

Pentaethylenehexaminemanganese(II) pentaborate

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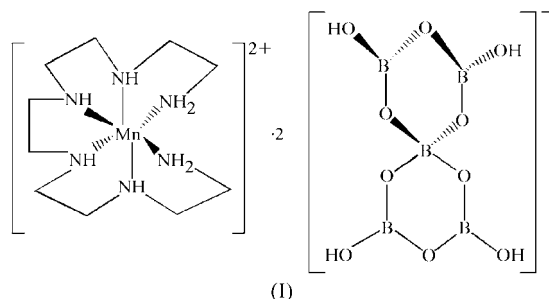
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The title compound, (pentaethylenehexamine- κ^6N)manganese(II) 4,4',6,6'-tetrahydroxy-2,2'-spirobi(cyclotriboroxane)-(1-), $[\text{Mn}(\text{C}_{10}\text{H}_{28}\text{N}_6)][\text{B}_5\text{O}_6(\text{OH})_4]_2$, was synthesized under mild solvothermal conditions. The $\text{B}_5\text{O}_6(\text{OH})_4^-$ units are connected to one another *via* hydrogen bonds, forming a three-dimensional framework with large channels along the *a* and *c* axes, in which the templating $[\text{Mn}(\text{C}_{10}\text{H}_{28}\text{N}_6)]^{2+}$ cations are located. The Mn^{II} complex cation has a twofold axis and the coordination geometry of the MnN_6 group is that of a distorted trigonal prism.

Comment

From a structural point of view, B atoms are easy to condense into clusters, example being $\text{B}_4\text{O}_5(\text{OH})_4$ (Touboul *et al.*, 1999), B_5O_8 (Penin *et al.*, 2001), B_8O_{18} (Li *et al.*, 2003), $\text{B}_{12}\text{O}_{24}$ (Menchetti & Sabelli, 1979; Choudhury *et al.*, 2002), $\text{B}_{16}\text{O}_{24}(\text{OH})_8$ (Behm, 1985), *etc.* As a result of the flexible threefold (BO_3 , triangular) or fourfold (BO_4 , tetrahedral) coordination of the B atom, borates are the most complex compounds containing oxide polyanions. Many inorganic frameworks constructed from BO polyhedra exhibiting one-dimensional chains (Grice *et al.*, 1999; Yu *et al.*, 2002; Schubert *et al.*, 2003), two-dimensional layers (Bubnova *et al.*, 2002; Penin, Seguin *et al.*, 2002; Penin, Touboul & Nowogrock, 2002, 2003) and three-dimensional open structures (Harrison *et al.*,



1993; Penin *et al.*, 2001; Choudhury *et al.*, 2002; Huppertz & von der Eltz, 2002; Rowsell *et al.*, 2002; Huppertz & Heymann,

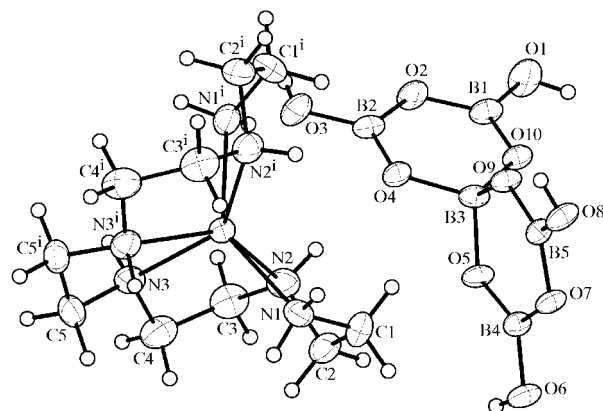


Figure 1

The cation and anion in (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 30% probability level. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

2003) have been reported in the past few decades, and these borate crystals were usually grown under the templating effect of inorganic cations. Recently, the templating effects of metal-organic complexes have been demonstrated for many inorganic systems (Bruce *et al.*, 1995, 1996; Gray *et al.*, 1997; Yu *et al.*, 2001). However, the formation of metallo-organically templated borates is less well explored, and only one such material, namely $[\text{Cu}(\text{en})_2](\text{B}_7\text{O}_{13}\text{H}_3)$ (en is ethylenediamine; Sung *et al.*, 2000), has been reported to date. The aim of our work is to construct new borate structures by using common BO clusters as fundamental building blocks (FBBs) in the presence of transition metal coordination complexes. A novel borate, *viz.* the title compound, (I), has been isolated successfully.

