

# 过渡金属硼酸盐 $K_7\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\} \cdot H_2O$ 的合成与量子化学研究

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**摘要:** 通过水热的方法合成了一例新的过渡金属硼酸盐  $K_7\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\} \cdot H_2O$  (**1**), 并对其进行了红外, 热重, 能谱以及 X-射线单晶衍射和粉末衍射分析。晶体学测试结果表明, 化合物 **1** 属于正交晶系,  $Pmn2_1$  空间群, 晶胞参数  $a=1.236\ 51(4)\text{ nm}$ ,  $b=0.909\ 61(3)\text{ nm}$ ,  $c=1.304\ 05(5)\text{ nm}$ ,  $V=1.466\ 72(9)\text{ nm}^3$ ,  $Z=2$ ,  $R_1=0.049\ 7$ ,  $wR_2=0.146\ 8$ 。对  $\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\}^{7-}$  阴离子簇的量化分析显示此簇中的端基  $BO_3$  基团对前线分子轨道的贡献最大。除端 O 原子外,  $BO_3$  端基的原子电荷较其它 B 和 O 原子电荷低。

**关键词:** 过渡金属; 硼酸盐; 聚阴离子簇; 量子化学

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## Synthesis of Transitional Metal Borate $K_7\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\} \cdot H_2O$ and Quantum Chemistry Study

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**Abstract:** A new transitional metal borate  $K_7\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\} \cdot H_2O$  (**1**) has been synthesized under hydrothermal conditions and characterized by means of IR spectrum, TG, EDS single X-ray and PXRD diffraction. The X-ray crystallography indicates **1** crystallizes in a orthorhombic lattice,  $Pmn2_1$  space group, with  $a=1.236\ 51(4)\text{ nm}$ ,  $b=0.909\ 61(3)\text{ nm}$ ,  $c=1.304\ 05(5)\text{ nm}$ ,  $V=1.466\ 72(9)\text{ nm}^3$ ,  $Z=2$ ,  $R_1=0.049\ 7$ ,  $wR_2=0.146\ 8$ . Quantum chemistry calculation discovers the terminal  $BO_3$  group has a major contribution to the frontier molecular orbitals (FMOs) of the  $\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\}^{7-}$  cluster. The atom charges in the terminal  $BO_3$  group are lower than that of the other B and O atoms, except for the terminal O atom in the  $BO_3$  group. ICSD: 424019.

**Key words:** transitional metal; borate; polyanion cluster; quantum chemistry

## 0 Introduction

Borate materials containing transitional metals have attracted much research interest due to their rich structural chemistry and diverse applications in mineralogy and industry<sup>[1-5]</sup>. From the point of chemistry, boron atoms coordinate with oxygen not only in three-fold (triangular,  $BO_3$ ) but also in four-fold coordination

(tetrahedral,  $BO_4$ ). These  $BO_3$  and  $BO_4$  can further polymerize to all kinds of large oxoborate clusters through common corners (oxygen atoms). Such polyanion clusters can be considered as the secondary building units (SBUs) to take part in the construction of novel borates. In the past seven decades, borates have formed the following systems: main group and transition metal (TM) borates<sup>[6]</sup>, rare earth borates<sup>[7-8]</sup>, organically<sup>[9-11]</sup>

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and TM-complex templated borates<sup>[12-14]</sup>. Wherein, the most borates with framework containing metal were made by temperature solid state method or boric acid flux method. It's very rare for the metal borates synthesized by the hydrothermal conditions<sup>[15]</sup>. Although people have discovered about 30 borate polyanion clusters, the theoretic research about the electronic structures of the clusters has only attracted relatively little attention<sup>[16]</sup>. In this paper, we report a novel transitional metal borates  $K_7\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\} \cdot H_2O$  (**1**) with framework containing a distorted  $O_2ZnO_3$  square pyramid. Besides, we using density functional theory (DFT)<sup>[17]</sup> calculated the electronic structure of  $\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\}^{7-}$  cluster at B3LYP/(6-31G(d)+LanL2DZ) level and natural bond orbital (NBO) population was analyzed under the Gaussian 09 program.

