

A novel metallo-organically templated pentaborate: acetato[*N,N'*-bis(2-aminoethyl)ethane-1,2-diamine]zinc(II) 4,4',6,6'-tetrahydroxy-2,2'-spiro-bi[cyclotriboroxane](1—)

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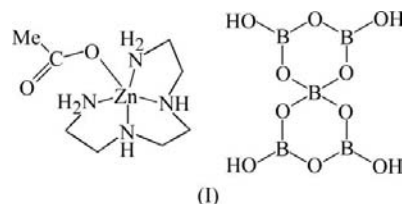
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The title compound, $[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_6\text{H}_{18}\text{N}_4)][\text{B}_5\text{O}_6(\text{OH})_4]$, contains mixed-ligand $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})]^+$ complex cations (teta is triethylenetetramine) and pentaborate $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ anions. The $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ anions are connected to one another through hydrogen bonds, forming a three-dimensional supramolecular network, in which the $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})]^+$ cations are located.

Comment

Borate materials have attracted a great deal of attention in the past because of their rich structural chemistry and potential applications in mineralogy and industry (Christ & Clark, 1977; Becker, 1998; Burns, 1995; Grice *et al.*, 1999; Chen *et al.*, 1995). Borate materials with various alkali metals, alkaline earth metals, main group metals, rare earths and transition metals have been widely explored. In contrast, less work has been carried out on organic borates. To date, only a few organic amines have been successfully introduced into borate systems, such as $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3][\text{B}_6\text{O}_9(\text{OH})_2]$ (Li *et al.*, 2006), $[\text{H}_3\text{N}(\text{C}_6\text{H}_{10})\text{NH}_3][\text{B}_4\text{O}_5(\text{OH})_4]$ and $[\text{H}_3\text{N}(\text{C}_6\text{H}_{10})\text{NH}_3][\text{B}_5\text{O}_8(\text{OH})]$ (Wang *et al.*, 2004) and $[\text{C}_6\text{H}_{13}\text{N}_2][\text{B}_5\text{O}_6(\text{OH})_4]$ (Liu *et al.*, 2008), or metals coordinated by amines, such as $[\text{Cu}(\text{en})_2][\text{B}_7\text{O}_{13}\text{H}_3]_n$ (en is ethylenediamine; Sung *et al.*, 2000), $[\text{Mn}(\text{C}_{10}\text{H}_{18}\text{N}_6)][\text{B}_5\text{O}_6(\text{OH})_4]_2$ (Zhang *et al.*, 2004), $[\text{Ni}(\text{C}_4\text{H}_{10}\text{N}_2)(\text{C}_2\text{H}_8\text{N}_2)_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$ (Liu *et al.*, 2006) and $[\text{Zn}(\text{dien})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$ and $[\text{B}_5\text{O}_7(\text{OH})_3\text{Zn}(\text{tren})]$ [dien is diethylenetriamine and tren is tris(2-aminoethyl)amine; Wang *et al.*, 2005]. However, borates involving organic acids are extremely rare (Tombul *et al.*, 2007). We describe here the synthesis and crystal structure of the title novel metallo-organically templated borate, $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})][\text{B}_5\text{O}_6(\text{OH})_4]$ (teta is

triethylenetetramine), (I), in which the $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})]^+$ complex cation contains both organic amine and organic acid ligands.



The asymmetric unit of (I) consists of a $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})]^+$ cation and a $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ polyborate anion (Fig. 1). In the $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})]^+$ metal complex cation, the Zn centre is coordinated by four N atoms from teta and one carboxylate O atom, forming a square pyramid with an O atom as the vertex. The Zn—N bond lengths are in the range 2.0549 (19)–2.207 (2) Å and the N—Zn—N angles are between 80.46 (8) and 157.06 (8)°. The Zn—O bond length is 2.0020 (16) Å. The second O atom of the carboxylate group is disordered over three positions (see *Experimental*).