Compound (I) is composed of $\text{B}_5\text{O}_6(\text{OH})_4^-$ anions and $[\text{Mn}(\text{C}_{10}\text{H}_{28}\text{N}_6)]^{2+}$ cations (Fig. 1 and Table 1). The

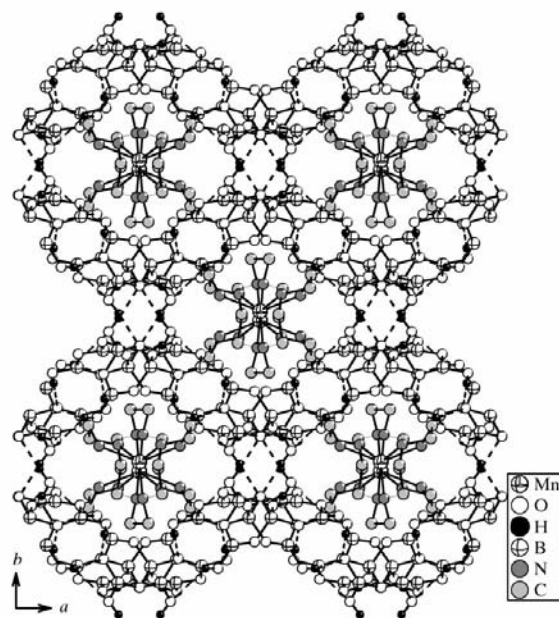


Figure 2

The crystal packing of (I), projected along the *c* axis. The broken lines indicate hydrogen-bonding interactions. H atoms of the Mn complex cations have been omitted for clarity.

$B_5O_6(OH)_4^-$ polyanion consists of two B_3O_3 rings, each containing one tetrahedral and two trigonal B atoms. The B—O distances for the trigonal B atoms (B1, B2, B4 and B5) range between 1.347 (7) and 1.382 (6) Å, and the B—O distances for the tetrahedral B atom (B3) range from 1.454 (7) to 1.477 (7) Å. The O—B—O angles involving trigonal B atoms are in the range 115.6 (5)–123.1 (5)° and the O—B—O angles involving atom B3 are in the range 108.3 (5)–112.0 (4)°. The two B_3O_3 rings are connected *via* their shared tetrahedral B atom. The $B_5O_6(OH)_4^-$ clusters are further connected by hydrogen-bonding interactions into a three-dimensional structure, with large channels along the *a* (as shown in Fig. 2) and *c* axes [O···O = 2.717 (6)–3.060 (5) Å]. The Mn atom lies on a twofold axis and is bonded to the six N atoms of the ligand. The MnN_6 coordination geometry is that of a distorted trigonal prism. The Mn—N distances range from 2.256 (5) to 2.332 (5) Å and the N—Mn—N angles are between 75.1 (3) and 144.1 (2)°. The $[Mn(C_{10}H_{28}N_6)]^{2+}$ cations are located in the inorganic channel and interact with the framework both electrostatically and *via* hydrogen bonds, with N···O distances in the range 3.059 (6)–3.362 (6) Å (Table 2).

Experimental

Compound (I) was prepared from a mixture of $NH_4B_5O_8 \cdot 4H_2O$ (0.816 g), $[Mn(C_{10}H_{28}N_6)](CH_3COO)_2$ (0.398 g), pyridine (3.2 ml), distilled water (1.1 ml) and hydrofluoric acid (40%, 0.1 ml) in the molar ratio 3.0:1.0:4.0:4.8:2.0. The mixture was stirred mechanically at room temperature (the final pH was 9.0) and then placed in an autoclave at 443 K for 7 d. Yellow block-shaped crystals of (I) were obtained. The powder X-ray diffraction pattern of the bulk product is in good agreement with the pattern calculated on the basis of the present crystal structure determination, indicating the phase purity of the sample. Analysis calculated for $C_{10}H_{36}B_{10}MnN_6O_{20}$: C 15.13, H 7.11, N 10.59%; found: C 15.27, H 7.23, N 10.53%. Thermogravimetric analysis (TGA) was performed in a dry N_2 atmosphere (303–1673 K), with heating rates of 30 K min^{-1} between 303 and 1273 K, and 15 K min^{-1} between 1273 and 1673 K. TGA showed that there were two steps of weight loss. The initial weight loss (about 10%; 553–593 K) corresponds to the total removal of hydroxy groups (calculated 9.7%). The weight loss from 593 to 743 K is attributed to the partial release of organic molecules. When heated further, the organic molecules were lost fully at about 1283 K, and finally the volatile boron oxide phases were partially released. The IR spectrum of (I) contains the characteristic bands of the BO_3 and BO_4 groups, corresponding to strong bands at ~ 1390 and 1040 cm^{-1} , respectively (Yu *et al.*, 2002). A peak at 1602 cm^{-1} corresponds to the bending of NH_2 . The stretching bands of the OH and NH_2 groups are observed at $\sim 3435\text{ cm}^{-1}$ (Yang *et al.*, 2001).