## 1 Experimental

### 1.1 Materials and methods

All chemicals were purchased from commercial sources and used without further purification. The FT-IR spectrum (KBr pellet) was recorded on an ABB Bomen MB 102 spectrometer. Thermogravimetric analysis was performed on a Mettler TGA/SDTA 851e analyzer with a heating rate of  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$  under an air atmosphere. Energy dispersive spectroscopy (EDS) scanning was analyzed by JEOL JSM6700F Field Emission Scanning Electron Microscope (FESEM). Powder X-ray diffraction (PXRD) patterns were

collected on a Rigaku DMAX 2500 diffractometer using graphite-monochromated Cu  $K\alpha$  radiation ( $\lambda=0.154\text{ nm}$ ) in the angular range  $2\theta=5^\circ\sim65^\circ$  with a step size of  $0.05^\circ$ .

### 1.2 Synthesis and characterization

Synthesis of the compound **1** was achieved by a hydrothermal technique in a Teflon-lined stainless steel bomb under synthetic reaction conditions determined empirically. A mixture of  $Zn(CH_3COO)_2 \cdot 2H_2O$  (0.219 g),  $K_2B_4O_7 \cdot 4H_2O$  (0.307 g),  $H_2O$  (1.0 mL) and DMF (5.0 mL) in a molar ratio of about 1:1:56:68 was sealed in a 30 mL stainless reactor with a Teflon liner at  $180\text{ }^\circ\text{C}$  for 7 d, then cooled to room temperature. Colorless block crystals of **1** were recovered by filtration, washed with distilled water and dried in air, respectively. Yield: 40% (based on Zn).

### 1.3 Single-crystal structure determination

The intensity data sets were collected on Rigaku Mercury CCD with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda=0.071\text{ nm}$ ) in the  $\omega$  scanning mode at room temperature. All absorption corrections were performed using the multiscan program. The structure was solved by direct methods and refined by full-matrix least squares on  $F^2$  with the SHELX-97 program<sup>[18]</sup>. All nonhydrogen atoms were refined anisotropically. The hydrogen atoms associated with the hydroxyl groups were added in the riding model and refined isotropically. The hydrogen atoms of the water molecule couldn't be identified because of the disorder of the oxygen atom

Table 1 Crystal data for compound 1

Empirical formula	$H_8B_{13}K_7O_{28}Zn$	Absorption correction	Empirical
Formula weight	935.66	$F(000)$	920
Temperature / K	293(2)	Crystal size / mm	0.2×0.2×0.3
Wavelength / nm	0.071073	$\theta$ range / $^\circ$	2.24~25.73
Crystal system	Orthorhombic	Limiting indices	$-15 \leq h \leq 15, -10 \leq k \leq 11, -12 \leq l \leq 15$
Space group	$Pmn2_1$	Reflections collected / unique ( $R_{int}$ )	7 825 / 2 463 (0.029 0)
$a$ / nm	1.236 51(4)	Completeness to $\theta$ / %	100.0
$b$ / nm	0.909 61(3)	Refinement method	Full-matrix least-squares on $F^2$
$c$ / nm	1.304 05(5)	Data / restraints / parameters	2 463 / 1 / 244
Volume / nm <sup>3</sup>	1.466 72(9)	Goodness-of-fit on $F^2$	1.183
$Z$	2	Final $R$ indices ( $I>2\sigma(I)$ )	$R_1=0.049\text{ 7}, wR_2=0.146\text{ 8}$
$D_c$ / (g·cm <sup>-3</sup> )	2.119	$R$ indices (all data)	$R_1=0.052\text{ 9}, wR_2=0.149\text{ 8}$
Absorption coefficient / mm <sup>-1</sup>	1.938	Largest diff. peak and hole/ (e <sup>-</sup> ·nm <sup>-3</sup> )	1 405 and -985

