

## Two new transition metal inorganic–organic hybrid borates: [tris(2-aminoethoxy)trihydroxyhexaborato]-cobalt(II) and its nickel(II) analogue

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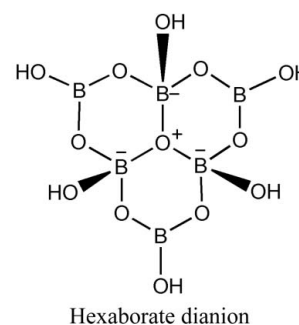
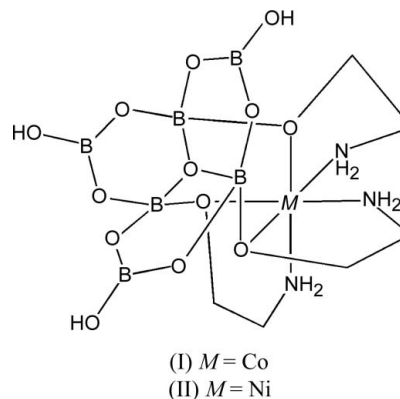
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The two isomorphous title compounds, [1,5,9-tris(2-aminoethoxy)-3,7,11-trihydroxy-3,7,11-tribora-1,5,9-triborata-2,4,6,8,10,12-hexaoxa-13-oxoniatricyclo[7.3.1.0<sup>5,13</sup>]tridecane]cobalt(II), [Co(C<sub>6</sub>H<sub>21</sub>B<sub>6</sub>N<sub>3</sub>O<sub>13</sub>)] or Co{B<sub>6</sub>O<sub>7</sub>(OH)<sub>3</sub>[O(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>3</sub>}, and the Ni<sup>II</sup> analogue, [Ni(C<sub>6</sub>H<sub>21</sub>B<sub>6</sub>N<sub>3</sub>O<sub>13</sub>)], each consist of an M<sup>II</sup> cation and an inorganic–organic hybrid {B<sub>6</sub>O<sub>7</sub>(OH)<sub>3</sub>[O(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>3</sub>}<sup>2-</sup> anion. The M<sup>II</sup> cation lies on a crystallographic threefold axis (as does one O atom) and is octahedrally coordinated by three N atoms from the organic component. Three O atoms covalently link the B–O cluster and the organic component. Molecules are connected to one another through N–H···O and O–H···O hydrogen bonds, forming a three-dimensional supramolecular network.

### Comment

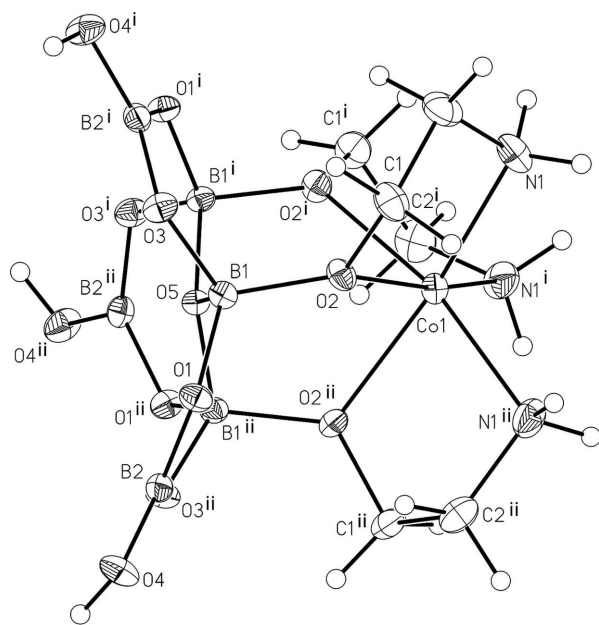
In recent decades, borate materials have been extensively studied because of their rich structural chemistry and potential applications, especially in mineralogy, nonlinear optics and photoluminescence (Christ & Clark, 1977; Heller, 1986; Becker, 1998; Burns, 1995; Grice *et al.*, 1999; Chen *et al.*, 1995; Sasaki *et al.*, 2000; Lin *et al.*, 2007). The synthesis of new inorganic–organic hybrid compounds is a relatively new research area, which has been growing rapidly in recent years. In the search for useful inorganic–organic borate materials, the synthesis and structure of the metallo-organically templated borates have been investigated: examples include [Cu(en)<sub>2</sub>][B<sub>7</sub>O<sub>13</sub>H<sub>3</sub>]<sub>n</sub> (en is ethylenediamine; Sung *et al.*, 2000), [Mn(C<sub>10</sub>H<sub>18</sub>N<sub>6</sub>)][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub> (Zhang *et al.*, 2004), [Ni(C<sub>4</sub>H<sub>10</sub>N<sub>2</sub>)(C<sub>2</sub>H<sub>8</sub>N<sub>2</sub>)<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub> (Liu *et al.*, 2006), [Zn(dien)<sub>2</sub>][B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>]<sub>2</sub> and [B<sub>5</sub>O<sub>7</sub>(OH)<sub>3</sub>Zn(tren)] [dien is diethylenetriamine and tren is tris(2-aminoethyl)amine; Wang *et al.*, 2005], [Ag(py)<sub>2</sub>]<sub>2</sub>[B<sub>10</sub>O<sub>14</sub>(OH)<sub>4</sub>] (py is pyridine; Wang *et al.*, 2008), [Zn(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)(C<sub>6</sub>H<sub>18</sub>N<sub>4</sub>)] [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>] (Wu *et al.*, 2009)

