Aqua[η^1-dihydrobis(1,2,4-triazolyl)borato]-(5,10,15,20-*meso*-tetraphenylporphyrinato-κ^4N)-manganese(III) monohydrate

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The crystal structure of the title compound, [Mn(TPP)(η^1-H$_2$Btz$_2$)(H$_2$O)]·H$_2$O [where H$_2$Btz = dihydrobis(1,2,4-triazolyl)borate, C$_4$H$_6$BN$_6$, and TPP = tetraphenylporphyrin, C$_{44}$H$_{20}$N$_4$], contains a singly coordinated H$_2$Btz$_2$. The TPP ligand is highly distorted even though the coordination environment around Mn^{III} has regular octahedral geometry. Both coordinated and uncoordinated water molecules are involved in intermolecular hydrogen bond through O—H···O, O—H···N and O—H···(π-arene) interactions to form a three-dimensional network.

Comment

Manganese(III) porphyrins are versatile building blocks for a variety of polymeric coordination compounds, because additional axial coordination is possible around the Mn^{III} center. They are structurally rigid and can also form very well defined extended zeotype structures. In principle, various bridging ligands can form unique functional porous materials through the bridging of two Mn^{III} porphyrin complexes. Recent review articles highlight detailed examples and applications of these materials (Kitakawa *et al.*, 2004; Yaghi *et al.*, 2003). In order to investigate unsymmetrical coordination networks based on Mn^{III} porphyrins, we chose the dihydrobis(1,2,4-triazolyl)borate anion as a potential bridging ligand. Unlike the most commonly adopted planar 4,4′-bipyridyl ligand (Eddaoudi *et al.*, 2001), the two triazolyl rings of dihydrobis(1,2,4-triazolyl)borate, [H$_2$Btz$_2$]$^-$, are not coplanar. The ligand has a tetrahedral stucture and the bite angle of the two triazolyl rings can vary upon coordination to metals. Moreover, this
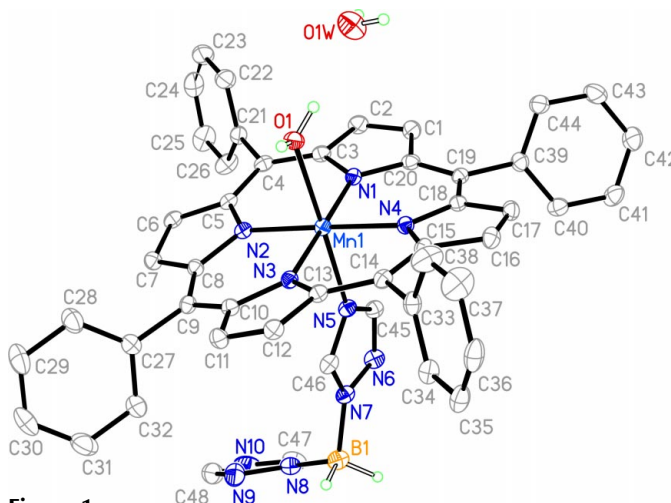

Figure 1
The structure of (I), showing 30% probability displacement ellipsoids and the atomic numbering scheme. H atoms bonded to C atoms have been omitted.

ligand has a negative charge and it would be beneficial to construct a coordination network free of counteranions by using cationic Mn[III] porphyrins. Janiak *et al.* (1995) also pointed out the rich hydrogen-bonding ability of the poly-(triazolyl)borate family because of the extra ring N atoms, *e.g.* the 4-position N atoms of dihydrobis(1,2,4-triazolyl)borate, which are also known as exodentate N atoms (Janiak & Scharmann, 2003). Therefore, a large number of topologically interesting hydrogen-bonding networks from this family may be possible.

The reaction between equimolar amounts of [Mn(TPP)]ClO$_4$ and K[H$_2$Btz$_2$] produced a dark-green crystalline compound. To our surprise, only the neutral [Mn(TPP)(η^1-H$_2$Btz$_2$)(H$_2$O)] as its hydrate, (I) (Fig. 1), was obtained, in 68% yield.