Table 2 Selected bond distances (nm) and bond angles ( $^\circ$ ) for compound 1

Zn(1)-O(2)	0.201 5(7)	Zn(1)-O(1) <sup>i</sup>	0.205 0(4)	Zn(1)-O(1)	0.205 0(4)
Zn(1)-O(11) <sup>i</sup>	0.215 6(7)	Zn(1)-O(11)	0.215 6(7)	O(1)-B(2)	0.148 5(9)
O(1)-B(1)	0.149 9(8)	O(2)-B(4) <sup>i</sup>	0.149 1(8)	O(2)-B(4)	0.149 1(8)
O(3)-B(1)	0.143 1(8)	O(3)-B(1) <sup>i</sup>	0.143 1(8)	O(4)-B(3)	0.135 2(10)
O(4)-B(1)	0.147 5(8)	O(5)-B(3)	0.133 2(10)	O(5)-B(2)	0.147 9(8)
O(6)-B(5)	0.136 2(8)	O(6)-B(4)	0.146 5(9)	O(7)-B(6)	0.135 6(10)
O(7)-B(4)	0.146 6(9)	O(8)-B(2)	0.142 9(10)	O(8)-B(4)	0.144 8(8)
O(9)-B(6)	0.136 1(9)	O(10)-B(6)	0.137 0(9)	O(10)-B(2)	0.146 9(8)
O(11)-B(8)	0.128 8(8)	O(12)-B(8)	0.124 8(13)	O(13)-B(3)	0.139 9(10)
O(14)-B(7)	0.134 5(7)	O(14)-B(1)	0.1481(9)	O(15)-B(7)	0.140 8(13)
O(16)-B(5)	0.138 2(15)	B(5)-O(6) <sup>i</sup>	0.136 2(8)	B(7)-O(14) <sup>i</sup>	0.134 5(7)
B(8)-O(11) <sup>i</sup>	0.128 8(8)				
O(2)-Zn(1)-O(1) <sup>i</sup>	102.14(19)	O(2)-Zn(1)-O(1)	102.14(19)	O(1) <sup>i</sup> -Zn(1)-O(1)	101.9(2)
O(2)-Zn(1)-O(11) <sup>i</sup>	105.5(3)	O(1) <sup>i</sup> -Zn(1)-O(11) <sup>i</sup>	92.5(2)	O(1)-Zn(1)-O(11) <sup>i</sup>	145.3(3)
O(2)-Zn(1)-O(11)	105.5(3)	O(1) <sup>i</sup> -Zn(1)-O(11)	145.3(3)	O(1)-Zn(1)-O(11)	92.5(2)
O(11) <sup>i</sup> -Zn(1)-O(11)	60.2(3)	B(2)-O(1)-B(1)	125.5(5)	B(4) <sup>i</sup> -O(2)-B(4)	127.1(8)
B(1)-O(3)-B(1) <sup>i</sup>	121.1(7)	B(3)-O(4)-B(1)	121.5(5)	B(3)-O(5)-B(2)	122.1(6)
B(5)-O(6)-B(4)	123.5(6)	B(6)-O(7)-B(4)	120.4(5)	B(2)-O(8)-B(4)	120.3(5)
B(6)-O(10)-B(2)	120.4(6)	B(7)-O(14)-B(1)	118.2(6)	O(3)-B(1)-O(4)	107.9(6)
O(3)-B(1)-O(14)	111.4(5)	O(4)-B(1)-O(14)	107.5(5)	O(3)-B(1)-O(1)	111.1(5)
O(4)-B(1)-O(1)	111.1(5)	O(14)-B(1)-O(1)	107.9(5)	O(8)-B(2)-O(10)	110.5(5)
O(8)-B(2)-O(5)	108.2(6)	O(10)-B(2)-O(5)	107.5(5)	O(8)-B(2)-O(1)	111.9(5)
O(10)-B(2)-O(1)	107.6(6)	O(5)-B(2)-O(1)	111.1(5)	O(5)-B(3)-O(4)	126.1(7)
O(5)-B(3)-O(13)	117.7(7)	O(4)-B(3)-O(13)	116.2(7)	O(8)-B(4)-O(6)	108.1(6)
O(8)-B(4)-O(7)	111.0(5)	O(6)-B(4)-O(7)	107.6(5)	O(8)-B(4)-O(2)	111.8(5)
O(6)-B(4)-O(2)	109.8(6)	O(7)-B(4)-O(2)	108.5(6)	O(6)-B(5)-O(6) <sup>i</sup>	123.0(11)
O(6)-B(5)-O(16)	118.5(5)	O(6) <sup>i</sup> -B(5)-O(16)	118.5(5)	O(7)-B(6)-O(9)	119.4(6)
O(7)-B(6)-O(10)	123.0(6)	O(9)-B(6)-O(10)	117.5(7)	O(14) <sup>i</sup> -B(7)-O(14)	126.8(10)
O(14) <sup>i</sup> -B(7)-O(15)	116.6(5)	O(14)-B(7)-O(15)	116.6(5)	O(12)-B(8)-O(11) <sup>i</sup>	122.8(5)
O(12)-B(8)-O(11)	122.8(5)	O(11) <sup>i</sup> -B(8)-O(11)	114.2(10)		

Symmetry transformations used to generate equivalent atoms: <sup>i</sup> -x, y, z.

in the water molecule. Crystal data and structural refinement parameters for **1** are summarized in Table 1 and selected bond lengths and angles are listed in Table 2.

