

Syntheses and crystal structures of three new borates templated by transition-metal complexes in situ

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Abstract

Three new cobalt borate compounds, $[\text{Co}(\text{DIEN})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$ (DIEN = diethylenetriamine) (**1**), $[\text{B}_5\text{O}_7(\text{OH})_3\text{Co}(\text{TREN})]$ (TREN = *tris*(2-aminoethyl)amine) (**2**), and $[\text{Co}_2(\text{TETA})_3][\text{B}_5\text{O}_6(\text{OH})_4]_4$ (TETA = triethylenetetramine) (**3**) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction, IR, elemental analysis and thermogravimetry. The structures exhibit interesting 3D supramolecular hydrogen-bonded architectures, involving the similar borate polyanion $[\text{B}_5\text{O}_{6+n}(\text{OH})_{4-n}]^{(n+1)-}$ ($n = 0$ for **1** and **3**, and $n = 1$ for **2**) and the templating transition metal complexes which are generated in situ under mild solvothermal conditions. Crystal data: **1**, monoclinic, space group $C2/m$ (No. 12), $a = 15.2372(3) \text{ \AA}$, $b = 11.5987(2) \text{ \AA}$, $c = 8.4163(3) \text{ \AA}$, $\beta = 93.601(4)^\circ$, $V = 1484.49(7) \text{ \AA}^3$, $Z = 2$; **2**, monoclinic, $P2_1/c$ (No. 14), $a = 8.9881(3) \text{ \AA}$, $b = 20.7648(5) \text{ \AA}$, $c = 9.3681(2) \text{ \AA}$, $\beta = 99.926(4)^\circ$, $V = 1722.25(8) \text{ \AA}^3$, $Z = 4$; **3**, triclinic, space group $P-1$ (No. 2), $a = 12.3717(4) \text{ \AA}$, $b = 12.9653(8) \text{ \AA}$, $c = 19.0925(3) \text{ \AA}$, $\alpha = 77.009(5)^\circ$, $\beta = 80.095(2)^\circ$, $\gamma = 82.334(3)^\circ$, $V = 2925.3(2) \text{ \AA}^3$, $Z = 2$.

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1. Introduction

Borate materials have been a research field with rapid expansion in the past decades, mainly because of their rich structural chemistry and potential applications in mineralogy and industry [1–5]. From the structural point of view, boron atoms coordinate with oxygen not only in four-fold coordination (tetrahedral, BO_4) but also in three-fold coordination (triangular, BO_3). These BO_3 and BO_4 groups can further polymerize to form polynuclear anions, including isolated rings (or cages), infinite chains, sheets and frameworks [4,6–12]. Burns et al. [2,4] have developed a comprehensive description based on fundamental building blocks (*FBBs*) to have a clearer nomenclature for the borates with more complicated borate anions.

So far, many borate materials with alkali metal, alkaline earth metal, rare earth and transition metal have been widely studied. In contrast, less work has been carried out on metallo-organically templated borates [13–16]. Different from borate materials traditionally prepared under high-temperature/pressure solid-state conditions, hydrothermal approach has been recently proved to be very effective in the construction of novel borate compounds [14–20]. And our aim is to synthesize such materials with various templates such as inorganic species, organic agents or transition metal complexes by the hydrothermal technique. Our success in assembling the various borate *FBBs* with different transition metal complexes templates in $[\text{Mn}(\text{C}_{10}\text{H}_{28}\text{N}_6)][\text{B}_5\text{O}_6(\text{OH})_4]_2$ [14], $[\text{Zn}(\text{DIEN})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$ and $[\text{B}_5\text{O}_7(\text{OH})_3\text{Zn}(\text{TREN})]$ [16], led us to attempt the incorporation of other *d*-block elements, either as inherent cluster components or as extrinsic moieties of the borate cluster. Fortunately, this expectation has been realized in the preparation of three new cobalt borates, $[\text{Co}(\text{DIEN})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$ (**1**), $[\text{B}_5\text{O}_7(\text{OH})_3\text{Co}(\text{TREN})]$ (**2**), and $[\text{Co}_2(\text{TETA})_3][\text{B}_5\text{O}_6(\text{OH})_4]_4$ (**3**).

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2. Experimental section

2.1. Synthesis

Single crystals of the title compounds were obtained from a mixture of $\text{Co}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$, H_3BO_3 , organic amine (DIEN for **1**, TETA for **2** and **3**), pyridine and H_2O in the molar ratio of 1:3:2:40:30, 1:4:2:32:24 and 1:4:12:20:24, respectively. The final mixture was stirred for several hours at room temperature and then crystallized in a Teflon-lined autoclave at 160 °C for 7 days. The single crystals were obtained by filtration and dried in air (64% yield based on boron for **1**, 44% for **2** and 26% for **3**).

C, H, N-elemental analysis was carried out using the combustion method. Anal. found for **1**: C, 13.58; H, 4.80; N, 11.88. Calcd: C, 13.70; H, 4.89; N, 11.98. Anal. found for **2**: C, 17.01; H, 4.93; N, 13.21. Calcd: C, 17.07; H, 5.01; N, 13.27. Anal. Found for **3**: C, 15.04; H, 4.88; N, 11.71. Calcd: C, 15.13; H, 4.94; N, 11.77. The calculated values are based on the formula given above.

2.2. Characterization

Infrared (IR) spectra were obtained from sample powder pelletized with KBr on an ABB Bomen MB 102 series FTIR spectrophotometer over a range of 400–4000 cm^{-1} . The thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/SDTA 851e analyzer in N_2 atmosphere with a heating rate of 10 °C/min. The elemental analysis was carried out on an Elemental Vario EL III CHNOS elemental analyzer.

2.3. Determination of crystal structure

Crystals of **1** (red, prism, dimensions $0.56 \times 0.23 \times 0.12 \text{ mm}^3$), **2** (dark green, prism, dimensions $0.48 \times 0.22 \times 0.10 \text{ mm}^3$) and **3** (red, prism, dimensions $0.58 \times 0.35 \times 0.16 \text{ mm}^3$) were carefully selected under an optical microscope and glued to thin glass fiber with epoxy resin. Single-crystal X-ray diffraction data were collected on a Siemens SMART CCD diffractometer with graphite-monochromated $\text{Mo } K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) in the ω scanning mode at room temperature. An empirical absorption correction was applied using the SADABS program [21]. The structures were all solved by direct method using the SHELXS-97 program package [22]. The cobalt atom was first located, and the boron, oxygen, carbon and nitrogen atoms were found in the successive difference-Fourier synthesis. In compound **1**, the O(2), O(7) and O(8) atoms are located on special positions and disordered over two positions with an equal site-occupation factor (SOF) of 0.25, and the N(1) atom is disordered over two positions with SOF of 0.8 and 0.2, respectively. In **2**, the C(1), C(2), C(3), and C(4) atoms are disordered over two positions with SOF of 0.8 and 0.2 (for C(1), C(3) atoms), and 0.6 and 0.4 (for C(2), C(4) atoms), respectively. In **3**, the Co atoms are both split into two positions with the occupancies of 60% and 40%, respectively. Similarly, the SOF values of 0.7 and 0.3 are assigned to the disordered atoms of the N(3), N(5), N(7), N(9) and N(12) atoms. The hydrogen atoms were positioned at idealized geometry and refined using a riding model. The structures were refined on F^2 by a full-matrix least-squares method using the SHELXL-97 program

