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Article

$Na_5[MB_{24}O_{34}(OH)_{12}] \cdot nH_2O$ (M = Cr^{3+}, Al^{3+}): Unprecedented Spherelike Polyborate Clusters from Boric Acid Flux Synthesis

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Two novel isotypic polyborate cluster compounds $Na_5[MB_{24}O_{34}(OH)_{12}] \cdot nH_2O$ (M = Cr^{3+}, Al^{3+}) have been synthesized in a boric acid flux closed system at 220 °C by using gel as precursors. The structure of the Cr compound was determined by low-temperature single-crystal X-ray diffraction, and the Al compound was confirmed to be isostructural by powder X-ray diffraction and similar FT-IR spectra and thermal behavior. $Na_5[CrB_{24}O_{34}(OH)_{12}] \cdot nH_2O$ crystallizes in the monoclinic space group $P2_1/c$ with the cell parameters $a = 17.4549(3)$ Å, $b = 11.1976(2)$ Å, $c = 21.2403(3)$ Å, $\beta = 94.644(2)°$, $V = 4137.85(12)$ Å^3, and $Z = 4$. The predominant feature of the structure are the spherelike polyborate clusters $[MB_{24}O_{34}(OH)_{12}]^{5-}$. The M^{3+} cation is located at the center of the cluster, around which four hexaborate units ($[B_6O_{10}(OH)_3]^{5-}$) are tetrahedrally assembled in almost a perfect T_d symmetry. To the best of our knowledge, $[MB_{24}O_{34}(OH)_{12}]^{5-}$ is the first example of a polyborate cluster that contains 24 boron atoms. Upon heating, the compounds show two steps of weight loss, including the loss of the disengaged water and dehydration of the hydroxy groups. The first step is reversible, retaining the structure framework. The second weight loss is continuous and irreversible.

Introduction

Borate compounds have been an active subject in inorganic chemistry for many years. From a structural chemistry point of view, a myriad of structure types can be obtained by linkage of triangular BO_3 and tetrahedral BO_4 groups.[1–6] In many cases, the BO_3 and/or BO_4 groups are linked via sharing corners, forming diverse polyborate anions such as isolated rings or cages, 1D chains, 2D sheets, and 3D networks.[7–17] Current interest in borates stems from their nonlinear optical properties, originating mostly from their complex structures, often with noncentrosymmetric structures. BBO (β-BaB_2O_4),[18] BIBO (α-BiB_3O_6),[19,20] and LBO (LiB_3O_5)[21] are well-known examples. The transition-metal

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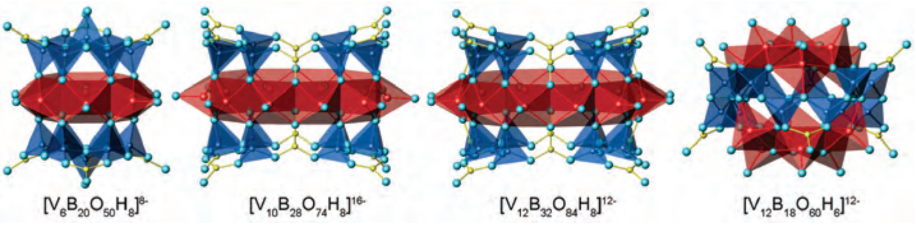

Figure 1. Structures of various well-known vanadoborate clusters: $[V_6B_{20}O_{50}H_8]^{8-}$, $[V_{10}B_{28}O_{74}H_8]^{16-}$, $[V_{12}B_{32}O_{84}H_8]^{12-}$, and $[V_{12}B_{18}O_{60}H_6]^{12-}$: (red pyramid) VO_5; (blue tetrahedron) BO_4; (red sphere) vanadium; (blue sphere) 4-fold coordinated boron; (yellow sphere) 3-fold coordinated boron; (cyan sphere) oxygen. All of the hydrogen atoms are omitted for clarity.

borates, on the other hand, are also very interesting, due to their magnetic behavior[22–27] and reversible Li-ion uptake.[28–30] Recently, a number of transition-metal borates with open frameworks have been reported.[31–34] For example, $MCuB_7O_{12}\cdot nH_2O$ (M = Na, K)[33] contains one-dimensional 14-ring channels formed by CuO_6, BO_4, and BO_3. The water molecules and alkali-metal cations located in the 14-ring channels are removable.