ICSD: 424019.

#### 1.4 Computational description

The energy of polyanion  $\{(\text{BO}_3)\text{Zn}[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\}^{7-}$  was calculated at the gradient-correction DFT level using the three-parameter fit of exchange and correlation functionals of Becke (B3LYP)<sup>[19]</sup>, which includes the correlation functional of Lee et al<sup>[20]</sup>. The 6-31G (d) Pople basis set was applied for B, H and O

atoms and the LanL2DZ effective core potential basis set was used for Zn atom. Natural bond orbital (NBO) analysis<sup>[21-22]</sup> was carried out at B3LYP/(6-31G(d)+LanL2DZ) level of theory to reveal the partial charge of atom and donor and acceptor interactions. All computations were done by Gaussian09<sup>[23]</sup>.

## 2 Results and discussion

### 2.1 Description of the structure

Single-crystal X-ray analysis indicates the asymmetric unit of compound **1** contains 30 independent non-H atoms, including 1 Zn, 5 K, 7 B and 17 O atoms.

As shown in Fig.1, four independent B atoms B3, B5, B6, B7, B8 adopt triangle coordination models. Among them, B3, B5, B6 and B7 are coordinated by two O atoms and one -OH forming  $\text{BO}_2(\text{OH})$  triangles with B-O bond distances vary from 0.133 1 to 0.141 0 nm. Different from the B3, B5, B6 and B7 atoms, the B8 atom is coordinated by two  $\mu_2\text{-O}$  atoms and one terminal O atom forming the B (8) $\text{O}_3$  triangle and the B-O bond lengths varying from 0.124 8 to 0.1286 nm in the B (8) $\text{O}_3$  triangle, which are significantly shorter than the other B-O bonds in the  $\text{BO}_2(\text{OH})$  triangles. In the asymmetric unit, B1, B2 and B4 atoms are coordinated by four O atoms forming  $\text{BO}_4$  tetrahedra with bond distances varying from 0.143 0 to 0.150 3 nm. The Zn atom is coordinated by three  $\mu_3\text{-O}$  atoms with Zn-O bonds changing from 0.2016 to 0.2019 nm and two  $\mu_2\text{-O}$  atoms with the same Zn-O bonds 0.2153 nm. The Zn atom and the terminal  $\text{BO}_3$  group are joined together by the sharing-edge linking of two  $\mu_2\text{-O}$  atoms forming a crown structure of  $\text{BO}_3\text{ZnO}_3$  (Fig. 2a). Six  $\text{BO}_4$  are linked together by six O vertexes and each adjacent two  $\text{BO}_4$  tetrahedra are bridged by one  $\text{BO}_2(\text{OH})$  triangle to form  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  polyanion cluster<sup>[24]</sup> (Fig.2b), which is further linked with the  $\text{BO}_3\text{ZnO}_3$  crown through three  $\mu_3\text{-O}$  atoms constructing the  $\{(\text{BO}_3)\text{Zn}[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\}^{7-}$  polyanion cluster (Fig.2c). Then, the  $\{(\text{BO}_3)\text{Zn}[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\}^{7-}$  clusters are further connected by H-bonding interaction into a 2D supermolecular framework. The  $\text{K}^+$  cations reside between adjacent clusters compensating the negative charges of

the clusters and hold them together into a 3D structure through bonding with oxygen atoms of the polyanion clusters (Fig.2d).

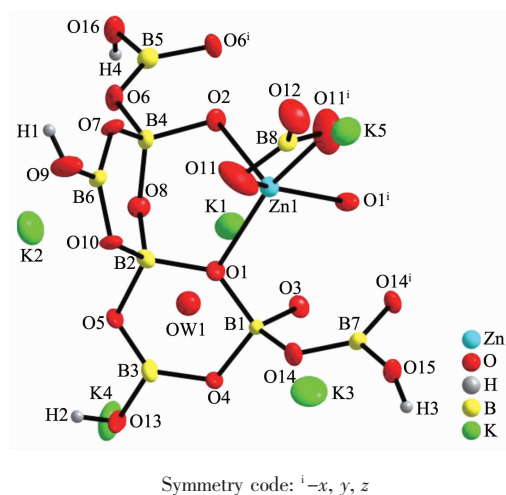


Fig.1 ORTEP drawing of the asymmetric unit of the compound **1** with 50% probability ellipsoid for non-H atoms

## 2.2 Thermogravimetric (TG) analysis

TG analysis shows the compound **1** has two step losing water (Fig.3). The loss of 2% weight in the first step from 30 to 360 °C corresponds to the release of the free water molecule (Calcd. 1.8%). Above 360 °C, a graduate weight loss of 11.0% up to 600 °C is observed and was assigned to the removal of the hydroxyl groups (Calcd. 10.9%).

