



Three new vanadoborates functionalized with zinc complexes



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ABSTRACT

Three new vanadoborates $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}](\text{H}_2\text{dap})_4(\text{dap})_2 \cdot 9\text{H}_2\text{O}$ (**1**), $[\text{Zn}(\text{H}_2\text{teta})_2\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6] \cdot 4\text{H}_3\text{O}$ (**2**) and $[\text{Zn}(\text{H}_3\text{tepa})\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6][\text{H}_2\text{en}]_2 \cdot \text{H}_3\text{O} \cdot 3\text{H}_2\text{O}$ (**3**) have been hydrothermally synthesized and structurally characterized. **1** consists of new cluster $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}]^{8-}$ with the rare $[\text{Zn}_4\text{B}_4\text{O}_{18}]$ unit, protonated $\text{H}_2\text{dap}^{2+}$, free dap and H_2O molecules. Both **2** and **3** contain $[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6(\text{H}_2\text{O})]^{10-}$ clusters, which are connected by $[\text{Zn}(\text{H}_2\text{teta})_2]^{2+}/[\text{Zn}(\text{H}_3\text{tepa})]^{2+}$ groups as bridges into 1-D chain. The magnetic susceptibility of **3** shows the antiferromagnetic interaction between V^{IV} cations.

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The study of new polyoxovanadates is a very active and expanding research area, because various types of valence states of V^{n+} ions ($n = +3, +4, +5$) could provide interesting catalytic or magnetic properties [1]. The vanadoborates are a growing family among the polyoxovanadates, where different B–O–V clusters are observed, as exemplified by $[\text{V}_{12}\text{B}_{18}\text{O}_{60}]$ [2], $[\text{V}_6\text{B}_{22}\text{O}_{53}]$ [3], $[\text{V}_{12}\text{B}_{16}\text{O}_{58}]$ [4], and $[\text{V}_6\text{B}_{22}\text{O}_{54}]$ [5]. These vanadoborate clusters with many exposed surface O atoms can act as good donors to coordinate to electrophiles of transition metal (TM) ions or TM complex moieties, resulting in the formation of one-, two-, and three-dimensional extended solid vanadoborates [2–5]. The introduction of TM ions or TM complex moieties can not only enrich structural moieties of vanadoborates, but can also modify their electronic and magnetic properties. Among vanadoborates, the B–O–V clusters are mainly constructed by $[\text{VO}_5]$ square-pyramids and $[\text{BO}_x]$ ($x = 3, 4$) polyhedra, but a few vanadoborate clusters incorporating other polyhedral atoms have been documented [2–5]. Hence, the synthesis of the new vanadoborate clusters containing other heteroatoms has become an attractive but challenging goal. Herein we report the hydrothermal synthesis and crystal structure of the three new vanadoborates $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}](\text{H}_2\text{dap})_4(\text{dap})_2 \cdot 9\text{H}_2\text{O}$ (**1**), $[\text{Zn}(\text{H}_2\text{teta})_2\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6] \cdot 4\text{H}_3\text{O}$ (**2**) and $[\text{Zn}(\text{H}_3\text{tepa})\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6][\text{H}_2\text{en}]_2 \cdot \text{H}_3\text{O} \cdot 3\text{H}_2\text{O}$ (**3**). The $[\text{ZnO}_4]$ tetrahedron in **1** is incorporated into vanadoborate framework to form an interesting vanadoborate cluster, while the $[\text{Zn}(\text{H}_2\text{teta})_2]^{2+}/[\text{Zn}(\text{H}_3\text{tepa})]^{2+}$ complexes in **2** and **3** acting as bridges link $[\text{V}_{12}\text{B}_{18}]$ clusters up into 1-D extended vanadoborates.

Abbreviations: dap, diaminopropane; teta, triethylenetetramine; en, ethylenediamine; teпа, tetraethylenepentamine.

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Green block crystals of **1** were obtained by solvothermal reaction of NH_4VO_3 , H_3BO_3 , ZnO, dap and H_2O at 135 °C for 5 days. **1** contains new cluster $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}]^{8-}$, protonated $\text{H}_2\text{dap}^{2+}$, free dap and H_2O molecules. The B atoms adopt two kinds of coordination models, namely the $[\text{BO}_3]$ triangles and $[\text{BO}_4]$ tetrahedral. The interconnection of the $[\text{BO}_3]$ triangles and $[\text{BO}_4]$ tetrahedral leads to a quadrilateral $[\text{B}_{14}\text{O}_{32}]$ ring (Fig. 1a). Ten edge-sharing $[\text{VO}_5]$ units construct an ellipsoidal $[\text{V}_{10}\text{O}_{30}]$ ring (Fig. 1b). Each Zn^{2+} ion adopts a tetrahedral $[\text{ZnO}_4]$ coordination geometry. The $[\text{ZnO}_4]$ and $[\text{BO}_3]$ units are connected by edge and corner-sharing O atoms to form a dumbbell-like $[\text{Zn}_4\text{B}_4\text{O}_{18}]$ unit with a center of inversion (Fig. 1c). One $[\text{V}_{10}\text{O}_{30}]$ ring is sandwiched between two $[\text{B}_{14}\text{O}_{32}]$ units, resulting in a hollow barrel-like $[\text{V}_{10}\text{B}_{28}\text{O}_{74}]$ cluster. The $[\text{Zn}_4\text{B}_4\text{O}_{18}]$ unit is fixed within the $[\text{V}_{10}\text{B}_{28}\text{O}_{74}]$ cluster via four $\text{Zn}-(\mu_3\text{-O})-\text{B}_2$ bonds to form a $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}]^{8-}$ cluster (Fig. 1d). The $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}]^{8-}$ clusters adopt the NaCl-type stacking mode and each $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}]^{8-}$ cluster is surrounded by other $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}]^{8-}$ clusters (Fig. 2). Bond valence sum calculations [6] indicate clearly a charge of V^{4+} for each vanadium center. The framework stoichiometry of $[\text{Zn}_4\text{V}_{10}\text{B}_{34}\text{O}_{84}\text{H}_{10}]$ creates a charge of -8 , which can be balanced by four $\text{H}_2\text{dap}^{2+}$ ions.

