetrakis(4-bromophenyl)porphyrinato-$\kappa^4 N$]magnesium

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The title compound, [Mg(C$_{44}$H$_{24}$Br$_4$N$_4$)(H$_2$O)$_2$] or [Mg(TBrPP)(H$_2$O)$_2$], where TBrPP is the 5,10,15,20-tetrakis(4-bromophenyl)porphyrinato ligand, was obtained unintentionally as a by-product of the reaction of the [Mg(TBrPP)] complex with an excess of dimethylglyoxime in dichloromethane. The entire molecule exhibits point group symmetry $4/m$. In the asymmetric unit, except for two C atoms of the phenyl ring, all other atoms lie on special positions. The Mg^{II} atom is situated at a site with symmetry $4/m$, while the N and the C atoms of the porphyrin macrocycle, as well as two C atoms of the phenyl ring and the Br atom lie in the mirror plane containing the porphyrin core. The H atoms of the axially bonded water molecule are incompatible with the fourfold rotation axis and are disordered over two sites. In the crystal, molecules are packed in rows along [001]. Weak intermolecular C—H⋯π and C—H⋯Br interactions, as well as O—H⋯Br hydrogen bonds, stabilize the crystal packing.

1. Related literature

For general background to magnesium porphyrin species and their applications, see: Ghosh et al. (2010). For the synthesis of the [Mg^{II}(TPP)(H$_2$O)] complex (TPP is the 5,10,15,20-tetraphenylporphyrinate ligand), see: Timkovich & Tulinsky (1969). In the Cambridge Structural Database (CSD, Version

5.35; Groom & Allen, 2014), there are six magnesium porphyrin structures with aqua ligands deposited. Four from these structures are monoaqua species, derived from [Mg(TOMePP)(H$_2$O)] (TOMePP is the 5,10,15,20-tetrakis(4-methoxyphenyl)porphyrinate ligand; Yang & Jacobson, 1991) and one is a diaqua derivative, [Mg(TPP)(H$_2$O)$_2$]·(18-C-6) where 18-C-6 is 18-crown-6 ether (Ezzayani et al., 2013). For the related porphyrin species [Mg(TPP)(4-pic)$_2$] (4-pic = 4-picoline) and [Mg(TPP)(H$_2$O)], see: McKee et al. (1984) and Ong et al. (1986), respectively. The H atom position of the aqua axial ligand was calculated with the program CALC-OH (Nardelli, 1999).
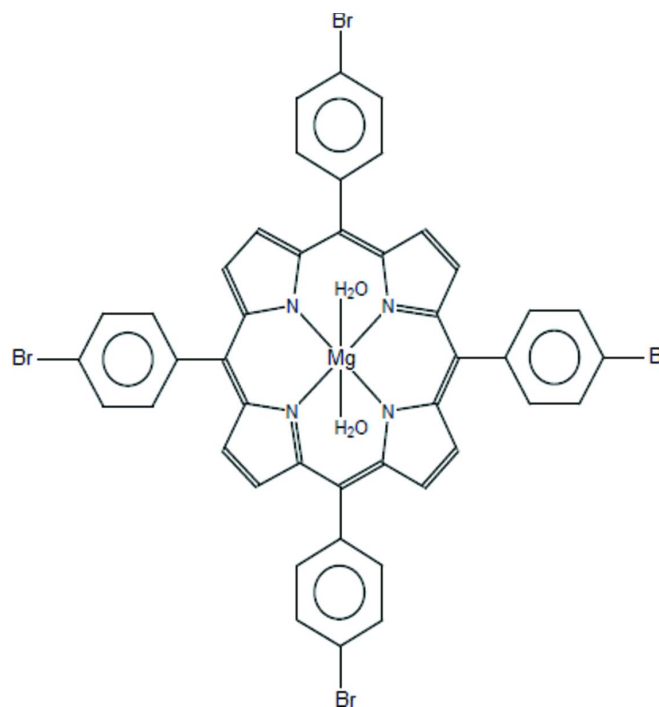
2. Experimental

2.1. Crystal data

[Mg(C$_{44}$H$_{24}$Br$_4$N$_4$)(H$_2$O)$_2$]	$Z = 2$
$M_r = 988.65$	Mo $K\alpha$ radiation
Tetragonal, $I4/m$	$\mu = 3.95$ mm^{-1}
$a = 14.8313$ (10) Å	$T = 150$ K
$c = 9.3966$ (8) Å	$0.37 \times 0.27 \times 0.14$ mm
$V = 2066.9$ (2) Å^3	