## 2.3 Powder X-ray diffraction (PXRD) analysis

To investigate the effect of water loss on the structure of the compound **1**, the PXRD patterns were recorded before and after water loss of compound **1**.

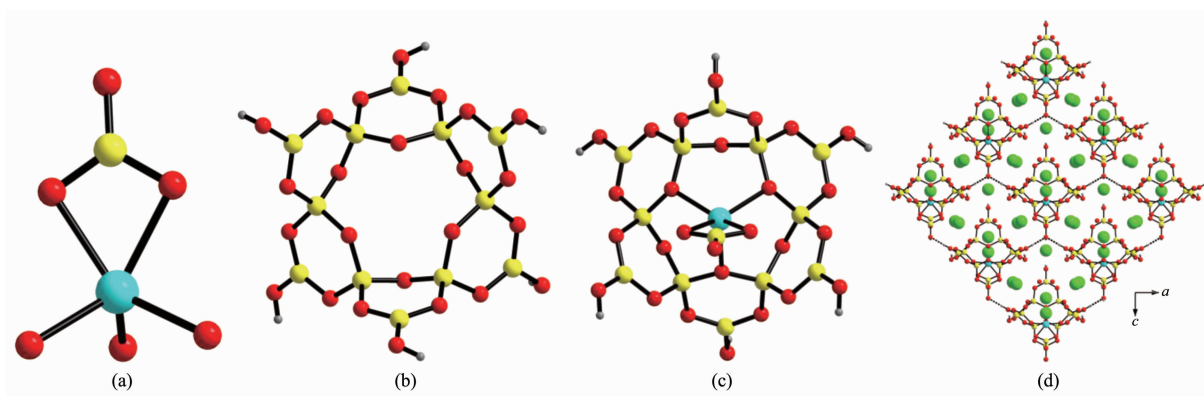
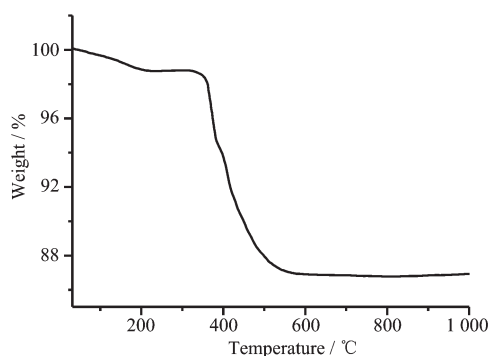
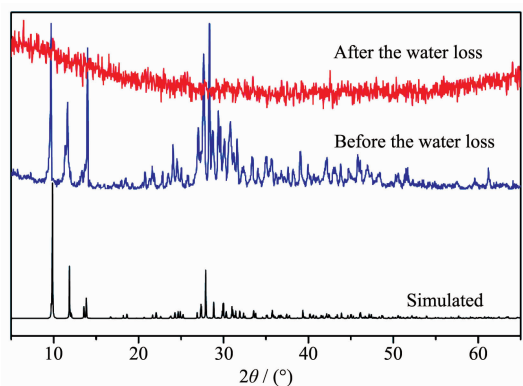


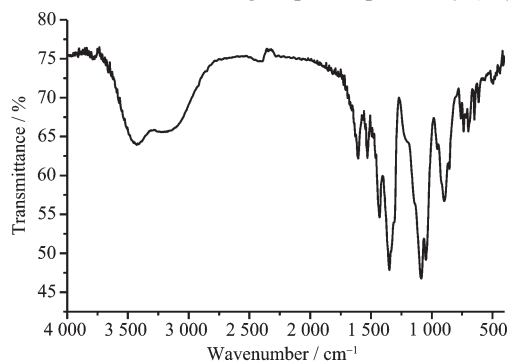
Fig.2 (a)  $\text{BO}_3\text{ZnO}_3$  crown structure; (b)  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  cluster formed by six  $\text{BO}_4$  tetrahedra and six  $\text{BO}_2(\text{OH})$  triangles; (c)  $\{(\text{BO}_3)\text{Zn}[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\}^{7-}$  polyanion cluster constructed by the linking of the  $\text{BO}_3\text{ZnO}_3$  crown and the  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  cluster; (d) View of the compound **1** along the  $b$  axis

Fig.3 TG curve of the compound **1**Fig.4 Experimental and simulated PXRD patterns of the compound **1** before and after the water loss

As showed in Fig.4, before the water loss, the experimental diffraction peaks of the compound **1** correspond well with those simulated on the basis of single crystal structure, which indicates the structure is stable at room temperature. After heating at 600 °C, however, all the diffraction peaks of the remainder disappeared, which confirms the structure of the compound **1** is corrupted after losing water at 600 °C.