(I)
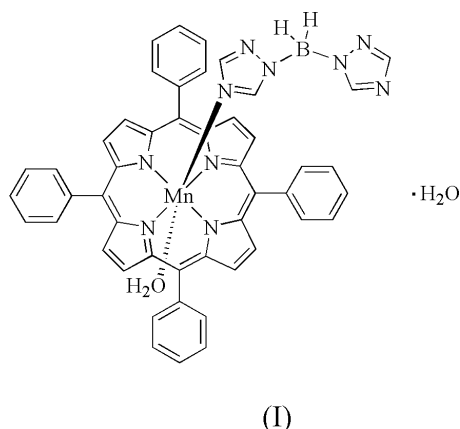
Although the dihydrobis(1,2,4-triazolyl)borate ligand can bridge two Mn[III] centers through the two exodentate N atoms of the two triazolyl rings, in (I) only one N atom is involved in coordination, while the other forms a hydrogen bond with the water molecule coordinated to a neighboring molecule. Steric congestion between the Mn(TPP)$^+$ unit and the dihydrobis(1,2,4-triazolyl)borate anion may only allow single coordination of the latter. The dihedral angle between the two triazolyl rings is 110.02 (10)°. The tetrahedral geometry of the BN$_2$H$_2$ moiety of the dihydrobis(1,2,4-triazolyl)borate ligand is normal. The N7—B1—N8 angle is 109.2 (2)°. The B1—N7 and B1—N8 bond distances [1.561 (3) and 1.540 (4) Å, respectively] are comparable with each other and are quite similar to those of dihydrobis(pyrazol-1-yl)borates chelated to Ru[II] (Huh *et al.*, 1999, 2000).

In (I), both of the H atoms bonded to the coordinated water molecule are involved in either O—H···O or O—H··· strong hydrogen bonds. One H atom of the uncoordinated water molecule is involved in an O—H···N hydrogen bond, while the other forms a weak O—H···(π arene) interaction. Detailed information of the hydrogen-bonding scheme is shown in Fig. 2 and summarized in Table 2.

The coordination geometry around Mn1 in (I) is slightly distorted octahedral. The Mn1—N5 and Mn1—O1 distances [2.2836 (18) and 2.2198 (17) Å, respectively] are quite normal,
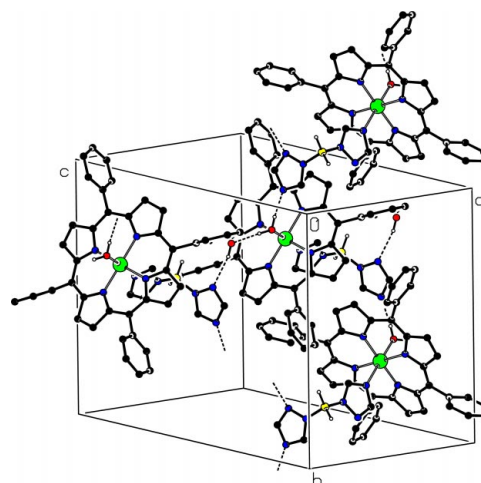
Figure 2
The molecular packing diagram for (I), with hydrogen bonds indicated by dashed lines. The weak O—H···(π-arene) bond is not shown.

as observed in previously structurally determined complexes (Park *et al.*, 2003). The O1—Mn1—N5 bond angle of 175.59 (7)° deviates slightly from linearity. All bond distances between Mn1 and the N donors of the TPP ligand, from 2.0012 (19) Å for Mn1—N4 to 2.0049 (18) Å for Mn1—N2, are in good agreement with those in similar Mn(TPP)$^+$ compounds (Munro & Camp, 2003). The deviations of atoms N1, N2, N3 and N4 from the mean plane of the TPP ligand are −0.0720 (17), −0.0176 (17), 0.0133 (17) and 0.0234 (17) Å, respectively. However, the Mn(TPP)$^+$ moiety shows a highly distorted saddle-type structure. The deviations of the *meso*-position atoms C4, C9, C14 and C19 from the mean plane of the TPP ligand are 0.327 (2), 0.304 (2), −0.227 (2) and 0.309 (2) Å, respectively. In fact, we also observed such a large distortion of the TPP rings when we used metallocyanide bridging ligands, even though we could obtain heterometallic trimers (Huh *et al.*, 2004).