Table 1
Crystal data and structure refinement for **1–3**

Compounds	1	2	3
Empirical formula	$\text{C}_8\text{H}_{34}\text{N}_6\text{B}_{10}\text{O}_{26}\text{Co}$	$\text{C}_6\text{H}_{21}\text{N}_4\text{B}_5\text{O}_{10}\text{Co}$	$\text{C}_{18}\text{H}_{70}\text{N}_{12}\text{B}_{20}\text{O}_{40}\text{Co}_2$
Formula weight	701.44	422.25	1428.92
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$C2/m$	$P2_1/c$	$P-1$
$a/\text{\AA}$	15.2372(3)	8.9881(3)	12.3717(4)
$b/\text{\AA}$	11.5987(2)	20.7648(5)	12.9653(8)
$c/\text{\AA}$	8.4163(3)	9.3681(2)	19.0925(3)
$\alpha/^\circ$	90	90	77.009(5)
$\beta/^\circ$	93.601(4)	99.926(4)	80.095(2)
$\gamma/^\circ$	90	90	82.334(3)
$V/\text{\AA}^3$	1484.49(7)	1722.25(8)	2925.3(2)
Z	2	4	2
$D_c/\text{g cm}^{-3}$	1.569	1.628	1.622
$\mu(\text{Mo } K\alpha)/\text{mm}^{-1}$	0.668	1.052	0.679
Reflection collected	2249	4814	15 568
Independent reflections	1178	2787	8875
Data/restraints/parameters	1178/3/152	2787/5/266	8875/0/901
θ range/ $^\circ$	2.68–25.00	2.30–25.00	3.24–25.00
Limiting indices	$-18 \leq h \leq 13$, $-13 \leq k \leq 13$, $-9 \leq l \leq 9$	$-10 \leq h \leq 9$, $-15 \leq k \leq 24$, $7 \leq l \leq 11$	$-14 \leq h \leq 14$, $-12 \leq k \leq 15$, $-21 \leq l \leq 22$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0573P)^2 + 11.7689P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0086P)^2 + 12.9063P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.1206P)^2 + 4.8498P]$, where $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	1.071	1.034	1.011
Final R_1 , wR_2 [$I > 2\sigma(I)$]	0.0911, 0.1801	0.0892, 0.1557	0.0715, 0.1945
Largest diff. peak and hole ($\text{e}\text{\AA}^{-3}$)	0.527 and -0.4447	0.714 and -0.524	0.829 and -0.612

package [22]. All the non-hydrogen atoms were refined anisotropically. Crystallographic data for **1–3** are presented in Table 1. The final atomic coordinates, the selected bond distances and angles are listed in Tables 2 and 3, respectively. The details of H-bonds are given in Table 4. CCDC 287020–287022 contain the supplementary crystallographic data for this paper.

Table 2
Final atomic coordinates ($\times 10^4$) and equivalent thermal isotropic displacement U_{eq} ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses of **1–3**

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
[Co(DIEN)₂][B₅O₆(OH)₄]₂				
Co	0	0	0	97(1)
B(1)	4600(7)	0	7226(13)	68(4)
B(2)	3447(7)	0	8872(15)	63(4)
B(3)	2126(4)	1034(6)	3968(8)	40(2)
B(4)	3088(6)	0	6024(12)	37(2)
O(1)	1771(3)	1979(4)	3278(6)	67(2)
O(2)	4336(9)	0	8690(16)	29(5)
O(2')	4279(13)	616(15)	8640(20)	33(7)
O(3)	2848(3)	0	7659(7)	44(2)
O(4)	1825(4)	0	3303(7)	49(2)
O(5)	2730(2)	1040(3)	5200(5)	42(1)
O(6)	4039(4)	0	5926(7)	43(2)
O(7)	5550(20)	0	7040(40)	78(2)
O(7')	5410(30)	0	7210(50)	50(2)
O(8)	3160(30)	0	10 600(60)	79(2)
O(8')	3120(20)	280(50)	10 210(50)	40(2)
N(1)	1139(10)	1200(13)	−130(20)	136(6)
N(1')	640(20)	1560(40)	210(30)	140(2)
N(2)	103(10)	0	−2390(20)	223(2)
C(1)	984(8)	1991(16)	−1388(16)	156(6)
C(2)	583(15)	1180(20)	−2790(20)	226(2)
[B₅O₇(OH)₃Co(TREN)]				
Co	1313(1)	5914(1)	6032(1)	56(1)
B(1)	−486(10)	6107(4)	3209(10)	49(2)
B(2)	−1518(11)	6873(5)	1382(12)	62(3)
B(3)	−3208(10)	6477(4)	3022(11)	51(2)
B(4)	−4815(11)	6903(5)	4721(12)	65(3)
B(5)	−5788(9)	6076(5)	3075(10)	50(2)
O(1)	690(5)	5792(3)	3882(5)	49(1)
O(2)	−376(6)	6480(3)	2001(7)	71(2)
O(3)	−1259(6)	7270(4)	298(8)	80(2)
O(4)	−1895(5)	6084(3)	3625(6)	60(2)
O(5)	−2844(6)	6882(3)	1849(6)	59(2)
O(6)	−4484(5)	6074(3)	2514(6)	57(1)
O(7)	−3513(6)	6924(3)	4203(6)	59(2)
O(8)	−5067(7)	7274(3)	5887(8)	91(2)
O(9)	−5939(6)	6469(3)	4237(6)	66(2)
O(10)	−6924(6)	5664(3)	2558(7)	66(2)
C(1)	1600(20)	7111(7)	7831(17)	94(5)
C(1')	2620(60)	7040(20)	7740(40)	110(30)
C(2)	2150(40)	6613(13)	8930(40)	99(12)
C(2')	2760(50)	6661(13)	8780(50)	90(16)
C(3)	−844(15)	5816(7)	8190(12)	76(3)
C(3')	−170(70)	5330(30)	8130(60)	110(20)
C(4)	870(40)	5914(15)	9140(30)	75(9)
C(4')	690(20)	5619(9)	9099(19)	80(7)
C(5)	4337(11)	5549(5)	7628(11)	79(3)
C(6)	3403(12)	5552(6)	8882(11)	96(4)
N(1)	1634(8)	6917(3)	6300(9)	69(2)
N(2)	−703(8)	5625(4)	6672(8)	71(2)

Table 2 (continued)