2.2. Data collection

Bruker APEXII diffractometer	4471 measured reflections
Absorption correction: multi-scan	1248 independent reflections
(SADABS; Bruker, 2006)	940 reflections with $I > 2\sigma(I)$
$T_{min} = 0.409$, $T_{max} = 0.575$	$R_{int} = 0.034$

2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	H atoms treated by a mixture of
$wR(F^2) = 0.073$	independent and constrained
$S = 1.06$	refinement
1248 reflections	$\Delta\rho_{max} = 0.50$ e Å^{-3}
81 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}

data reports

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

$Cg1$ is the centroid of the N1/C1–C4 pyrrole ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C13—H13$\cdots Cg1^{i}$	0.95	2.74	3.615 (3)	153
O1—H1$O1\cdots$Br1^{ii}	1.10 (5)	2.69 (5)	3.741 (3)	159 (4)
C2—H2$\cdots$Br1^{iii}	0.95	2.97	3.914 (3)	175 (1)

Symmetry codes: (i) $y, -x, -z$; (ii) $x+\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$; (iii) $y, -x, z$.

Data collection: *APEX2* (Bruker, 2006); cell refinement: *SAINT* (Bruker, 2006); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *WinGX* (Farrugia, 2012).

Acknowledgements

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supporting information

Crystal structure of diaqua[5,10,15,20-tetrakis(4-bromophenyl)porphyrinato-$\kappa^4 N$]magnesium

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S1. Synthesis and crystallization

To a solution of [Mg(TBrPP)] (15 mg, 0.015 mmol) in dichloromethane (10 ml) was added an excess of dimethyl-glyoxime (50 mg, 0.431 mmol). The reaction mixture was stirred at room temperature and at the end of the reaction, the color of the solution gradually changed from purple to blue–purple. Black coloured crystals of the title complex were obtained by diffusion of *n*-hexane through the dichloromethane solution. The two water molecules coordinating to the magnesium atom most probably originated from the undistilled dichloromethane solvent.

S2. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. The H atom position of the axially bonded aqua ligand was calculated with the CALC-OH program (Nardelli, 1999). The molecular symmetry of the water molecule is not compatible with the fourfold axis, hence the occupancy of this H atom was fixed to 0.5.
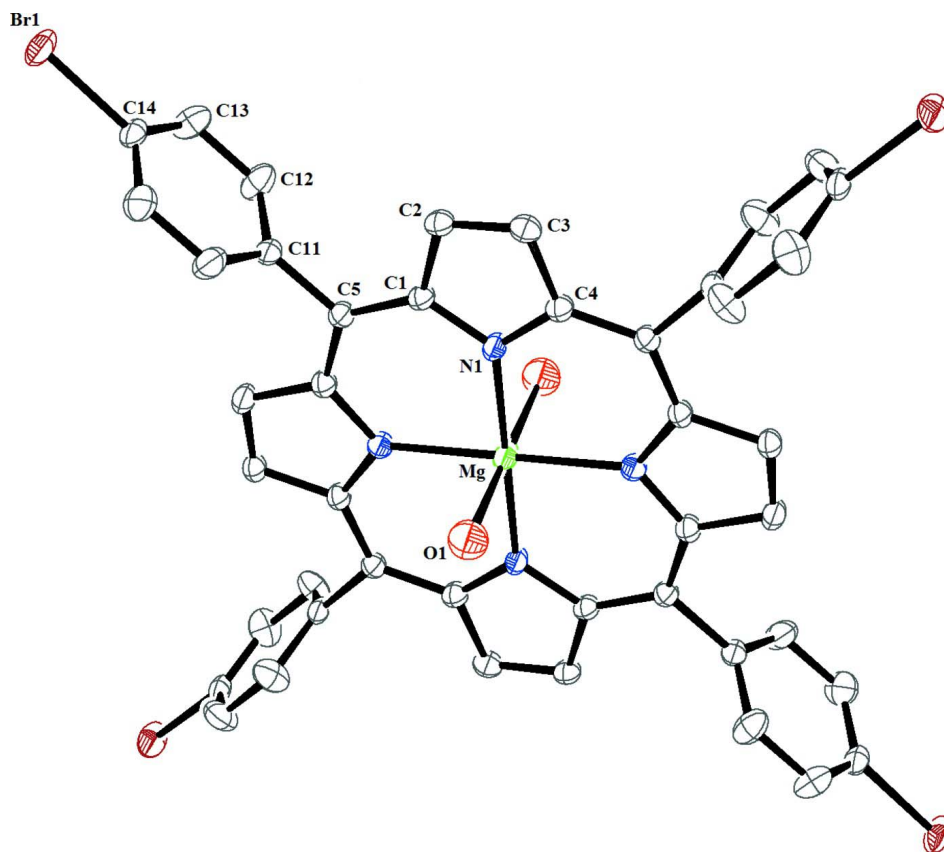
Figure 1