The $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ borate polyanion is formed by two $[\text{B}_3\text{O}_3]$ rings linked by a common BO_4 tetrahedron. Each ring is composed of two BO_3 triangles and a slightly distorted common BO_4 tetrahedron. The terminal O atoms are protonated. The trigonally coordinated B atoms have B—O distances in the range 1.344 (2)–1.381 (2) Å and the tetrahedral B atoms have longer B—O distances in the range 1.453 (2)–1.483 (2) Å. The O—B—O angles of the BO_3 triangles lie in the range 115.20 (15)–123.64 (16)° and those of the BO_4 tetrahedra range from 107.71 (13) to 111.59 (13)°.

Extensive hydrogen-bond interactions are important in the formation and stability of low-dimensional structures (Chang *et al.*, 2001; Dalrymple & Shimizu, 2007). The overall sheet-like structure of (I) is formed by extensive multipoint hydrogen bonding involving the $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ borate poly-

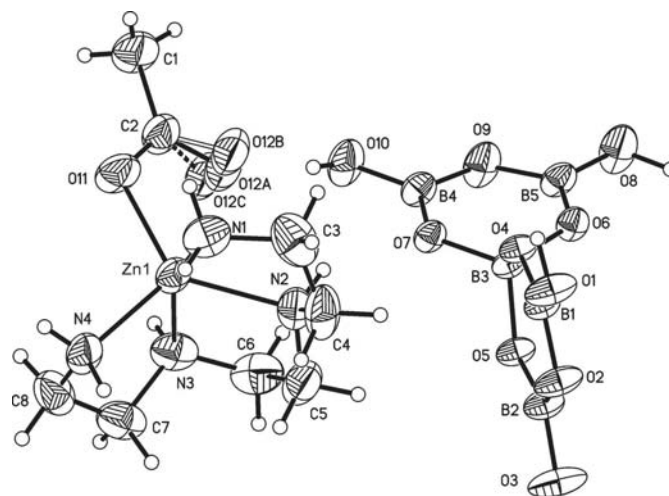
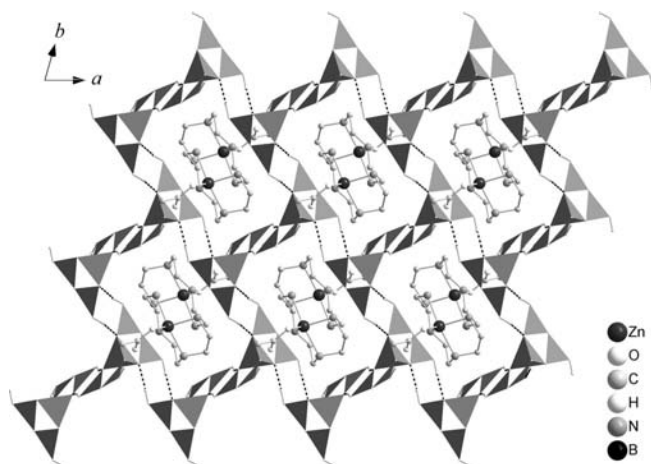


Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 45% probability level and H atoms are shown as small spheres of arbitrary radii. The O12 atom is disordered over three positions that refined to a ratio of 0.22 (2): 0.37 (4): 0.41 (4).

**Figure 2**

View, along the *c* axis, of the $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})]^+$ cations in the inorganic borate network. Dashed lines indicate hydrogen bonds.

anions. The $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ polyanions and the templating $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})]^+$ cations are further connected by hydrogen bonds to form a three-dimensional supramolecular network $[\text{N1}—\text{H1F}\cdots\text{O3}$, $\text{N2}—\text{H2A}\cdots\text{O7}$, $\text{N3}—\text{H3D}\cdots\text{O10}$ and $\text{N4}—\text{H4A}\cdots\text{O2}$; $\text{N}\cdots\text{O} = 3.054(3)–3.125(3)$ Å; Table 2]. The $[\text{Zn}(\text{CH}_3\text{COO})(\text{teta})]^+$ cations are located in the free space of the network and interact with the inorganic framework by extensive hydrogen bonding (Fig. 2 and Table 2).