Experimental

[Mn(TPP)]ClO$_4$ (38 mg, 0.05 mmol; Hill & Williamson, 1985) in acetone (20 ml) was mixed with a methanol (20 ml) solution of K[H$_2$Btz$_2$] (10 mg, 0.05 mmol; Janiak *et al.*, 1995). The reaction mixture was heated at 333 K for 1 h and then filtered on a glass frit. The filtrate was then completely evaporated on a rotary evaporator and the crude solids were dissolved in acetone (30 ml) and the solution was filtered. A dark-green crystalline solid was obtained; it was washed with hexane and dried in air (yield 29 mg). X-ray quality crystals of (I) were obtained by recrystallization from methanol. IR ν(BH): 2409.4 cm^{-1}.

Crystal data

[Mn(C$_{44}$H$_{20}$N$_4$)(C$_4$H$_6$BN$_6$)(H$_2$O)]·· H$_2$O	D_x = 1.345 Mg m^{-3}
M_r = 852.63	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 37 308
a = 12.2498 (2) Å	reflections
b = 16.0805 (5) Å	θ = 2.7–25.0°
c = 21.5391 (6) Å	μ = 0.37 mm^{-1}
β = 96.944 (2)°	T = 100 (1) K
V = 4211.71 (19) Å^3	Plate, dark green
Z = 4	0.30 × 0.30 × 0.15 mm

Data collection

Nonius KappaCCD area-detector diffractometer	7423 independent reflections
φ scans, and ω scans with κ offsets	5034 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*DENZO-SMN*; Otwinowski & Minor, 1997)	$R_{int} = 0.063$
	$\theta_{max} = 25.0°$
	$h = -14 \rightarrow 14$
$T_{min} = 0.898$, $T_{max} = 0.947$	$k = -19 \rightarrow 19$
37 308 measured reflections	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.2174P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.105$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.07$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
7423 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}
581 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected geometric parameters (Å).

Mn1—N4	2.0012 (19)	N6—C45	1.315 (3)
Mn1—N3	2.0042 (19)	N6—N7	1.368 (3)
Mn1—N2	2.0049 (18)	N7—C46	1.333 (3)
Mn1—N1	2.0050 (19)	N7—B1	1.561 (3)
Mn1—O1	2.2198 (17)	N8—C47	1.322 (3)
Mn1—N5	2.2836 (19)	N8—N9	1.372 (3)
N5—C46	1.330 (3)	N8—B1	1.540 (4)
N5—C45	1.357 (3)	N9—C48	1.331 (4)

Table 2
Hydrogen-bonding geometry (Å, °).

*Cg*1 is the centroid of the C21–C26 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H2O$\cdots$O1W	0.84 (2)	1.965 (12)	2.804 (3)	175 (2)
O1—H1O$\cdots$N10^i	0.84 (2)	1.898 (7)	2.728 (3)	169 (3)
O1W—H2$W\cdots$N9^{ii}	0.84 (2)	2.123 (10)	2.945 (3)	166 (3)
O1W—H1$W\cdots Cg$1^{iii}	0.84 (2)	2.90 (3)	3.673 (3)	154 (3)

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

All H atoms bonded to C atoms were located in difference maps and subsequently treated as riding atoms, with C—H distances of 0.95 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bonded to O atoms were refined, with an O—H bond distance restraint of 0.84 (2) Å. The isotropic displacement parameters of the H atoms bonded to the coordinated water were refined independently, but the $U_{iso}(H)$ values of the solvent water H atoms were fixed at $1.5U_{eq}(O)$. The H atoms bonded to B were refined independently with isotropic displacement parameters.

Data collection: *COLLECT* (Nonius, 1997–2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *SHELXTL/PC*; software used to prepare material for publication: *SHELXTL/PC*.

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