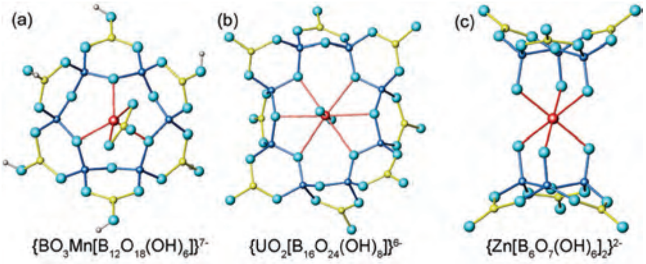

Figure 2. Structural fragments of three monometal-centered borate clusters: (red sphere) Mn, U, or Zn; (blue sphere) 4-fold coordinated boron; (yellow sphere) 3-fold coordinated boron; (cyan sphere) oxygen. All of the hydrogen atoms are omitted for clarity.

Achievements in metal borate cluster chemistry, however, have been limited, possibly due to the lack of model compounds, among which the vanadoborates and their derivates were most extensively studied because of their diverse constructions.[35–40] As shown in Figure 1, $[V_6B_{20}O_{50}H_8]^{8-}$, $[V_{10}B_{28}O_{74}H_8]^{16-}$, and $[V_{12}B_{32}O_{84}H_8]^{12-}$ all have toroidal $(O{=}VO_2)_n$ rings (n = 6, 10, 12) which are sandwiched by two polyborate (B_{10}, B_{14}, or B_{16}) rings on each side. However, $[V_{12}B_{18}O_{60}H_6]^{12-}$ has a $[B_{18}O_{36}(OH)_6]^{24-}$ ring in the middle and two hexavanadate V_6O_{12} groups as side caps. In the above cases, vanadium atoms are naturally coordinated in square-pyramidal symmetry and VO_5 trends to be connected via common basal edges. On further combination of the borate rings, multimetal-centered clusters are therefore formed. In addition, several monometal-centered borate clusters are also observed in other metal borate systems: for example, $K_7\{(BO_3)Mn[B_{12}O_{18}(OH)_6]\}\cdot H_2O$,[40] $K_6\{UO_2[B_{16}O_{24}(OH)_8]\}\cdot 12H_2O$,[41] and $[(CH_3)_2NH(CH_2)_2NH(CH_3)_2]\{Zn[B_6O_7(OH)_6]_2\}$[42] (see Figure 2). In the cases of manganese and uranium borates, there is a common characteristic: the cyclic borate polyanions ($[B_{12}O_{18}(OH)_6]^{6-}$ and $[B_{16}O_{24}(OH)_8]^{8-}$) provide planar or near-planar coordination environments to central metal cations, whose stereocoordination environments need to be completed by other additional atoms, such as a BO_3 in $\{(BO_3)Mn[B_{12}O_{18}(OH)_6]\}^{7-}$ and two oxygen atoms in $\{UO_2[B_{16}O_{24}(OH)_8]\}^{6-}$. A simple way to construct an octahedral site for zinc with two hexaborate $[B_6O_7(OH)_6]^{2-}$ units is seen in $\{Zn[B_6O_7(OH)_6]_2\}^{2-}$. Here, we report a novel type of monometal-centered borate cluster constructed by assembling four hexaborate subunits $[B_6O_{10}(OH)_3]^{5-}$ in a nearly T_d symmetry with the central cation being octahedrally coordinated. The model compounds $Na_5[MB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ (M = Cr^{3+}, Al^{3+}) are prepared in a boric acid flux closed system at 220 °C. The structure of the Cr compound was determined by low-temperature single-crystal X-ray diffraction. The interspaces of the clusters are filled by Na^+ countercations and disengaged water molecules. Crystals of Al analogues are generally small, and we only characterized their powder X-ray diffraction patterns, FT-IR spectra, and thermal

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behavior. To the best of our knowledge, $Na_5[MB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ (M = Cr^{3+}, Al^{3+}) represent the first examples of 24-boron polyborate anions.