and [Cd(TETA)(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)] [B<sub>5</sub>O<sub>6</sub>(OH)<sub>4</sub>] (TETA is triethylenetetramine; Yang *et al.*, 2011). These compounds usually contain isolated or layered boron polyanion hosts and interstitial transition metal complex cations. We describe herein the synthesis and crystal structures of two novel inorganic–organic hybrid borates, M{B<sub>6</sub>O<sub>7</sub>(OH)<sub>3</sub>[O(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>3</sub>} [M = Co<sup>II</sup>, (I), and Ni<sup>II</sup>, (II)].

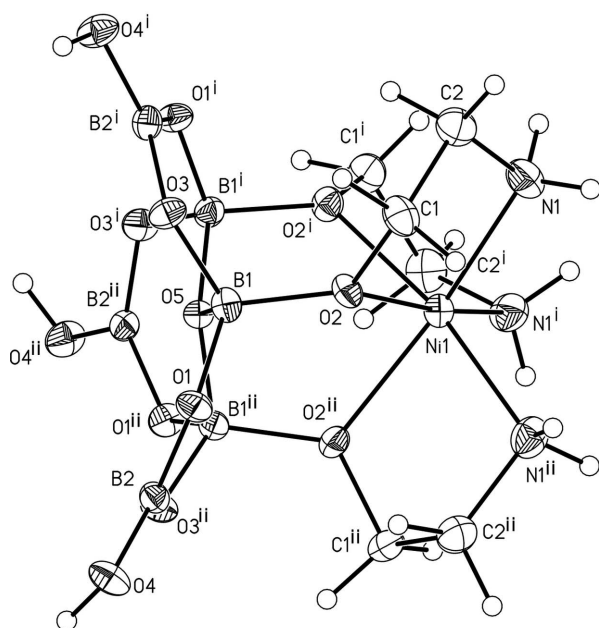


Compounds (I) and (II) (see Scheme) were obtained under mild solvothermal conditions. Both compounds crystallize in the cubic system (space group *Pa* $\bar{3}$ ) and they are isomorphous (Figs. 1*a* and 1*b*). Each compound consists of an inorganic–organic hybrid {B<sub>6</sub>O<sub>7</sub>(OH)<sub>3</sub>[O(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>3</sub>}<sup>2-</sup> anion and an M<sup>II</sup> cation residing on a crystallographic threefold axis. The M<sup>II</sup> cation is octahedrally coordinated by three N atoms from the organic component, and three O atoms covalently linking the B–O cluster and organic component (Figs. 1*a* and 1*b*). The three M–N bond lengths [2.1330 (14) Å for (I) and 2.081 (3) Å for (II)] are equivalent by symmetry. The N–M–N angles are 100.13 (5)° for (I) and 98.72 (12)° for (II). The three M–O bond lengths are equivalent by symmetry [2.1359 (12) Å for (I) and 2.102 (3) Å for (II)]. These structural differences between (I) and (II) may be attributed to the different ionic radii of the Co<sup>II</sup> and Ni<sup>II</sup> cations (0.72 and 0.69 Å, respectively; Purnell *et al.*, 1991).