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
N(3)	3245(8)	5331(4)	6286(8)	72(2)
N(4)	2021(8)	5963(4)	8412(8)	64(2)
[Co₂(TETA)₃][B₅O₆(OH)₄]₄				
Co(1)	2601(1)	7295(1)	4916(1)	14(1)
Co(1')	2474(2)	7660(2)	5019(1)	22(1)
Co(2)	2575(1)	7268(1)	−57(1)	13(1)
Co(2')	2440(2)	7631(2)	52(1)	22(1)
B(1)	9987(3)	−1131(3)	3415(2)	18(1)
B(2)	8939(3)	−2068(4)	4473(2)	19(1)
B(3)	7950(3)	−1034(3)	3462(2)	16(1)
B(4)	6458(4)	372(4)	3171(2)	22(1)
B(5)	6748(3)	−1075(4)	2549(2)	20(1)
B(6)	10 022(3)	1010(3)	1559(2)	17(1)
B(7)	11 024(3)	2159(3)	576(2)	15(1)
B(8)	12 048(3)	1024(3)	1551(2)	16(1)
B(9)	13 520(4)	1291(4)	2204(3)	24(1)
B(10)	13 804(4)	−123(3)	1570(2)	18(1)
B(11)	11 207(4)	5135(4)	3424(2)	21(1)
B(12)	11 466(3)	3659(3)	2833(2)	19(1)
B(13)	12 954(3)	3972(3)	3458(2)	16(1)
B(14)	13 993(3)	2837(3)	4425(2)	14(1)
B(15)	14 984(3)	3935(3)	3428(2)	19(1)
B(16)	5000(3)	6155(3)	1601(2)	13(1)
B(17)	6071(4)	7071(3)	529(2)	20(1)
B(18)	7068(3)	6034(3)	1531(2)	15(1)
B(19)	8318(4)	6076(4)	2406(3)	23(1)
B(20)	8549(3)	4601(3)	1833(2)	18(1)
O(1)	11 024(2)	−872(2)	3084(2)	27(1)
O(2)	9944(2)	−1759(2)	4104(1)	18(1)
O(3)	8958(2)	−2658(2)	5157(2)	26(1)
O(4)	9076(2)	−778(2)	3104(1)	18(1)
O(5)	8002(2)	−1780(2)	4167(1)	18(1)
O(6)	7502(2)	−1576(2)	2981(1)	16(1)
O(7)	7271(2)	−73(2)	3573(1)	20(1)
O(8)	5836(2)	1255(2)	3323(2)	33(1)
O(9)	6267(2)	−55(2)	2610(2)	27(1)
O(10)	6410(3)	−1514(2)	2058(2)	35(1)
O(11)	9052(2)	618(2)	1838(1)	22(1)
O(12)	10 053(2)	1749(2)	909(1)	19(1)
O(13)	10 969(2)	2888(2)	−58(1)	23(1)
O(14)	10 963(2)	682(2)	1874(1)	18(1)
O(15)	11 975(2)	1836(2)	866(1)	17(1)
O(16)	12 466(2)	1524(2)	2057(1)	16(1)
O(17)	12 786(2)	101(2)	1390(1)	18(1)
O(18)	13 940(3)	1831(3)	2618(2)	42(1)
O(19)	14 210(2)	507(2)	1939(2)	29(1)
O(20)	14 452(3)	−990(2)	1394(2)	33(1)
O(21)	10 611(2)	6040(2)	3561(2)	32(1)
O(22)	10 775(2)	4466(2)	3095(2)	27(1)
O(23)	11 018(2)	3105(3)	2444(2)	35(1)
O(24)	12 514(2)	3450(2)	2967(1)	17(1)
O(25)	12 250(2)	4916(2)	3599(1)	17(1)
O(26)	13 025(2)	3185(2)	4149(1)	18(1)
O(27)	14 054(2)	4277(2)	3117(1)	19(1)
O(28)	14 024(2)	2134(2)	5080(2)	23(1)
O(29)	14 962(2)	3209(2)	4075(1)	19(1)
O(30)	15 974(2)	4317(2)	3142(2)	24(1)
O(31)	3991(2)	5882(2)	1930(1)	21(1)
O(32)	5048(2)	6800(2)	918(1)	16(1)
O(33)	6031(2)	7656(2)	−151(1)	21(1)
O(34)	5937(2)	5789(2)	1908(1)	15(1)
O(35)	7004(2)	6733(2)	814(1)	17(1)
O(36)	7731(2)	5041(2)	1432(1)	16(1)
O(37)	7536(2)	6573(2)	1993(1)	15(1)

Table 2 (continued)

Atoms	x	y	z	U_{eq}^a
O(38)	8680(3)	6553(3)	2883(2)	40(1)
O(39)	8795(2)	5074(2)	2355(2)	28(1)
O(40)	9119(2)	3670(2)	1723(2)	33(1)
C(1)	1310(4)	7854(6)	6320(4)	68(2)
C(2)	1033(7)	8879(7)	5801(6)	127(5)
C(3)	2106(7)	9677(5)	4500(5)	79(2)
C(4)	3349(6)	9549(6)	4540(6)	83(3)
C(5)	3956(10)	8673(11)	3630(4)	134(6)
C(6)	3758(6)	7537(6)	3430(4)	69(2)
C(7)	1724(6)	5318(4)	5563(4)	61(2)
C(8)	2839(5)	4973(5)	5289(4)	62(2)
C(9)	4658(6)	5467(5)	4828(4)	59(2)
C(10)	1552(6)	5367(6)	646(4)	69(2)
C(11)	1384(12)	5917(11)	1292(4)	152(7)
C(12)	1642(11)	7682(6)	1370(4)	129(5)
C(13)	711(6)	8285(8)	892(4)	86(3)
C(14)	1888(7)	9749(8)	-49(6)	116(5)
C(15)	3052(7)	9610(5)	-419(4)	73(2)
C(16)	3803(5)	7379(5)	-1496(3)	50(1)
C(17)	4246(5)	6358(5)	-1111(4)	60(2)
C(18)	4415(5)	5230(5)	57(4)	63(2)
N(1)	2434(3)	7426(3)	6107(2)	31(1)
N(2)	1397(7)	8776(4)	5007(5)	127(4)
N(3)	3810(4)	8449(4)	4434(3)	33(1)
N(3')	3498(8)	8970(13)	5023(7)	32(3)
N(4)	2779(4)	7231(4)	3763(3)	29(1)
N(4')	2912(14)	8246(14)	3885(8)	51(4)
N(5)	3719(12)	6397(11)	4826(8)	33(3)
N(5')	3592(4)	5755(5)	5220(3)	28(1)
N(6)	1322(3)	6320(3)	5130(2)	29(1)
N(7)	1542(4)	5996(4)	-13(3)	36(1)
N(7')	1201(11)	6568(12)	569(7)	10(3)
N(8)	2129(5)	6762(5)	1112(3)	59(1)
N(9)	1299(4)	8582(6)	141(4)	36(2)
N(9')	1453(12)	9249(14)	-219(8)	37(3)
N(10)	3619(3)	8605(3)	-81(2)	33(1)
N(11)	2630(3)	7623(3)	-1178(2)	28(1)
N(12)	4139(4)	6293(4)	-341(3)	22(1)
N(12')	3527(14)	6219(15)	13(11)	60(6)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

3.1. Infrared spectra

The IR spectra of 1–3 showed typical peaks, with little differences between the spectra, as shown in Fig. 1. The strong bands at ~ 1414 and 1317 cm^{-1} in the spectra are characteristic of trigonally coordinated boron, while the bands at ~ 1160 , 1062 , 1020 and 920 cm^{-1} are characteristic of tetrahedral boron [23]. In addition, the stretching vibration of the O–H, and N–H, C–H bands are observed at ~ 3406 , 3221 , 2940 and 2892 cm^{-1} , respectively.