Experimental Section

Syntheses. All reagents were of analytical grade and were used as obtained from commercial sources without further purification. A typical synthesis was to charge $Cr(NO_3)_3\cdot 9H_2O$ or $Al(NO_3)_3\cdot 9H_2O$ (2.5 mmol), $Na_2B_4O_7\cdot 10H_2O$ (20 mmol), H_3BO_3 (80 mmol), and 10 mL of water in a 50 mL unsealed Teflon container. Then the mixture was heated at 140 °C in an oven for 2−4 h to obtain a gel-like precursor. Then the Teflon container was sealed in a steel autoclave and further heated at 220 °C for 5 days. The solid product was washed with hot water (80 °C), and the yield was about 80%. One-step synthesis using the same starting materials was unsuccessful.

Structure Determination. Single-crystal X-ray diffraction data on a crystal of the Cr compound that was about 0.03 × 0.3 × 0.5 mm^3 were collected at 100 K, on an Oxford Diffraction Excalibur-II diffractometer equipped with a Sapphire-III CCD area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å) from an Enhance-II sealed tube source. Empirical absorption correction was applied. The crystal structure was solved by direct methods (SHELXS97) and refined by full-matrix least-squares refinement.[43] Chromium, sodium, and some of the boron and oxygen atoms of the cluster were readily located by direct methods, and all of the remaining non-hydrogen atoms were found from residual peaks. All of the positions of the hydrogens bonded to the main cluster were initially located in the difference map; for the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined in the riding model. The hydrogen atoms bonded to the disengaged water molecules were not presented, since their positions could not be found beyond doubt on the Fourier map and several water molecules are disordered. The last cycles of refinement included atomic positions for all of the atoms, anisotropic thermal parameters for all of the non-hydrogen atoms, and isotropic thermal parameters for all of the hydrogen atoms and disordered water molecules. Detailed crystallographic information is given in Table 1. Selected bond distances and angles are given in Tables S1 and S2, respectively (Supporting Information). Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax, (+49)7247-808-666; e-mail, crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-418440.

Table 1. Crystallographic and Structure Refinement Parameters for $Na_5[CrB_{24}O_{34}(OH)_{12}]\cdot nH_2O$

formula	$H_{25}Na_5CrB_{24}O_{52.5}$
CSD no.	418440
formula wt	1291.59
cryst size (mm)	0.03 × 0.3 × 0.5
morphology, color	tablet, light pink
temp (K)	100
space group	$P2_1/c$
a (Å)	17.4549(3)
b (Å)	11.1976(2)
c (Å)	21.2403(3)
β (deg)	94.644(2)
V (Å^3)	4137.85(12)
Z	4
ρ_{calcd} (g/cm^3)	2.073
λ (Å)	0.710 73
μ(Mo Kα) (mm^{-1})	0.487
no. of refined params	693
no. of indep rflns	13 402
no. of rflns with $I > 2\sigma(I)$	7578
θ range (deg)	3.76–32.32
R_{int}	0.0415
R1/wR2[a] ($I > 2\sigma(I)$)	0.0562/0.1683
R1/wR2 (all data)	0.0944/0.1849

[a] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0700P)^2 + 7.26P]$ with $P = \max(F_o^2 + 2F_c^2)/3$.