The hexaborate anion (see Scheme), [B<sub>6</sub>O<sub>7</sub>(OH)<sub>6</sub>]<sup>2-</sup>, found in aksaite, mcallisterite and rivadavite (Hanic *et al.*, 1971; Dal Negro *et al.*, 1969, 1971; Dal Negro & Ungaretti, 1973), is a common fundamental building block in borates. The {B<sub>6</sub>O<sub>7</sub>(OH)<sub>3</sub>[O(CH<sub>2</sub>)<sub>2</sub>NH<sub>2</sub>]<sub>3</sub>}<sup>2-</sup> anion in (I) can be regarded as resulting from the dehydration reaction of three 2-aminoethanol molecules with the three hydroxy groups attached to the four-coordinate B atoms in [B<sub>6</sub>O<sub>7</sub>(OH)<sub>6</sub>]<sup>2-</sup>, to form an



(a)

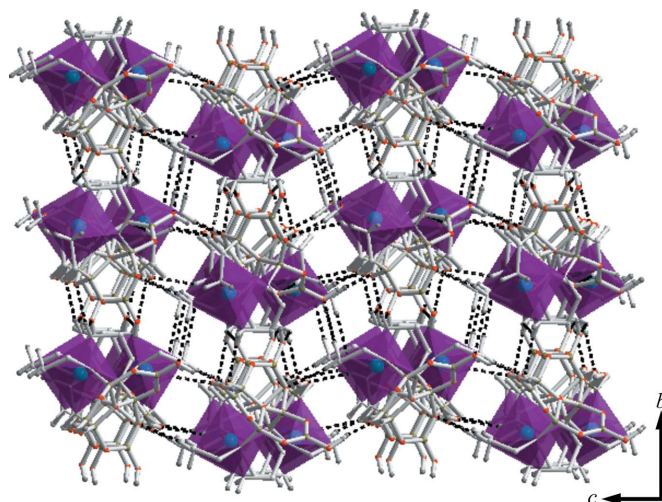


(b)

**Figure 1**

The molecular structures of (a) (I) and (b) (II), showing the atom-labelling schemes. Displacement ellipsoids are drawn at the 45% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i)  $y, z, x$ ; (ii)  $z, x, y$ .]

isolated cage-like structure. The B–O cluster moiety in  $\{B_6O_7(OH)_3[O(CH_2)_2NH_2]_3\}^{2-}$  is composed of three trigonal  $BO_3$  units and three  $BO_4$  tetrahedra linked to each other. This B–O cluster is characterized by three  $[B_3O_3]$  rings linked by three shared  $BO_4$  tetrahedra and a central common O atom (O5) which lies on a crystallographic threefold axis. Each ring is produced by two shared  $BO_4$  tetrahedra and one trigonal  $BO_3$  unit. The trigonally coordinated B atoms have B–O distances in the range 1.356 (2)–1.379 (2) Å, similar to those observed in the hexaborate anion  $[B_6O_7(OH)_6]^{2-}$  [B–O =

**Figure 2**

A view of the packing structure of (I) down the  $a$  axis. Dashed lines indicate hydrogen bonds.