3.2. Crystal structures

3.2.1. Structure description of FBBs

As shown in Fig. 2, all these cobalt borates consist of the similar polyanion $[\text{B}_5\text{O}_6+n(\text{OH})_{4-n}]^{(n+1)-}$ ($n = 0$ for 1 and

Table 3

Selected bond length (\AA) and angles ($^\circ$) for 1–3

$[\text{Co}(\text{DIEN})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$			
Co–N(1)	2.231(14)	B(3)–O(1)	1.337(8)
Co–N(2)	2.03(3)	B(3)–O(4)	1.389(8)
B(1)–O(2)	1.32(2)	B(3)–O(5)	1.348(8)
B(1)–O(6)	1.352(12)	B(4)–O(3)	1.439(12)
B(1)–O(7)	1.37(7)	B(4)–O(5)	1.478(7)
B(2)–O(2)	1.36(2)	B(4)–O(5)#2	1.479(6)
B(2)–O(3)	1.315(12)	B(4)–O(6)	1.458(11)
B(2)–O(8)	1.38(10)		
O(2)–B(1)–O(6)	121.9(11)	O(1)–B(3)–O(4)	114.6(5)
O(2)–B(1)–O(7)	119(3)	O(5)–B(3)–O(4)	121.0(6)
O(6)–B(1)–O(7)	119(2)	O(3)–B(4)–O(6)	111.6(7)
O(3)–B(2)–O(2)	124.2(12)	O(3)–B(4)–O(5)	109.7(5)
O(3)–B(2)–O(8)	122(3)	O(6)–B(4)–O(5)	108.2(5)
O(2)–B(2)–O(8)	113(3)	O(5)#2–B(4)–O(5)	109.4(6)
O(1)–B(3)–O(5)	124.4(6)		
$[\text{B}_5\text{O}_7(\text{OH})_3\text{Co}(\text{TREN})]$			
Co–O(1)	2.012(5)	B(3)–O(4)	1.466(11)
Co–N(1)	2.112(7)	B(3)–O(5)	1.465(10)
Co–N(2)	2.092(7)	B(3)–O(6)	1.433(10)
Co–N(3)	2.097(7)	B(3)–O(7)	1.505(10)
Co–N(4)	2.213(7)	B(4)–O(7)	1.342(10)
B(1)–O(1)	1.309(10)	B(4)–O(8)	1.387(12)
B(1)–O(2)	1.388(10)	B(4)–O(9)	1.370(12)
B(1)–O(4)	1.388(10)	B(5)–O(6)	1.365(9)
B(2)–O(2)	1.361(11)	B(5)–O(9)	1.386(10)
B(2)–O(3)	1.358(11)	B(5)–O(10)	1.356(10)
B(2)–O(5)	1.339(10)		
O(1)–B(1)–O(2)	120.4(7)	O(6)–B(3)–O(7)	111.6(6)
O(1)–B(1)–O(4)	123.2(7)	O(5)–B(3)–O(7)	106.9(6)
O(2)–B(1)–O(4)	116.4(7)	O(4)–B(3)–O(7)	107.3(7)
O(5)–B(2)–O(3)	120.9(8)	O(7)–B(4)–O(9)	122.8(9)
O(5)–B(2)–O(2)	121.2(8)	O(7)–B(4)–O(8)	122.5(9)
O(3)–B(2)–O(2)	117.9(7)	O(9)–B(4)–O(8)	114.4(7)
O(6)–B(3)–O(5)	110.8(8)	O(10)–B(5)–O(6)	120.3(8)
O(6)–B(3)–O(4)	110.3(6)	O(10)–B(5)–O(9)	118.8(6)
O(5)–B(3)–O(4)	109.8(6)	O(6)–B(5)–O(9)	120.7(7)
$[\text{Co}_2(\text{TETA})_3][\text{B}_5\text{O}_6(\text{OH})_4]_4$			
Co(1)–N(1)	2.290(4)	B(9)–O(16)	1.360(5)
Co(1)–N(2)	2.287(6)	B(9)–O(18)	1.370(5)
Co(1)–N(3)	2.197(6)	B(9)–O(19)	1.366(5)
Co(1)–N(4)	2.193(5)	B(10)–O(17)	1.340(5)
Co(1)–N(5)	2.213(6)	B(10)–O(19)	1.381(5)
Co(1)–N(6)	2.085(4)	B(10)–O(20)	1.362(5)
Co(2)–N(7)	2.197(5)	B(11)–O(21)	1.353(5)
Co(2)–N(8)	2.175(6)	B(11)–O(22)	1.383(5)
Co(2)–N(9)	2.214(5)	B(11)–O(25)	1.367(5)
Co(2)–N(10)	2.284(4)	B(12)–O(22)	1.388(5)
Co(2)–N(11)	2.078(4)	B(12)–O(23)	1.366(5)
Co(2)–N(12)	2.220(5)	B(12)–O(24)	1.345(5)
B(1)–O(1)	1.379(5)	B(13)–O(24)	1.480(5)
B(1)–O(2)	1.378(5)	B(13)–O(25)	1.453(5)
B(1)–O(4)	1.343(5)	B(13)–O(26)	1.483(5)
B(2)–O(2)	1.382(5)	B(13)–O(27)	1.469(5)
B(2)–O(3)	1.358(5)	B(14)–O(26)	1.373(5)
B(2)–O(5)	1.358(5)	B(14)–O(28)	1.374(5)
B(3)–O(4)	1.488(5)	B(14)–O(29)	1.360(5)
B(3)–O(5)	1.477(5)	B(15)–O(27)	1.361(5)
B(3)–O(6)	1.488(4)	B(15)–O(29)	1.373(5)
B(3)–O(7)	1.443(5)	B(15)–O(30)	1.361(5)
B(4)–O(7)	1.358(5)	B(16)–O(31)	1.352(5)
B(4)–O(8)	1.351(5)	B(16)–O(32)	1.378(5)
B(4)–O(9)	1.378(5)	B(16)–O(34)	1.369(5)

Table 3 (continued)