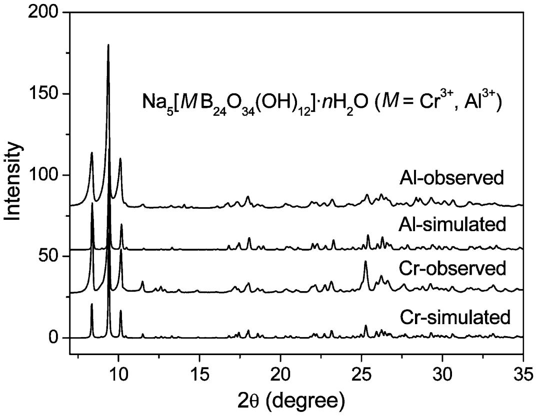

Figure 3. Observed powder X-ray diffraction patterns of $Na_5[MB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ (M = Cr^{3+}, Al^{3+}), consistent with the calculated patterns from the crystal structure.

Other Analyses. Powder X-ray diffraction data were collected at room temperature on a Rigaku D/Max-2000 diffractometer (Cu Kα, $\lambda = 1.5406$ Å, 40 kV and 100 mA, graphite monochromator, scintillator detector, step scan 0.02°/3 s). Figure 3 gives the calculated X-ray diffraction patterns from the crystal structures and the observed patterns of $Na_5[MB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ (M = Cr^{3+}, Al^{3+}) in the range of 7–35°, which are consistent and prove that the title compounds are isostructural. Because of the lack of single-crystal data for the Al compound, we calculated its X-ray diffraction pattern on the basis of the positional parameters of the Cr compound and the refined lattice parameters of the Al compound. The lattice parameters were refined on powder data using Topas:[44] Cr compound, $P2_1/c$, $a = 17.481(6)$ Å, $b = 11.249(5)$ Å, $c = 21.228(7)$ Å, $\beta = 94.85(8)°$, $V = 4159.7(6)$ Å^3; Al compound, $P2_1/c$, $a = 17.458(6)$ Å, $b = 11.148(5)$ Å, $c = 21.113(9)$ Å, $\beta = 94.94(9)°$, $V = 4094.3(8)$ Å^3. The lattice parameters determined from the powder and the single -crystal data agree well. Magnetic measurements were carried out on a Quantum Design MPMS XL-7 SQUID magnetometer from $T = 2$ to 300 K under an applied field of 100 Oe. The chemical analysis was carried out using ICP methods on an ESCALAB2000 analyzer. FT-IR spectroscopy was measured with a Nicolet Magna-IR-750 Series II spectrometer. Thermogravimetric−differential scanning calorimetric−mass spectrometric (TG-DSC-MS) measurements were carried out on a NETZSCH STA449C instrument with a heating rate of 10 °C/min from 30 to 800 °C under a flow of argon.

Results and Discussion

Structure Description. $Na_5[MB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ (M = Cr^{3+}, Al^{3+}) were isostructural compounds because of their similar powder X-ray diffraction patterns (see Figure 3). Therefore, we describe the structure of the Cr analogue as being representative. The main feature is the spherelike 24-

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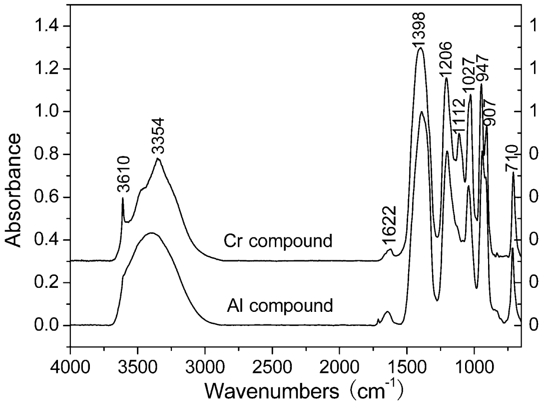

Figure 4. FT-IR spectra of $Na_5[MB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ ($M = Cr^{3+}, Al^{3+}$), showing the coexistence of BO_4 (the band between 907 and 1206 cm^{-1}) and BO_3 (the band at 1398 cm^{-1}) groups in roughly the same amounts. H_2O (1622, 3354 cm^{-1}) and $-OH$ (3610 cm^{-1}) groups are also presented in the structure.