1.343 (6)–1.398 (1) Å; Genkina *et al.*, 1976; Dal Negro *et al.*, 1971]. The tetrahedral B atoms have longer B–O distances [1.435 (5)–1.518 (4) Å], lengths that are also comparable with those reported for  $[B_6O_7(OH)_6]^{2-}$  [B–O = 1.445 (5)–1.517 (2) Å; Genkina *et al.*, 1976; Dal Negro *et al.*, 1971]. The O–B–O angles of the trigonal  $BO_3$  units are in the range 115.81 (14)–122.45 (14)° and those of the  $BO_4$  tetrahedra are in the range 105.3 (3)–113.0 (3)° (see Tables 1 and 3). The esterification of  $[B_6O_7(OH)_6]^{2-}$  with 2-aminoethanol shows no substantial influence on the structure of the B–O cluster moiety. It is interesting to compare compound (I) with a 2-aminoethanol borate, *i.e.*  $[HOCH_2CH_2NH_3][B_5O_6(OH)_4] \cdot H_2O$ , obtained from a 2-aminoethanol–boric acid solution containing a significant excess of boric acid (Schubert *et al.*, 2008). In this example, 2-aminoethanol is protonated. However, under the present reaction conditions with a large excess of 2-aminoethanol, the free base 2-aminoethanol can react with the B–O cluster anion to form a borate ester analogue.

Molecules are connected *via* N–H···O and O–H···O hydrogen bonds in both (I) and (II) (Fig. 2), forming three-dimensional supramolecular networks. Hydrogen-bonding parameters for (I) and (II) are listed in Tables 2 and 4, respectively.

## Experimental

Compounds (I) and (II) were prepared under mild solvothermal conditions. For the synthesis of (I), typically  $Co(CH_3COO)_2 \cdot 4H_2O$  (1 mmol, 248 mg),  $H_3BO_3$  (6 mmol, 368 mg) and  $H_2O$  (0.6 ml) were placed in a Teflon-lined autoclave and stirred at room temperature, then 2-aminoethanol (3 ml) was added and thorough mixing was carried out. The mixture was heated at 453 K for 3 d, and then cooled to room temperature at a rate of 5 K  $h^{-1}$ . Pale-pink crystals of (I) were obtained. For the synthesis of (II), the same procedure was used, but using  $Ni(CH_3COO)_2 \cdot 4H_2O$  (1 mmol, 248 mg) in place of  $Co(CH_3COO)_2 \cdot 4H_2O$ , to yield blue block-shaped crystals of (II).

Compound (I)

Crystal data

[Co(C<sub>6</sub>H<sub>21</sub>B<sub>6</sub>N<sub>3</sub>O<sub>13</sub>)]  
*M<sub>r</sub>* = 467.05  
 Cubic, *Pa* $\bar{3}$   
*a* = 15.2796 (18) Å  
*V* = 3567.3 (7) Å<sup>3</sup>  
*Z* = 8  
 Mo *K*α radiation  
 μ = 1.04 mm<sup>-1</sup>  
*T* = 293 K  
 0.34 × 0.32 × 0.27 mm

Data collection

Rigaku R-AXIS RAPID diffractometer  
 Absorption correction: empirical (using intensity measurements) (*ABSCOR*; Higashi, 1995)  
*T<sub>min</sub>* = 0.710, *T<sub>max</sub>* = 0.756  
 25748 measured reflections  
 1057 independent reflections  
 1025 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.022

Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.023  
*wR*(*F*<sup>2</sup>) = 0.065  
*S* = 1.11  
 1057 reflections  
 91 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 Δρ<sub>max</sub> = 0.64 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.20 e Å<sup>-3</sup>

Compound (II)

Crystal data

[Ni(C<sub>6</sub>H<sub>21</sub>B<sub>6</sub>N<sub>3</sub>O<sub>13</sub>)]  
*M<sub>r</sub>* = 466.83  
 Cubic, *Pa* $\bar{3}$   
*a* = 15.2217 (18) Å  
*V* = 3526.9 (7) Å<sup>3</sup>  
*Z* = 8  
 Mo *K*α radiation  
 μ = 1.17 mm<sup>-1</sup>  
*T* = 293 K  
 0.14 × 0.14 × 0.14 mm

Data collection

Rigaku R-AXIS RAPID diffractometer  
 Absorption correction: empirical (using intensity measurements) (*ABSCOR*; Higashi, 1995)  
*T<sub>min</sub>* = 0.849, *T<sub>max</sub>* = 0.849  
 25821 measured reflections  
 1042 independent reflections  
 885 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.075

Table 1

Selected geometric parameters (Å, °) for (I).