Crystal data

$[Mn(C_{10}H_{28}N_6)][B_5O_6(OH)_4]_2$	Mo $K\alpha$ radiation
$M_r = 723.49$	Cell parameters from 36 reflections
Monoclinic, $C2/c$	
$a = 11.9060$ (1) Å	$\theta = 2.2\text{--}25.1^\circ$
$b = 14.7950$ (6) Å	$\mu = 0.49\text{ mm}^{-1}$
$c = 18.6611$ (7) Å	$T = 293$ (2) K
$\beta = 97.057$ (2)°	Block, yellow
$V = 3262.24$ (18) Å ³	$0.28 \times 0.28 \times 0.20\text{ mm}$
$Z = 4$	
$D_x = 1.473\text{ Mg m}^{-3}$	

Data collection

Siemens SMART CCD diffractometer	1738 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.045$
Absorption correction: empirical (<i>SADABS</i> ; Sheldrick, 1996)	$\theta_{max} = 25.1^\circ$
$T_{min} = 0.714$, $T_{max} = 0.907$	$h = -8 \rightarrow 14$
5263 measured reflections	$k = -17 \rightarrow 10$
2906 independent reflections	$l = -21 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0247P)^2 + 10.2326P]$
$R[F^2 > 2\sigma(F^2)] = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.150$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.19$	$\Delta\rho_{max} = 0.32\text{ e \AA}^{-3}$
2890 reflections	$\Delta\rho_{min} = -0.27\text{ e \AA}^{-3}$
213 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Mn—N1	2.256 (5)	O5—B3	1.477 (7)
Mn—N3	2.277 (5)	O6—B4	1.345 (6)
Mn—N2	2.332 (5)	O7—B5	1.372 (7)
O1—B1	1.349 (8)	O7—B4	1.382 (6)
O2—B1	1.365 (8)	O8—B5	1.352 (6)
O2—B2	1.377 (8)	O9—B5	1.349 (6)
O3—B2	1.353 (8)	O9—B3	1.471 (6)
O4—B2	1.347 (7)	O10—B1	1.350 (7)
O4—B3	1.454 (7)	O10—B3	1.466 (7)
O5—B4	1.348 (6)		
N1 ⁱ —Mn—N1	139.5 (2)	O3—B2—O2	120.9 (5)
N1 ⁱ —Mn—N3	97.53 (17)	O4—B3—O10	112.0 (4)
N1—Mn—N3	114.71 (17)	O4—B3—O9	109.1 (5)
N3 ⁱ —Mn—N3	75.1 (3)	O10—B3—O9	108.7 (5)
N1 ⁱ —Mn—N2	89.83 (17)	O4—B3—O5	108.3 (5)
N1—Mn—N2	75.81 (19)	O10—B3—O5	108.7 (5)
N3 ⁱ —Mn—N2	144.1 (2)	O9—B3—O5	109.9 (4)
N3—Mn—N2	76.0 (2)	O6—B4—O5	123.1 (5)
N2—Mn—N2 ⁱ	138.0 (3)	O6—B4—O7	116.1 (5)
O1—B1—O10	122.8 (7)	O5—B4—O7	120.7 (5)
O1—B1—O2	115.6 (5)	O9—B5—O8	122.3 (5)
O10—B1—O2	121.6 (6)	O9—B5—O7	121.2 (5)
O4—B2—O3	117.8 (6)	O8—B5—O7	116.5 (5)
O4—B2—O2	121.2 (6)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H1···O10 ⁱⁱ	0.82	1.90	2.717 (6)	173
O3—H2···O2 ⁱⁱⁱ	0.82	2.19	2.995 (5)	166
O3—H2···O1 ⁱⁱⁱ	0.82	2.43	3.060 (5)	134
O6—H3···O5 ^{iv}	0.82	1.93	2.751 (5)	179
O8—H4···O9 ⁱ	0.82	1.92	2.736 (4)	174
N1—H1D···O3 ^v	0.90	2.17	3.059 (6)	168
N1—H1E···O8 ^v	0.90	2.29	3.150 (6)	160
N1—H1E···O7 ^v	0.90	2.62	3.362 (6)	141
N2—H2C···O4	0.91	2.18	3.092 (6)	177
N3—H3D···O7 ^{vi}	0.91	2.29	3.181 (5)	165
N3—H3D···O6 ^{vi}	0.91	2.59	3.321 (6)	138

Symmetry codes: (i) $1 - x, y, \frac{1}{2} - z$; (ii) $1 - x, -y, -z$; (iii) $\frac{3}{2} - x, \frac{1}{2} - y, -z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, -z$; (v) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (vi) $\frac{1}{2} + x, \frac{1}{2} + y, z$.

H atoms bonded to O atoms were located from difference density maps, and H atoms bonded to C and N atoms were positioned geometrically; all H atoms were then allowed to ride on their parent atoms ($C-H = 0.97 \text{ \AA}$, $N-H = 0.91 \text{ \AA}$ and $O-H = 0.82 \text{ \AA}$). In (I), the $[B_5O_6(OH)_4]^-$ anions are connected *via* strong hydrogen-bonding interactions into an open-framework structure, which may give rise to voids of 57 \AA^3 . Such voids in the crystal structure are familiar in microporous materials. For example, the 24-MR zinc phosphate (ND-1; Yang *et al.*, 1999) possesses voids of 285 \AA^3 , resulting from the exceptionally porous structure.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1173). Services for accessing these data are described at the back of the journal.

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