A view of the molecular structure of [Mg(C$_{44}$H$_{24}$N$_4$Br$_4$)(H$_2$O)$_2$] showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.
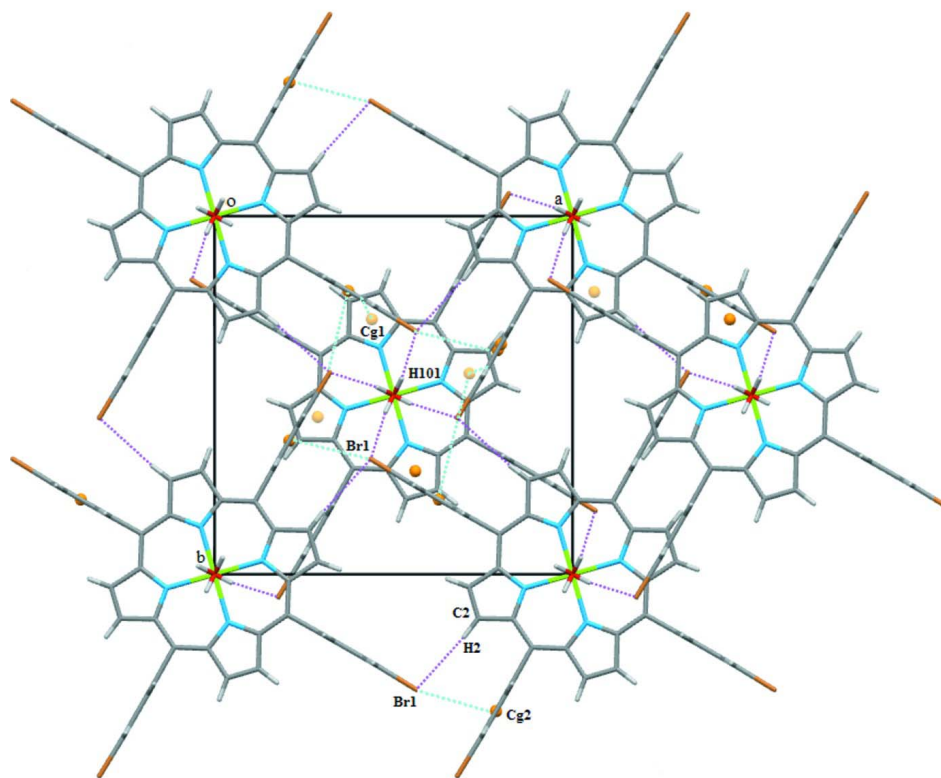
Figure 2

A portion of the crystal packing of the title complex, viewed down [001], showing C—H⋯π interactions (dotted light-blue lines) and C—H⋯Br and O—H⋯Br hydrogen bonds (dashed pink lines).

Diaqua[5,10,15,20-tetrakis(4–bromophenyl)porphyrinato-κ^4N]magnesium

Crystal data

[Mg($C_{44}H_{24}Br_4N_4$)(H_2O)$_2$]	D_x = 1.589 Mg m^{-3}
M_r = 988.65	Mo $K\alpha$ radiation, λ = 0.71073 Å
Tetragonal, $I4/m$	Cell parameters from 1411 reflections
Hall symbol: -I 4	θ = 2.6–26.9°
a = 14.8313 (10) Å	μ = 3.95 mm^{-1}
c = 9.3966 (8) Å	T = 150 K
V = 2066.9 (2) Å^3	Prism, black
Z = 2	0.37 × 0.27 × 0.14 mm
$F(000)$ = 976	