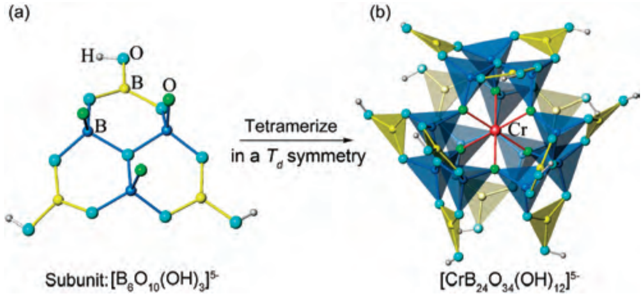

Figure 5. (a) Schematic representation of a single $[B_6O_{10}(OH)_3]^{5-}$ hexaborate subunit. Three oxygen atoms, which are bridged to another three hexaborate subunits, are specifically marked as green spheres. (b) View of the spherelike cluster $[CrB_{24}O_{34}(OH)_{12}]^{5-}$, obtained by tetramerizing four subunits in a nearly T_d symmetry.

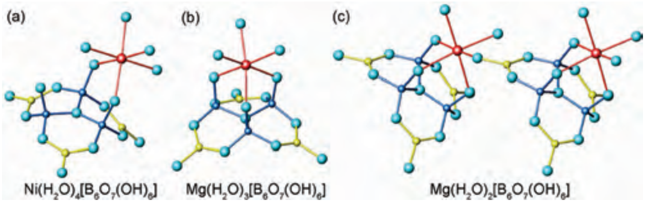

Figure 6. Structural fragments of three already known metal borates possessing the hexaborate $[B_6O_7(OH)_6]^{2-}$: (red sphere) Ni or Mg; (blue sphere) 4-fold coordinated boron; (yellow sphere) 3-fold coordinated boron; (cyan sphere) oxygen or water molecule. All of the hydrogen atoms are omitted.

boron cluster $[CrB_{24}O_{34}(OH)_{12}]^{5-}$, which consists of 71 crystallographic independent non-hydrogen atoms, including 1 Cr, 24 B, and 46 O. The intercluster void is occupied by 5 Na^+ countercations and 8 disengaged water molecules. All atoms are located in general positions. Twelve boron atoms (B1−B12) are 4-fold coordinated as regular tetrahedra with bond distances in the range of 1.428(4)−1.525(4) Å and bond angles in the range of 104.6(2)−115.3(2)°. Another 12 boron atoms (B13−B24) are 3-fold coordinated as regular triangles, whose bond distances and angles vary from 1.347(4) to 1.392(4) Å and from 114.0(3) to 124.4(3)°, respectively. The FT-IR spectra (see Figure 4) also show that two kinds of boron atoms coexist in roughly the same amounts in 3- and 4-coordination environments. The chromium atom is coordinated by 6 oxygen atoms in an ideal octahedral environment with an average Cr−O distance of 1.980 Å.

The concept of fundamental building blocks (FBBs) was introduced by Christ and Clark and then extended by Burns et al. as a comprehensive description of complicated borate polyanions.[1–5] Herein, the FBB in the title compounds is the isolated polyanion $[B_{24}O_{34}(OH)_{12}]^{8-}$, which can be expressed as $24{:}4[(6{:}3\Delta+3T)]$. For a better understanding, this FBB can be described as a tetramer of hexaborate subunits $[B_6O_{10}(OH)_3]^{5-}$. As shown in Figure 5a, such a hexaborate subunit is formed by 3 $BO_2(OH)$ and 3 BO_4 groups linked through the oxygen atoms. The three BO_4 units are bonded together via a single μ_3-oxygen atom. Each $BO_2(OH)$ is linked to 2 BO_4 group and possesses one terminal OH group. In every subunit, there are in total 13 oxygen atoms: one oxygen is of μ_3 type and six oxygens are of μ_2 type and connect BO_4 and BO_3 groups. The other six oxygen atoms are terminal. These six terminal oxygen atoms can also be divided into two types; three BO_3 groups are bonded to protons of hydroxy groups, and three BO_4 tetrahedra (shown as green spheres in Figure 5a) are bridged to three other $[B_6O_{10}(OH)_3]^{5-}$ subunits in the title compounds. In fact, another similar hexaborate anion $[B_6O_7(OH)_6]^{2-}$ has already been reported previously in some known metal borates as shown in Figure 6 and Figure 2c.[42,47–49] The constructions are the same; the only difference is that all the six terminal oxygen atoms in $[B_6O_7(OH)_6]^{2-}$ are bonded to hydrogens of hydroxy groups. The possible reason is that the $[B_6O_7(OH)_6]^{2-}$ groups are truly isolated from each other, while ours are polymerized into large clusters.