B(5)–O(6)	1.354(5)	B(17)–O(32)	1.397(5)
B(5)–O(9)	1.397(5)	B(17)–O(33)	1.354(5)
B(5)–O(10)	1.347(5)	B(17)–O(35)	1.340(5)
B(6)–O(11)	1.343(5)	B(18)–O(34)	1.498(5)
B(6)–O(12)	1.384(5)	B(18)–O(35)	1.470(5)
B(6)–O(14)	1.375(5)	B(18)–O(36)	1.463(5)
B(7)–O(12)	1.374(5)	B(18)–O(37)	1.470(4)
B(7)–O(13)	1.364(5)	B(19)–O(37)	1.357(5)
B(7)–O(15)	1.362(5)	B(19)–O(38)	1.372(5)
B(8)–O(14)	1.460(5)	B(19)–O(39)	1.370(5)
B(8)–O(15)	1.492(5)	B(20)–O(36)	1.360(5)
B(8)–O(16)	1.471(5)	B(20)–O(39)	1.375(5)
B(8)–O(17)	1.462(5)	B(20)–O(40)	1.354(5)
O(4)–B(1)–O(1)	122.9(4)	O(21)–B(11)–O(22)	120.4(4)
O(2)–B(1)–O(1)	115.1(3)	O(25)–B(11)–O(22)	121.1(4)
O(5)–B(2)–O(3)	123.1(4)	O(24)–B(12)–O(23)	123.2(3)
O(5)–B(2)–O(2)	121.3(3)	O(24)–B(12)–O(22)	120.5(3)
O(3)–B(2)–O(2)	115.6(3)	O(23)–B(12)–O(22)	116.3(3)
O(7)–B(3)–O(5)	109.7(3)	O(25)–B(13)–O(27)	109.0(3)
O(7)–B(3)–O(6)	111.7(3)	O(25)–B(13)–O(24)	111.8(3)
O(5)–B(3)–O(6)	108.0(3)	O(27)–B(13)–O(24)	108.6(3)
O(7)–B(3)–O(4)	110.0(3)	O(25)–B(13)–O(26)	109.8(3)
O(5)–B(3)–O(4)	110.4(3)	O(27)–B(13)–O(26)	110.4(3)
O(6)–B(3)–O(4)	107.0(3)	O(24)–B(13)–O(26)	107.3(3)
O(8)–B(4)–O(7)	119.1(4)	O(29)–B(14)–O(26)	121.1(3)
O(8)–B(4)–O(9)	119.7(4)	O(29)–B(14)–O(28)	117.0(3)
O(7)–B(4)–O(9)	121.2(4)	O(26)–B(14)–O(28)	121.8(3)
O(10)–B(5)–O(6)	123.5(3)	O(30)–B(15)–O(27)	122.9(4)
O(10)–B(5)–O(9)	116.8(3)	O(30)–B(15)–O(29)	115.8(3)
O(6)–B(5)–O(9)	119.7(3)	O(27)–B(15)–O(29)	121.2(4)
O(11)–B(6)–O(14)	123.1(3)	O(31)–B(16)–O(34)	122.7(3)
O(11)–B(6)–O(12)	116.6(3)	O(31)–B(16)–O(32)	116.2(3)
O(14)–B(6)–O(12)	120.2(3)	O(34)–B(16)–O(32)	121.0(3)
O(15)–B(7)–O(13)	123.1(3)	O(35)–B(17)–O(33)	124.1(4)
O(15)–B(7)–O(12)	121.1(3)	O(35)–B(17)–O(32)	121.2(4)
O(13)–B(7)–O(12)	115.8(3)	O(33)–B(17)–O(32)	114.6(3)
O(14)–B(8)–O(17)	108.9(3)	O(36)–B(18)–O(37)	111.6(3)
O(14)–B(8)–O(16)	109.3(3)	O(36)–B(18)–O(35)	108.8(3)
O(17)–B(8)–O(16)	111.4(3)	O(37)–B(18)–O(35)	110.0(3)
O(14)–B(8)–O(15)	110.6(3)	O(36)–B(18)–O(34)	109.1(3)
O(17)–B(8)–O(15)	109.2(3)	O(37)–B(18)–O(34)	107.0(3)
O(16)–B(8)–O(15)	107.4(3)	O(35)–B(18)–O(34)	110.3(3)
O(16)–B(9)–O(19)	121.3(4)	O(37)–B(19)–O(39)	121.1(3)
O(16)–B(9)–O(18)	121.8(4)	O(37)–B(19)–O(38)	122.0(4)
O(19)–B(9)–O(18)	116.9(4)	O(39)–B(19)–O(38)	117.0(3)
O(17)–B(10)–O(20)	119.9(3)	O(36)–B(20)–O(39)	121.3(3)
O(17)–B(10)–O(19)	121.1(3)	O(40)–B(20)–O(36)	119.2(3)
O(20)–B(10)–O(19)	119.0(3)	O(40)–B(20)–O(39)	119.5(3)
O(21)–B(11)–O(25)	118.4(4)		

3, and $n = 1$ for **2**) as the fundamental building unit, with $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ anion in **1** and **3** and $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$ anion in **2**. As found in several known borates, such as $\text{LiB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ [24], $\text{NaB}_5\text{O}_6(\text{OH})_4 \cdot 3\text{H}_2\text{O}$ [25], $\text{KB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ [26], $\text{CsB}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ [27], $(\text{NH}_4)\text{B}_5\text{O}_6(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ [28] and $\text{NaB}_5\text{O}_6(\text{OH})_4$ [29], the polyanion $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ is composed of one BO_4 tetrahedron and four $\text{BO}_2(\text{OH})$ triangles, which forms two B_3O_3 cycles linked by the common BO_4 tetrahedron. For compound **1**, there are four positions occupied by boron atoms: one general and three special; it is easy to see that the *FBB* (following the classical nomenclature of borates