Data collection

Bruker APEXII diffractometer	1248 independent reflections
Graphite monochromator	940 reflections with $I > 2\sigma(I)$
CCD rotation images, thin slices scans	R_{int} = 0.034
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)	θ_{max} = 27.5°, θ_{min} = 3.8°
T_{min} = 0.409, T_{max} = 0.575	h = −14→19
4471 measured reflections	k = −18→18
	l = −5→12

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.073$	
$S = 1.06$	H atoms treated by a mixture of independent and constrained refinement
1248 reflections	
81 parameters	$w = 1/[\sigma^2(F_o^2) + (0.0364P)^2 + 0.9155P]$
0 restraints	where $P = (F_o^2 + 2F_c^2)/3$
Primary atom site location: structure-invariant direct methods	$(\Delta/\sigma)_{max} = 0.009$
	$\Delta\rho_{max} = 0.50$ e Å^{-3}
	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Mg	0.5	0.5	0.5	0.0248 (5)	
O1	0.5	0.5	0.2636 (4)	0.0376 (9)	
H1O1	0.473 (4)	0.560 (3)	0.210 (6)	0.045*	0.5
N1	0.46158 (17)	0.36592 (17)	0.5	0.0192 (6)	
C1	0.3751 (2)	0.3337 (2)	0.5	0.0183 (7)	
C2	0.3771 (2)	0.2366 (2)	0.5	0.0195 (7)	
H2	0.3262	0.1977	0.5	0.023*	
C3	0.4643 (2)	0.2109 (2)	0.5	0.0219 (7)	
H3	0.4865	0.1508	0.5	0.026*	
C4	0.5177 (2)	0.2931 (2)	0.5	0.0196 (7)	
C5	0.2966 (2)	0.3872 (2)	0.5	0.0179 (7)	
C11	0.2081 (2)	0.33768 (19)	0.5	0.0192 (7)	
C12	0.16663 (16)	0.31403 (16)	0.6263 (3)	0.0307 (6)	
H12	0.1942	0.3299	0.714	0.037*	
C13	0.08517 (16)	0.26732 (17)	0.6273 (3)	0.0324 (6)	
H13	0.0572	0.2512	0.7146	0.039*	
C14	0.0463 (2)	0.2451 (2)	0.5	0.0229 (7)	
Br1	−0.06342 (2)	0.17805 (2)	0.5	0.03531 (15)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Mg	0.0142 (7)	0.0142 (7)	0.0461 (16)	0	0	0
O1	0.0376 (13)	0.0376 (13)	0.038 (2)	0	0	0

N1	0.0124 (13)	0.0162 (14)	0.0290 (16)	−0.0007 (10)	0	0
C1	0.0169 (16)	0.0150 (16)	0.0231 (18)	−0.0024 (12)	0	0
C2	0.0199 (16)	0.0152 (15)	0.0233 (18)	−0.0031 (12)	0	0
C3	0.0246 (17)	0.0137 (15)	0.0274 (19)	0.0007 (13)	0	0
C4	0.0186 (16)	0.0167 (16)	0.0234 (18)	−0.0014 (13)	0	0
C5	0.0164 (16)	0.0165 (16)	0.0209 (18)	−0.0009 (13)	0	0
C11	0.0166 (16)	0.0114 (15)	0.0296 (19)	0.0002 (12)	0	0
C12	0.0260 (13)	0.0389 (15)	0.0272 (14)	−0.0117 (11)	0.0002 (11)	−0.0054 (12)
C13	0.0295 (14)	0.0356 (15)	0.0321 (15)	−0.0096 (11)	0.0095 (12)	−0.0013 (12)
C14	0.0158 (16)	0.0129 (16)	0.040 (2)	−0.0010 (12)	0	0
Br1	0.01523 (19)	0.0223 (2)	0.0684 (3)	−0.00419 (14)	0	0

Geometric parameters (Å, º)