In Figure 6, the metal cations (Ni^{2+} and Mg^{2+}) are octahedrally coordinated by two, three, or four oxygen atoms (hydroxy groups) from $[B_6O_7(OH)_6]^{2-}$ and four, three, or two additional water molecules, respectively. In contrast, in the $\{Zn[B_6O_7(OH)_6]_2\}^{2-}$ cluster (see Figure 2c), the zinc cation is capped by two hexaborate anions. Six oxygen atoms from two opposite hexaborate anions build an ideal octahedral coordination environment.[42] Here in our study, $Na_5[MB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ ($M = Cr^{3+}, Al^{3+}$) exhibits a novel construction of a cluster with four $[B_6O_{10}(OH)_3]^{5-}$ subunits and an octahedrally coordinated central cation. As sketched in Figure 5b, each of the three terminal oxygen atoms (shown as green spheres in Figure 5a) is bridged to another subunit, forming a tetrameric 24-boron polyborate anion. Of course, there are 6 oxygen atoms in all (green spheres in Figure 5b), which join 4 hexaborate subunits into an intact FBB and also further coordinate to a Cr^{3+} with a perfect octahedral environment. In other words, it can also be considered that all four subunits are assembled by a Cr^{3+} cation into a nearly perfect T_d symmetry to form a tetrameric spherelike cluster. Eventually, the composition of the cluster is $[CrB_{24}O_{34}(OH)_{12}]^{5-}$.

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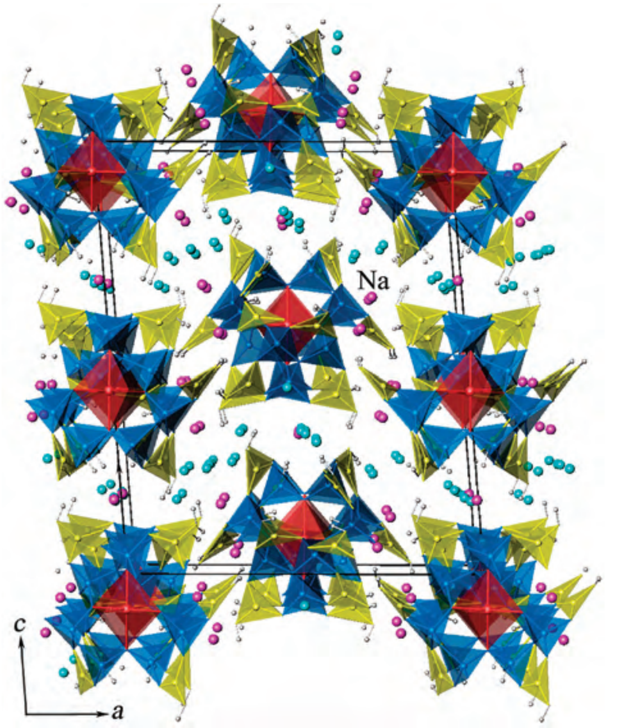

Figure 7. Perspective structural view of $Na_5[CrB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ along the *b* axis.

The negative charges of the clusters are all compensated by five Na^{5+} cations (purple spheres in Figure 7), which reside between adjacent clusters. All Na^+ cations are irregularly coordinated by six or seven oxygen atoms with Na−O distances between 2.336(3) and 2.844(2) Å. The remaining voids are further filled by disengaged water molecules, whose amount is defined by the single-crystal X-ray diffraction refinement. Finally, the molecular formula can be expressed as $Na_5[CrB_{24}O_{34}(OH)_{12}]\cdot 6.5H_2O$, which is also consistent with the chemical analysis (ICP) (Na:Cr:B ≈ 4.5:1:22.7) within an acceptable deviation.