Experimental

A mixture of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (1.1120 g), H_3BO_3 (1.2291 g) and H_2O (50 ml) was placed in a beaker and stirred at 363 K until the solution had evaporated to 2–3 ml, then *teta* (1 ml) was added and thorough mixing was carried out. The resulting viscous milky liquid was sealed in a Teflon-lined autoclave, heated at 453 K for 7 d and then cooled to room temperature. Colourless transparent block-like crystals of (I) were obtained, and these were washed with deionized water and dried at ambient temperature.

Crystal data

$[\text{Zn}(\text{C}_2\text{H}_3\text{O}_2)(\text{C}_6\text{H}_{18}\text{N}_4)](\text{B}_5\text{H}_4\text{O}_{10})$	$\gamma = 74.26(3)^\circ$
$M_r = 488.74$	$V = 1041.6(4) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.7778(18) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.260(2) \text{ \AA}$	$\mu = 1.24 \text{ mm}^{-1}$
$c = 12.882(3) \text{ \AA}$	$T = 295 \text{ K}$
$\alpha = 69.08(3)^\circ$	$0.57 \times 0.41 \times 0.27 \text{ mm}$
$\beta = 87.10(3)^\circ$	

Data collection

Rigaku R-Axis RAPID diffractometer	10240 measured reflections
Absorption correction: multi-scan (<i>ABSCOR</i> ; Higashi, 1995)	4703 independent reflections
$T_{\min} = 0.538$, $T_{\max} = 0.730$	3988 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.018$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$	1 restraint
$wR(F^2) = 0.080$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\max} = 0.28 \text{ e \AA}^{-3}$
4703 reflections	$\Delta\rho_{\min} = -0.24 \text{ e \AA}^{-3}$
284 parameters	

Table 1

Selected geometric parameters (Å, °).

$\text{Zn1}—\text{O11}$	2.0020 (16)	$\text{O4}—\text{B3}$	1.476 (2)
$\text{Zn1}—\text{N4}$	2.0549 (19)	$\text{O5}—\text{B2}$	1.344 (2)
$\text{Zn1}—\text{N2}$	2.1090 (18)	$\text{O5}—\text{B3}$	1.483 (2)
$\text{Zn1}—\text{N1}$	2.198 (2)	$\text{O6}—\text{B5}$	1.355 (2)
$\text{Zn1}—\text{N3}$	2.207 (2)	$\text{O6}—\text{B3}$	1.467 (2)
$\text{Zn1}—\text{O12A}$	2.44 (2)	$\text{O7}—\text{B4}$	1.351 (2)
$\text{O1}—\text{B1}$	1.350 (2)	$\text{O7}—\text{B3}$	1.453 (2)
$\text{O2}—\text{B1}$	1.376 (2)	$\text{O9}—\text{B5}$	1.370 (3)
$\text{O2}—\text{B2}$	1.381 (2)	$\text{O9}—\text{B4}$	1.371 (3)
$\text{O3}—\text{B2}$	1.351 (2)	$\text{O10}—\text{B4}$	1.354 (2)
$\text{O4}—\text{B1}$	1.349 (2)		
$\text{O11}—\text{Zn1}—\text{N4}$	105.65 (8)	$\text{O1}—\text{B1}—\text{O2}$	115.20 (15)
$\text{O11}—\text{Zn1}—\text{N2}$	132.06 (7)	$\text{O5}—\text{B2}—\text{O3}$	123.72 (17)
$\text{N4}—\text{Zn1}—\text{N2}$	122.28 (8)	$\text{O5}—\text{B2}—\text{O2}$	120.72 (16)
$\text{O11}—\text{Zn1}—\text{N1}$	95.43 (8)	$\text{O3}—\text{B2}—\text{O2}$	115.52 (16)
$\text{N4}—\text{Zn1}—\text{N1}$	97.20 (8)	$\text{O7}—\text{B3}—\text{O6}$	111.59 (13)
$\text{N2}—\text{Zn1}—\text{N1}$	80.78 (8)	$\text{O7}—\text{B3}—\text{O4}$	108.49 (14)
$\text{O11}—\text{Zn1}—\text{N3}$	106.94 (8)	$\text{O6}—\text{B3}—\text{O4}$	109.59 (14)
$\text{N4}—\text{Zn1}—\text{N3}$	81.88 (8)	$\text{O7}—\text{B3}—\text{O5}$	109.93 (14)
$\text{N2}—\text{Zn1}—\text{N3}$	80.46 (8)	$\text{O6}—\text{B3}—\text{O5}$	107.71 (13)
$\text{N1}—\text{Zn1}—\text{N3}$	157.06 (8)	$\text{O4}—\text{B3}—\text{O5}$	109.51 (13)
$\text{O11}—\text{Zn1}—\text{O12A}$	52.7 (8)	$\text{O7}—\text{B4}—\text{O10}$	122.83 (18)
$\text{N4}—\text{Zn1}—\text{O12A}$	153.3 (8)	$\text{O7}—\text{B4}—\text{O9}$	121.46 (17)
$\text{N2}—\text{Zn1}—\text{O12A}$	80.7 (8)	$\text{O10}—\text{B4}—\text{O9}$	115.72 (16)
$\text{N1}—\text{Zn1}—\text{O12A}$	100.2 (10)	$\text{O8}—\text{B5}—\text{O6}$	122.21 (18)
$\text{N3}—\text{Zn1}—\text{O12A}$	89.7 (10)	$\text{O8}—\text{B5}—\text{O9}$	117.05 (16)
$\text{O4}—\text{B1}—\text{O1}$	123.64 (16)	$\text{O6}—\text{B5}—\text{O9}$	120.74 (18)
$\text{O4}—\text{B1}—\text{O2}$	121.14 (15)		