O1—B1	1.4525 (18)	O3—B2 <sup>i</sup>	1.356 (2)
O1—B2	1.379 (2)	O4—B2	1.370 (2)
O2—B1	1.4790 (19)	O5—B1	1.5179 (15)
O3—B1	1.4403 (18)		
N1—Co1—O2	80.20 (5)	O3—B1—O1	110.66 (12)
N1 <sup>ii</sup> —Co1—O2	91.95 (5)	O3—B1—O2	112.68 (12)
N1 <sup>ii</sup> —Co1—O2 <sup>i</sup>	167.63 (5)	O3—B1—O5	108.44 (11)
O2 <sup>ii</sup> —Co1—O2	87.43 (4)	O3 <sup>ii</sup> —B2—O1	122.45 (14)
O1—B1—O2	110.78 (12)	O3 <sup>ii</sup> —B2—O4	121.74 (14)
O1—B1—O5	108.72 (11)	O4—B2—O1	115.81 (14)
O2—B1—O5	105.33 (12)		

Symmetry codes: (i) *z*, *x*, *y*; (ii) *y*, *z*, *x*.

Table 2

Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H4...O1 <sup>iii</sup>	0.76 (2)	2.07 (2)	2.7982 (15)	162 (2)
N1—H1B...O1 <sup>iv</sup>	0.90	2.33	3.1869 (17)	159
N1—H1A...O4 <sup>v</sup>	0.90	2.30	3.1559 (19)	160

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

Table 3

Selected geometric parameters (Å, °) for (II).

O1—B1	1.453 (4)	O3—B2 <sup>i</sup>	1.361 (5)
O1—B2	1.377 (5)	O4—B2	1.369 (5)
O2—B1	1.479 (4)	O5—B1	1.518 (4)
O3—B1	1.435 (5)		
N1 <sup>ii</sup> —Ni1—O2	91.09 (11)	O3—B1—O1	110.7 (3)
N1 <sup>i</sup> —Ni1—O2 <sup>i</sup>	81.68 (11)	O3—B1—O2	113.0 (3)
N1 <sup>ii</sup> —Ni1—O2 <sup>i</sup>	169.98 (12)	O3—B1—O5	108.6 (3)
O2 <sup>ii</sup> —Ni1—O2	88.30 (9)	O3 <sup>ii</sup> —B2—O1	122.3 (3)
O1—B1—O2	110.5 (3)	O3 <sup>ii</sup> —B2—O4	121.6 (3)
O1—B1—O5	108.5 (3)	O4—B2—O1	116.1 (3)
O2—B1—O5	105.3 (3)		

Symmetry codes: (i) *z*, *x*, *y*; (ii) *y*, *z*, *x*.

Table 4

Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H4...O1 <sup>iii</sup>	0.79 (5)	2.03 (5)	2.790 (3)	161 (5)
N1—H1B...O1 <sup>iv</sup>	0.90	2.33	3.175 (4)	156
N1—H1A...O4 <sup>v</sup>	0.90	2.31	3.151 (4)	156

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

Refinement

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.044  
*wR*(*F*<sup>2</sup>) = 0.107  
*S* = 1.14  
 1042 reflections  
 91 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 Δρ<sub>max</sub> = 0.38 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.50 e Å<sup>-3</sup>

All C- and N-bound H atoms were positioned geometrically and refined using a riding model, with C—H = 0.97 Å and N—H = 0.90 Å, and with *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(C or N). H atoms attached to O atoms were located in a difference Fourier map and refined using a riding model, with O—H = 0.82 Å and *U<sub>iso</sub>*(H) = 1.2*U<sub>eq</sub>*(O).

For both compounds, data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *Crystal-Structure* (Rigaku/MS, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: BM3109). Services for accessing these data are described at the back of the journal.

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