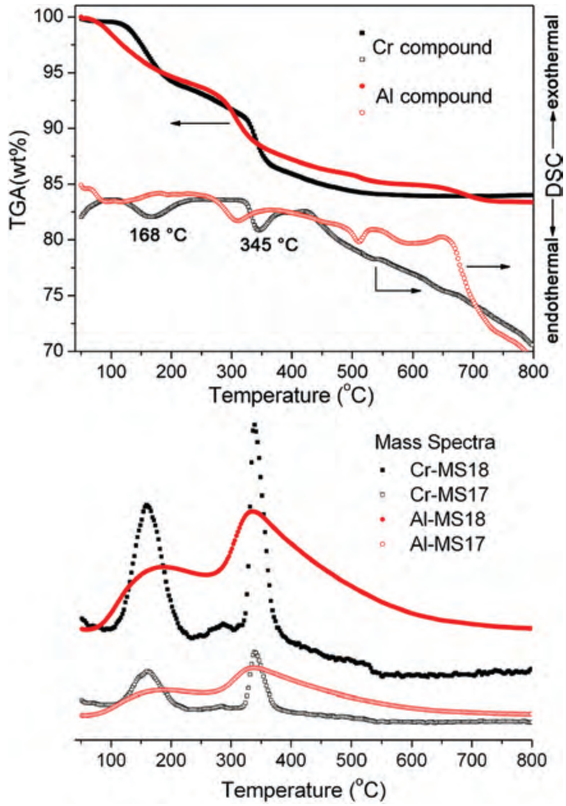

Figure 8. TG-DSC-MS curves of the title compounds.

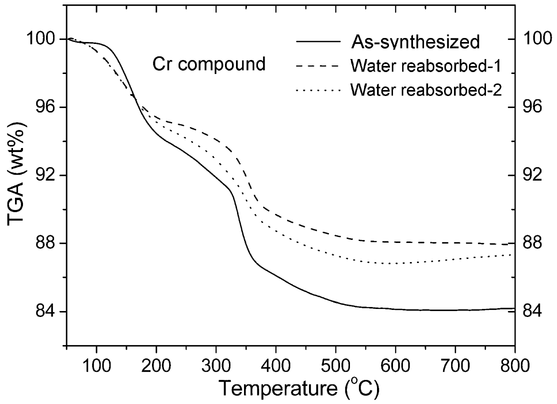

Figure 9. TG curves for as-synthesized and water-reabsorbed $Na_5[CrB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ samples, presented for comparison.

Thermal Stability and Magnetism. The thermal stabilities of the title compounds were investigated by TG-DSC-MS measurements (see Figure 8). For $Na_5[CrB_{24}O_{34}(OH)_{12}]\cdot nH_2O$, a total mass loss of about 15.9 wt % up to 800 °C was detected (calcd 17.4 wt % if $n = 6.5$), which includes two steps of losing water defined by the mass spectra. One is associated with the loss of the disengaged water in the cavity related to the prominent endothermic peak at 168 °C and the other with dehydration of the hydroxy groups at 345 °C. Interestingly, the first step of water loss is reversible. To prove that, we first heated the as-synthesized sample at 300 °C for 20 h. Then, the heated sample was kept in a crucible inserted in a covered beaker with some water in the bottom for 2 h. We did the TG analysis on the resulting sample, defined as the water-reabsorbed sample. After that, we repeated this absorption process on the water-reabsorbed sample to confirm the reversibility. The TG curves are all presented in Figure 9 for comparison. Clearly, the weight losses of water-reabsorbed samples also include two steps, which indicate that loss of the disengaged water is reversible. However, each weight loss is slightly smaller than that of the as-synthesized sample, suggesting that part of the hydroxy groups were dehydrated at 300 °C. The powder X-ray diffraction patterns, collected on the heated Cr compound at different temperatures, are shown in Figure 10. The framework largely persisted after removing the disengaged water molecules by annealing the sample at 300 °C for 20 h. Above 350 °C, the dehydration results in the phase **2**, which is characterized by five distinct peaks. These five peaks at low angle can be indexed as (002), (110), (102), (200), and (012) with a unit cell similar to that of $Na_5[CrB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ ($P2_1/c$, $a = 16.52$ Å, $b = 10.68$ Å, $c = 20.86$ Å, $\beta = 93.42°$). The reflections at high angles become a broad band at about $2\theta \approx 25°$, which indicates a partial decomposition. Thus, the fundamental packing of the cluster is retained in the phase **2**, but the structure is disordered on the atomic scale. At higher temperature (500 °C), the compound further transforms into a completely