Table 4

Details of hydrogen bonds for **1–3**

D–H...A	$d(\text{D–H})$ (Å)	$d(\text{H...A})$ (Å)	$d(\text{D...A})$ (Å)	$\angle(\text{DHA})$ (deg)
[Co(DIEN)]₂[B₅O₆(OH)₄]₂				
O(1)–H(1A)···O(5) ^a	0.82	1.90	2.714(6)	174(1)
O(7)–H(7A)···O(6) ^b	0.82	1.85	2.66(5)	168(3)
O(8)–H(8A)···O(7) ^c	0.82	1.99	2.74(8)	151(7)
N···O range	2.99(2)–3.11(3)			
[B₅O₇(OH)₃Co(TREN)]				
O(8)–H(8A)···O(5) ^d	0.82	1.88	2.69(4)	173(1)
O(10)–H(10A)···O(1) ^e	0.82	1.85	2.67(7)	175(2)
N···O range	3.00(3)–3.20(1)			
[Co₂(TETA)₃][B₅O₆(OH)₄]₄				
O(1)–H(1A)···O(14)	0.82	1.89	2.71(4)	175(8)
O(3)–H(3A)···O(26) ^f	0.82	1.86	2.68(4)	173(6)
O(8)–H(8A)···O(18) ^g	0.82	2.02	2.84(5)	172(5)
O(10)–H(10A)···O(37) ^h	0.82	1.88	2.70(4)	177(8)
O(11)–H(11A)···O(4)	0.82	1.85	2.67(4)	173(1)
O(13)–H(13A)···O(35) ⁱ	0.82	1.89	2.71(4)	176(1)
O(18)–H(18A)···O(24)	0.82	1.86	2.68(4)	176(5)
O(20)–H(20A)···O(10) ^j	0.82	2.04	2.86(4)	173(5)
O(21)–H(21A)···O(38)	0.82	2.02	2.84(5)	174(4)
O(23)–H(23A)···O(16)	0.82	1.86	2.68(4)	178(1)
O(28)–H(28A)···O(5) ^k	0.82	1.89	2.71(4)	174(7)
O(30)–H(30A)···O(34) ^l	0.82	1.87	2.69(4)	174(2)
O(31)–H(31A)···O(27) ^m	0.82	1.90	2.72(4)	174(4)
O(33)–H(33A)···O(15) ⁿ	0.82	1.88	2.70(4)	174(6)
O(38)–H(38A)···O(6) ^k	0.82	1.86	2.70(5)	177(1)
O(40)–H(40A)···O(23)	0.82	2.04	2.85(4)	173(9)
N···O range	2.89(2)–3.10(2)			

^a $-x + 1/2, -y + 1/2, -z + 1$.^b $-x + 1, -y, -z + 1$.^c $-x + 1, -y, -z + 2$.^d $x, -y + 3/2, z + 1/2$.^e $x - 1, y, z$.^f $-x + 2, -y, -z + 1$.^g $x - 1, y, z$.^h $x, y - 1, z$.ⁱ $-x + 2, -y + 1, -z$.^j $x + 1, y, z$.^k $x, y + 1, z$.

[1–7]) is: $5: 2 [(2.5: \Delta + 2 \times 0.5\Delta + 0.5T)]$ with Δ for trigonal BO_3 , and T for tetrahedral BO_4 . In the compound **3**, a usual polyanion with 20 crystallographically independent boron atoms is pointed out; its symbolic shorthand notation is: $20: [4(4\Delta + T)]$. The $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$ cluster in the compound **2**, however, is unusual and constructed from three trigonal $\text{BO}_2(\text{OH})$ units, one trigonal BO_3 unit and one tetrahedral BO_4 unit, which can be written as $5: 4\Delta + T$.

In compounds **1–3**, the B atoms have both triangular and tetrahedral coordination. The triangularly coordinated boron atoms have B–O distances in the range 1.309(2)–1.397(5) Å [av. = 1.364 Å] and the tetrahedral B atoms have longer B–O distances in the range 1.433(2)–1.505(2) Å [av. = 1.470 Å]. These values are in good agreement with the other borate compounds reported previously [15,16,24–29]. The O–B–O angles of the BO_4 tetrahedra lie in the 106.9(6)–111.8(3)° range and those of the BO_3 triangles span from 113.0(3)° to 124.4(6)°; the

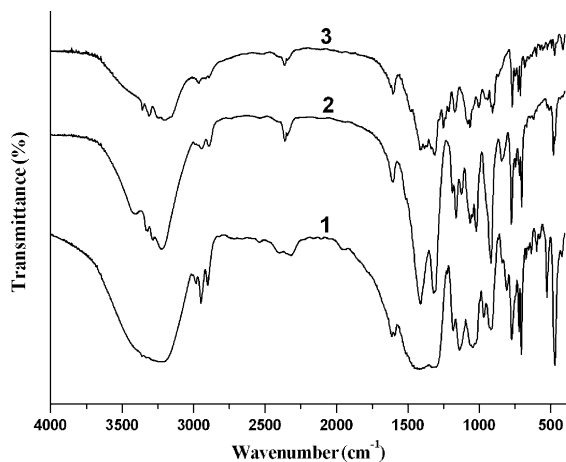


Fig. 1. IR spectra of 1–3.

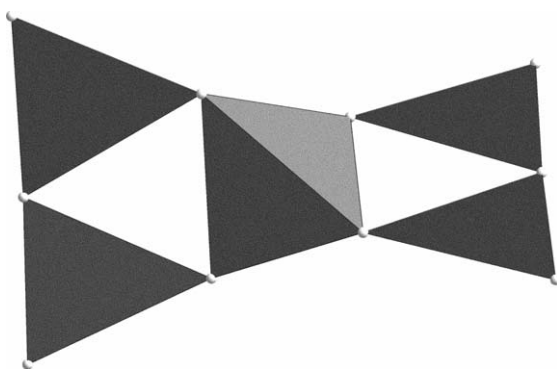


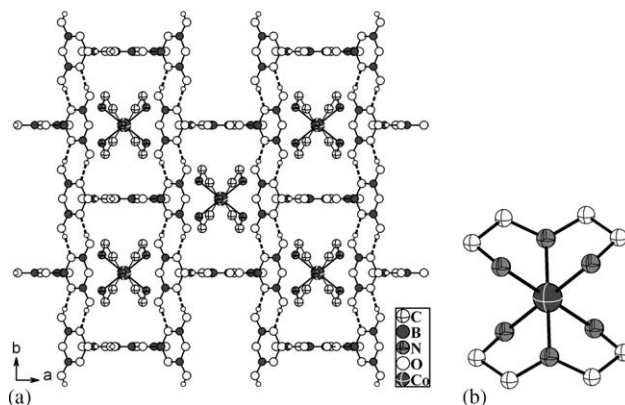
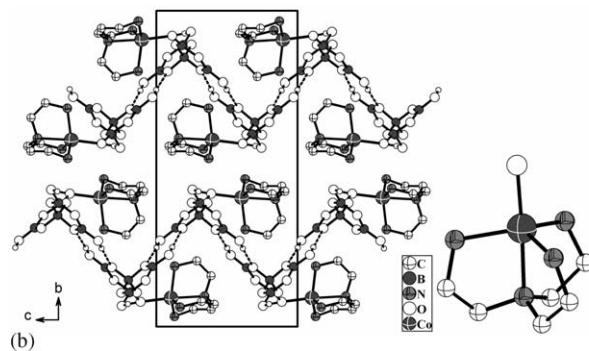
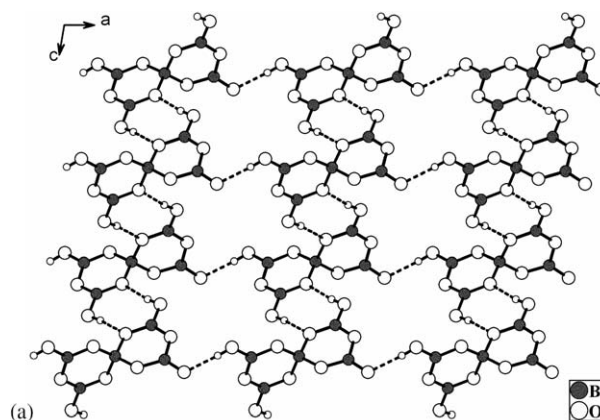
Fig. 2. Polyhedral representation of FBBs.

averages for corresponding angles are very close to 109.5° and 120° , respectively.