Table 2

Hydrogen-bond geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$\text{O1}—\text{H1A}\cdots\text{O4}^{\text{i}}$	0.84	1.87	2.703 (2)	174
$\text{O3}—\text{H3A}\cdots\text{O5}^{\text{ii}}$	0.84	1.85	2.692 (3)	171
$\text{O8}—\text{H8A}\cdots\text{O6}^{\text{iii}}$	0.84	1.94	2.751 (2)	162
$\text{N1}—\text{H1F}\cdots\text{O3}^{\text{iv}}$	0.92	2.21	3.112 (3)	165
$\text{N2}—\text{H2A}\cdots\text{O7}$	0.93	2.30	3.125 (3)	148
$\text{N3}—\text{H3D}\cdots\text{O10}^{\text{v}}$	0.93	2.34	3.116 (3)	141
$\text{N4}—\text{H4A}\cdots\text{O2}^{\text{iv}}$	0.92	2.16	3.054 (3)	164
$\text{N4}—\text{H4D}\cdots\text{O11}^{\text{vi}}$	0.92	2.02	2.939 (4)	173
$\text{O10}—\text{H10A}\cdots\text{O12A}$	0.84	1.98	2.799 (2)	164
$\text{O10}—\text{H10A}\cdots\text{O12B}$	0.84	1.88	2.682 (2)	159
$\text{O10}—\text{H10A}\cdots\text{O12C}$	0.84	1.80	2.565 (2)	149

Symmetry codes: (i) $-x, -y+1, -z$; (ii) $-x+1, -y, -z$; (iii) $-x, -y, -z$; (iv) $-x+1, -y+1, -z$; (v) $-x+1, -y, -z+1$; (vi) $-x+1, -y+1, -z+1$.

All H atoms were placed at calculated positions and were included in the refinement in the riding-model approximation, with hydroxyl $\text{O}—\text{H}$ distances of 0.84 Å, imine $\text{N}—\text{H}$ distances of 0.93 Å, amine $\text{N}—\text{H}$ distances of 0.92 Å, methylene $\text{C}—\text{H}$ distances of 0.99 Å and methyl $\text{C}—\text{H}$ distances of 0.98 Å, and with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$, $1.2U_{\text{eq}}(\text{N})$, $1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{methyl C})$.

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MS, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP11* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FN3025). Services for accessing these data are described at the back of the journal.

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