Mg—N1^i	2.069 (2)	C3—C4	1.454 (4)
Mg—N1	2.069 (2)	C3—H3	0.95
Mg—N1^{ii}	2.069 (2)	C4—C5^{iii}	1.412 (4)
Mg—N1^{iii}	2.069 (2)	C5—C4^i	1.412 (4)
Mg—O1^{ii}	2.221 (4)	C5—C11	1.504 (4)
Mg—O1	2.221 (4)	C11—C12	1.382 (3)
O1—H1O1	1.10 (5)	C11—C12^{iv}	1.382 (3)
N1—C4	1.363 (4)	C12—C13	1.393 (3)
N1—C1	1.368 (4)	C12—H12	0.95
C1—C5	1.409 (4)	C13—C14	1.369 (3)
C1—C2	1.440 (4)	C13—H13	0.95
C2—C3	1.348 (4)	C14—C13^{iv}	1.369 (3)
C2—H2	0.95	C14—Br1	1.906 (3)
N1^i—Mg—N1	89.998 (2)	N1—C4—C3	109.4 (3)
N1—Mg—N1^{ii}	180.00 (14)	C5^{iii}—C4—C3	125.1 (3)
O1^{ii}—Mg—O1	180	C1—C5—C4^i	126.4 (3)
Mg—O1—H1O1	117 (3)	C1—C5—C11	116.5 (3)
C4—N1—C1	107.1 (2)	C4^i—C5—C11	117.1 (3)
C4—N1—Mg	126.4 (2)	C12—C11—C12^{iv}	118.3 (3)
C1—N1—Mg	126.5 (2)	C12—C11—C5	120.85 (15)
N1—C1—C5	125.3 (3)	C12^{iv}—C11—C5	120.85 (15)
N1—C1—C2	109.3 (3)	C11—C12—C13	121.3 (2)
C5—C1—C2	125.5 (3)	C11—C12—H12	119.4
C3—C2—C1	107.6 (3)	C13—C12—H12	119.4
C3—C2—H2	126.2	C14—C13—C12	118.7 (2)
C1—C2—H2	126.2	C14—C13—H13	120.7
C2—C3—C4	106.6 (3)	C12—C13—H13	120.7
C2—C3—H3	126.7	C13—C14—C13^{iv}	121.9 (3)
C4—C3—H3	126.7	C13—C14—Br1	119.04 (15)
N1—C4—C5^{iii}	125.5 (3)	C13^{iv}—C14—Br1	119.05 (15)
N1^i—Mg—N1—C4	180	C1—N1—C4—C3	0
N1^{iii}—Mg—N1—C4	0	Mg—N1—C4—C3	180

O1ⁱⁱ—Mg—N1—C4	−90	C2—C3—C4—N1	0
O1—Mg—N1—C4	90	C2—C3—C4—C5ⁱⁱⁱ	180
N1ⁱ—Mg—N1—C1	0	N1—C1—C5—C4ⁱ	0
N1ⁱⁱⁱ—Mg—N1—C1	180	C2—C1—C5—C4ⁱ	180
O1ⁱⁱ—Mg—N1—C1	90	N1—C1—C5—C11	180
O1—Mg—N1—C1	−90	C2—C1—C5—C11	0
C4—N1—C1—C5	180	C1—C5—C11—C12	89.7 (3)
Mg—N1—C1—C5	0	C4ⁱ—C5—C11—C12	−90.3 (3)
C4—N1—C1—C2	0	C1—C5—C11—C12ⁱᵛ	−89.7 (3)
Mg—N1—C1—C2	180	C4ⁱ—C5—C11—C12ⁱᵛ	90.3 (3)
N1—C1—C2—C3	0	C12ⁱᵛ—C11—C12—C13	0.2 (5)
C5—C1—C2—C3	180	C5—C11—C12—C13	−179.3 (2)
C1—C2—C3—C4	0	C11—C12—C13—C14	−0.1 (4)
C1—N1—C4—C5ⁱⁱⁱ	180	C12—C13—C14—C13ⁱᵛ	0.1 (5)
Mg—N1—C4—C5ⁱⁱⁱ	0	C12—C13—C14—Br1	178.2 (2)

Symmetry codes: (i) y, −x+1, −z+1; (ii) −x+1, −y+1, −z+1; (iii) −y+1, x, z; (iv) x, y, −z+1.

Hydrogen-bond geometry (Å, º)

Cg1 is the centroid of the N1/C1–C4 pyrrole ring.

D—H···A	D—H	H···A	D···A	D—H···A
C13—H13···Cg1ᵛ	0.95	2.74	3.615 (3)	153
O1—H1O1···Br1ᵛⁱ	1.10 (5)	2.69 (5)	3.741 (3)	159 (4)
C2—H2···Br1ᵛⁱⁱ	0.95	2.97	3.914 (3)	175 (1)

Symmetry codes: (v) y, −x, −z; (vi) x+1/2, y+1/2, z−1/2; (vii) y, −x, z.