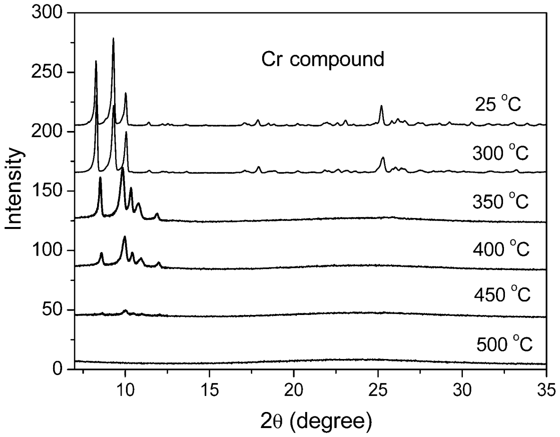

Figure 10. Powder X-ray diffraction patterns collected on the annealed $Na_5[CrB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ sample at different temperatures.

amorphous phase. Therefore, the dehydration of the hydroxy groups is a continuous and irreversible process. The TG-DSC-MS curves of the Al compound are also presented in Figure 8. It can be seen that the DSC curve is somewhat complex, but the TG curve is basically similar to that of the Cr compound and the mass spectral curves are dispersed, possibly due to the poor crystallization.

Magnetic susceptibility (χ) measurements were performed between 2 and 300 K on a polycrystalline sample of the Cr compound at an external field of 100 Oe. A Curie−Weiss fit of the reciprocal susceptibility provides a Curie constant C of 1.81 cm^3 K/mol (see Figure S1 in the Supportin Information), which is in good agreement with the expected value for isolated (high-spin) Cr^{3+} ions. No clear sign for long-range ordering was found above 2.0 K.

Conclusions

In this work, we have reported the synthesis, structure, and thermal properties of the two novel monometal-centered polyborate cluster compounds $Na_5[MB_{24}O_{34}(OH)_{12}]\cdot nH_2O$ ($M = Cr^{3+}, Al^{3+}$), which contain the first examples of a spherelike polyborate cluster with 24 boron atoms. This kind of cluster can be considered as a tetramer of $[B_6O_{10}(OH)_3]^{5-}$ hexaborate subunits having nearly T_d symmetry with one M^{3+} cation in the center. The nuclear site of the cluster is an ideal octahedral environment and is suitable for the location of one Cr^{3+} or Al^{3+} cation. The voids between polyborate clusters are filled by Na^+ cations and disengaged water molecules. When the title compounds are heated, they lose the weight in a stepwise fashion, corresponding to the loss of the disengaged water and the dehydration of the hydroxy groups. The former step is reversible, and the latter is continuous and irreversible. The search for novel borate compounds is intriguing, due to their rich structural diversity and potential industrial applications; these new polyborate clusters with novel structural features may inspire extensions in metal borate cluster chemistry.

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Supporting Information Available: A CIF file giving details of the crystal data, tables giving selected bond distances and angles for $Na_5[CrB_{24}O_{34}(OH)_{12}]\cdot 6.5H_2O$, and a figure giving the Curie–Weiss fit of χ^{-1}. This material is available free of charge via the Internet at http://pubs.acs.org.

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