3.2.2. Hydrogen-bonded borate host lattice for the accommodation of transition-metal complex template

As expected to be a good building block for supramolecular network, the FBBs, $[\text{B}_5\text{O}_{6+n}(\text{OH})_{4-n}]^{(n+1)-}$, connect with each other to form hydrogen-bonded architectures by the $-\text{OH}$ groups oriented in a planar triangular fashion. In **1** and **3**, the $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ units are linked together by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds to form a unidirectional rectangle-like borate anion host lattice with 12-membered boron rings, as shown in Figs. 3a and 5a. The $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$ cluster in **2**, however, is connected to four neighboring units by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, forming a puckered borate sheet with 8-membered boron rings, as shown in Fig. 4a.

In contrast to the borate species employed to construct the borate-anion hydrogen-bonded host lattices, the transition-metal complexes template guests were generated in situ and incorporated into the host lattices through hydrogen-bonding interactions with their nearest neighbors. In **1**, the templating $[\text{Co}(\text{DIEN})_2]^{2+}$ cations reside in the rectangle-like 12-membered boron rings and interact

Fig. 3. (a) View of the hydrogen-bonded borate anion host lattice with 12-membered boron rings in **1** and (b) $[\text{Co}(\text{DIEN})_2]^{2+}$ cations.Fig. 4. (a) View of the hydrogen-bonded sheet with 8-membered boron rings in **2** and (b) view of the packing structure and $[\text{Co}(\text{TREN})_2]^{2+}$ cations in **2**.

with the inorganic framework through H-bonds such as $\text{N}(1)\cdots\text{O}(1)$ [$d = 3.11 \text{ \AA}$] and $\text{N}(2)\cdots\text{O}(4)$ [$d = 2.99 \text{ \AA}$] (Fig. 6a). The Co atom is octahedrally coordinated by six nitrogen atoms from two DIEN molecules, with Co–N bond lengths in the range of $2.02(2)$ – $2.233(2) \text{ \AA}$ (Fig. 3b). In comparison with the previously reported zinc borate $[\text{Zn}(\text{DIEN})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$ [16], both structures seem to be similar and constructed from the same FBBs, $[\text{B}_5\text{O}_6(\text{OH})_4]^-$. However, it is of interest to note that a distinction can be made when considering the structure

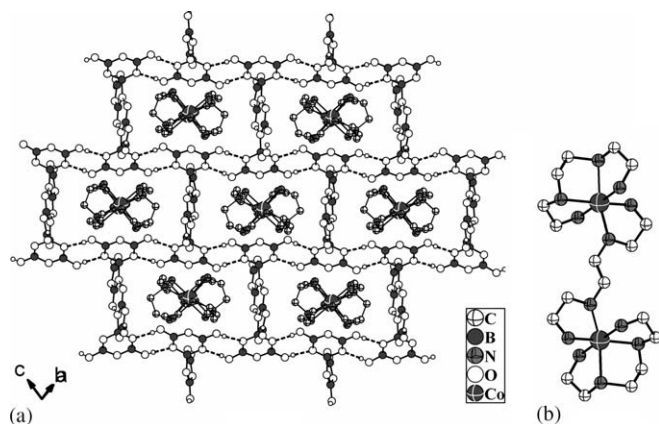


Fig. 5. (a) View of the hydrogen-bonded borate anion host lattice with 12-membered boron rings in **3** and (b) $[\text{Co}_2(\text{TETA})_3]^{4+}$ cations.

of the $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ unit. In the zinc borate, the $[\text{B}_5\text{O}_6(\text{OH})_4]^-$ anion has not a two-fold axis as in the present cobalt borate. And a similar case also exists in mineral borax, $\text{Na}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 8\text{H}_2\text{O}$ [30] and in other synthetic borates containing $[\text{B}_4\text{O}_5(\text{OH})_4]^{2-}$ anion, for example, $\text{NaRb}[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 4\text{H}_2\text{O}$ [31] and $\text{Cs}_2[\text{B}_4\text{O}_5(\text{OH})_4] \cdot 3\text{H}_2\text{O}$ [32]. In addition to these, compound **1** differs greatly from $[\text{Zn}(\text{DIEN})_2][\text{B}_5\text{O}_6(\text{OH})_4]_2$ [16] in the arrangement of templating complex cations in hydrogen-bonded host lattices, which can be attributed to the different space groups they crystallize in. In **2**, the “hanging” $[\text{Co}(\text{TREN})]^{2+}$ templates are attached to the $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$ clusters via the common O(1) atoms, and responsible for the forming of 3D supramolecular network through hydrogen bonds: $\text{N}(1) \cdots \text{O}(3)$ [$d = 3.12 \text{ \AA}$], $\text{N}(1) \cdots \text{O}(8)$ [$d = 3.15 \text{ \AA}$], $\text{N}(2) \cdots \text{O}(1)$ [$d = 3.00 \text{ \AA}$], $\text{N}(2) \cdots \text{O}(4)$ [$d = 3.06 \text{ \AA}$] and $\text{N}(3) \cdots \text{O}(4)$ [$d = 3.20 \text{ \AA}$] (Fig. 6b). The Co atom is square-pyramidally coordinated, bonded to one oxygen atom [Co–O 2.112 Å] from $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$ cluster and four nitrogen atoms [Co–N (av.) 2.128 Å] from TREN (Fig. 4b). Interestingly, the TREN, which possesses the same chemical formula ($\text{C}_6\text{H}_{18}\text{N}_4$) with TETA, should be the rearranged product of TETA under the hydrothermal condition. As is also found in the $[\text{Al}_3\text{P}_4\text{O}_{16}][\text{NH}_3(\text{CH}_2)_5\text{NH}_3][\text{C}_5\text{H}_{10}\text{NH}_2]$ [33], $[\text{B}_5\text{O}_7(\text{OH})_3\text{Zn}(\text{TREN})]$ [16] and $\text{Zn}_3(\text{tren})(\text{HPO}_3)_3 \cdot x\text{H}_2\text{O}$ [34], the decomposition and rearrangement of the organic amine can be realized under suitable synthesis conditions. It has to be pointed out that the structure of **2** is isostructural to $[\text{B}_5\text{O}_7(\text{OH})_3\text{Zn}(\text{TREN})]$ [16], which has similar unit cell parameters and identical $P2_1/c$ space group. The $[\text{Co}_2(\text{TETA})_3]^{4+}$ guest templates in **3**, however, locate in the rectangle-like borate host lattice and interact with the inorganic framework through extensive hydrogen-bonds with $\text{N} \cdots \text{O}$ distance in the range of 2.89–3.10 Å (Fig. 6c). It is worthy to note that TETA molecules adopt two different coordination manners, one serving as chelating ligand and the other acting as a bridge to connect two symmetry-related cobalt atoms (Fig. 5b). To our knowledge, the simultaneous