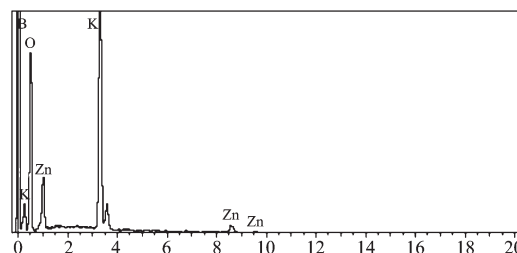
### 2.3 Infrared (IR) spectrum

The IR spectrum of **1** shows three obviously characteristic peaks at 1 346, 1 095 and 890  $cm^{-1}$  corresponding to  $BO_3$ ,  $BO_4$  and  $ZnO_5$  groups, respectively (Fig.5).

Fig.5 IR spectrum of the compound **1**

### 2.4 Energy dispersion spectroscopy (EDS) analysis

The Fig.6 shows the result by EDS analysis. It is further demonstrated that the compound **1** contains B, O, K and Zn atoms. H atom is too light to be detected by EDS.

Fig.6 EDS spectrum of the compound **1**

### 2.5 Quantum chemistry analysis

The frontier molecular orbitals (FMOs) and nature bond orbitals (NBOs) of the  $\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\}^{7-}$  polyanion cluster were analyzed through quantum chemistry method. The results show the main orbital components in the highest occupied orbital (HOMO) are concentrated on the terminal B (8) $O_3$  group linked with Zn atom. The contribution of the terminal O(12) atom orbital in  $BO_3$  group to HOMO orbital is 47%. Besides, each O atom of the bridged O(11) and O(11<sup>i</sup>) provides a 20% contribution to HOMO orbital and the contribution of the B(8) is 11%. Surprising is that the contribution of the Zn to the HOMO is only 3%. Similar with the composition of the HOMO orbital, the main components in the lowest unoccupied orbital (LUMO) come from the three O atoms from the terminal B (8) $O_3$  group. The contributions of the terminal O(12) and two bridged O atoms O(11) and O(11<sup>i</sup>) in the B (8) $O_3$  to the LUMO are 28%, 34% and 34%, respectively. The contribution of Zn to the LUMO is only 2%. Different from the HOMO, the B (8) atom doesn't take part in the construction of the LUMO. NBO analysis shows the atomic charges in B (8) $O_3$  group has a greatly different from the other atoms in the  $\{(BO_3)Zn[B_{12}O_{18}(OH)_6]\}^{7-}$  polyanion cluster. The charge of the B(8) is 0.99, which is remarkable lower than the average charge of 1.28 of the other B atoms. The two bridged O(11) and O(11<sup>i</sup>) atoms in the B(8) $O_3$  have the same charge -0.88 lower the average

charge  $-0.99$  of the O atoms in  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  group. The charge of the terminal O (12) in  $\text{B}(8)\text{O}_3$  is  $-0.98$  consistent with the average charge. Interestingly, the metal Zn atom has a charge of  $1.29$ , which is identical with the average charge of the B atoms in the  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  cluster.

### 3 Conclusions

In summary, a new transitional metal borates  $\text{K}_7\{(\text{BO}_3)\text{Zn}[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\} \cdot \text{H}_2\text{O}$  constructed with the terminal  $\text{BO}_3$  group, Zn atom,  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  and counter K cations has been successfully made under hydrothermal conditions. Quantum chemistry calculation for the  $\{(\text{BO}_3)\text{Zn}[\text{B}_{12}\text{O}_{18}(\text{OH})_6]\}^{7-}$  cluster shows the main components of the FMOs come from the contribution of the terminal  $\text{B}(8)\text{O}_3$  group. The atom charges except for O(12) in the  $\text{B}(8)\text{O}_3$  group are significantly lower than that of the  $[\text{B}_{12}\text{O}_{18}(\text{OH})_6]^{6-}$  cluster.

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