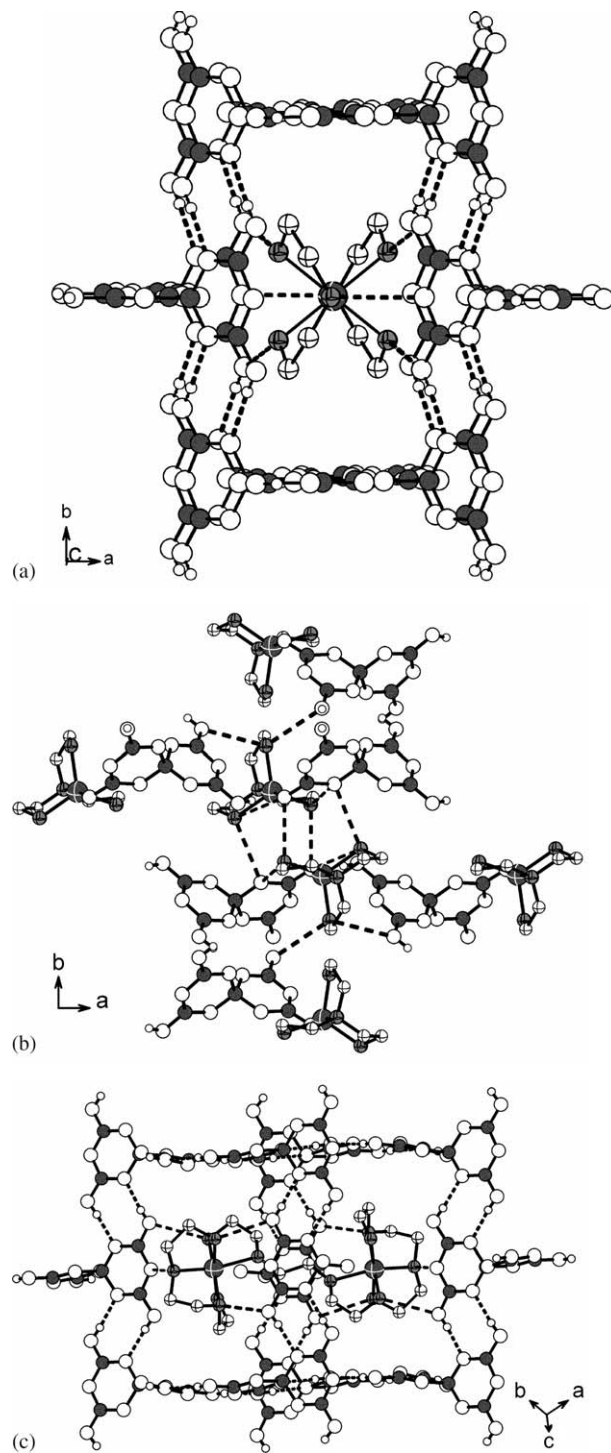


Fig. 6. (a) View of the H-bonds interactions between the $[\text{Co}(\text{DIEN})_2]^{2+}$ complex and the O atoms from inorganic framework; (b) view of the H-bonds interactions between $[\text{Co}(\text{TETA})_2]^{2+}$ cations and adjacent four $[\text{B}_5\text{O}_7(\text{OH})_3]^{2-}$ clusters and (c) side view of the hydrogen-bonded network with 12-membered boron rings, showing the H-bonds interactions between the $[\text{Co}_2(\text{TETA})_3]^{4+}$ complex and the O atoms from inorganic framework.

presence of such coordination patterns of TETA in this compound is unusual, though a similar instance was also found in $[\text{Cd}_2(\text{C}_2\text{N}_2\text{H}_8)_3][\text{Ge}_9\text{O}_{18}(\text{OH})_4]$ [35]. The cobalt

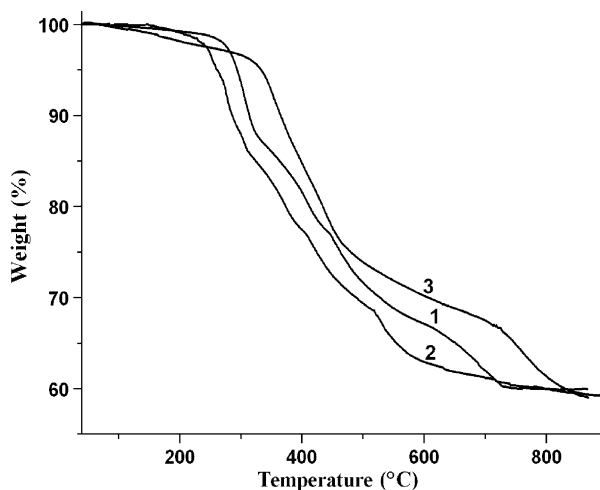


Fig. 7. TG curve of 1–3.

atoms are octahedrally coordinated with Co–N bond lengths in the range of 2.076(5)–2.296(7) Å (Fig. 6).

3.3. Thermal properties

Thermogravimetric (TG) analysis of 1–3 was carried out in N₂ atmosphere from 40 to 1000 °C with a heating rate of 10 °C/min. As shown in Fig. 7, the TG curve of 1 showed that the compound was stable up to about 150 °C, then a continuous weight loss between 150 and 725 °C, corresponding to the removal of two DIEN and four water molecules (Found: 39.07%; Calcd: 39.69%). For 2, a total weight loss of 40.35% was observed in the range between 170 and 830 °C, due to the release of the TREN and the dehydration of hydroxyls (Calcd: 41.03%). For 3, a two-step weight loss occurred between 140 and 900 °C. The initial weight loss between 140 and 600 °C corresponds to the departure of TETA molecules (Found: 30.14%; Calcd: 30.70%). The second step occurring between 600 and 900 °C is assigned to the dehydration process (Found: 10.42%; Calcd: 10.09%).

4. Conclusions

In summary, three new cobalt borates, [Co(DIEN)₂][B₅O₆(OH)₄]₂ (1), [B₅O₇(OH)₃Co(TREN)] (2) and [Co₂(TETA)₃][B₅O₆(OH)₄]₄ (3), have been synthesized under hydrothermal conditions. Based on the similar [B₅O_{6+n}(OH)_{4-n}]⁽ⁿ⁺¹⁾⁻ FBBs, the interesting hydrogen-bonded borate host lattices are formed and employed to accommodate the transition-metal complex templates, which are generated in situ. Given the various transition-metal elements that can be introduced into the borate architecture with different FBBs, it can be expected that many other novel structural complex borate materials will be realized.

Acknowledgments

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