Brown block crystals of **2** and **3** were prepared by a similar method used in the synthesis of the crystals of **1** except that dap was replaced by teta and teпа, respectively. Both **2** and **3** contain similar $[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6(\text{H}_2\text{O})]^{10-}$ cluster (Fig. S1). The $[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6(\text{H}_2\text{O})]^{10-}$ cluster can be considered as the puckered $[\text{B}_{18}\text{O}_{36}(\text{OH})_6]$ ring sandwiched between two triangular vanadium-oxo moieties. The V oxidation states were confirmed by valence bond calculation [6], which shows an average valence of about 4.14 for **2** and 4.16 for **3**. These values are close to the 4.17 expected for a $\text{V}^{\text{IV}}:\text{V}^{\text{V}}$ ratio of 5:1, so two of the twelve V atoms are V^{V} and ten are V^{IV} . The existence of V(IV) accounts for the brown color of the crystal. In **2** and **3**, the $[\text{V}_{12}\text{B}_{18}\text{O}_{54}(\text{OH})_6(\text{H}_2\text{O})]^{10-}$ clusters

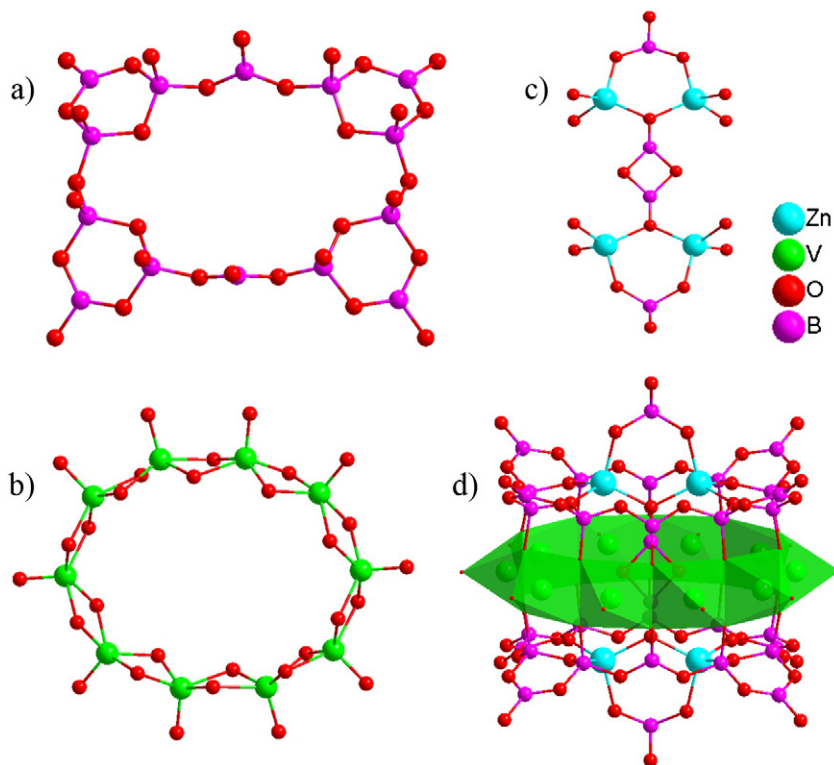


Fig. 1. The structures of the $[B_{14}O_{26}(OH)_4]$ ring (a), $[V_{10}O_{30}]$ ring (b), $[Zn_4B_4O_{18}]$ unit (c) and $[Zn_4V_{10}B_{34}O_{84}H_{10}]^{8-}$ cluster (d).

are linked to each other by μ_2 - $[Zn(H_2teta)_2]/[Zn(H_3tepa)]$ bridges, leading to two different 1-D hybrid chains (Fig. 3a–b).

In **2**, the Zn1 atom is coordinated by four N atoms of two tetra ligands and two O atoms from two adjacent $[V_{12}B_{18}O_{54}(OH)_6(H_2O)]^{10-}$ clusters, showing a slightly distorted octahedron (Fig. 3c). Tetra molecule of **2** adopts a rare bichelating coordination mode with two uncoordinated N atoms. Usually tetra displays a tetrachelating ligand [7,8]. The only example is $[Ni(teta)_2]_2Ge_4Se_{10} \cdot 0.5H_2O$ [8], where tetra acts as bi- and

tetrachelating ligand coordinating to the nickel atom and the uncoordinated N atoms are not protonated. But tetra of **2** is diprotonated (H_2teta^{2+} ion) and balance the charge of $[V_{12}B_{18}O_{54}(OH)_6(H_2O)]^{10-}$ cluster.

Although tepe was used as the structure-directing agent in the reaction of **3**, structural analysis identifies the presence of protonated H_2en^{2+} in the product, which suggests that part of tepe was converted into en via in-situ fragmentation reactions under the hydrothermal conditions. The Zn^{2+} ion is chelated by two bidentate tepe ligands and coordinated by two O atoms from two $[V_{12}B_{18}O_{54}(OH)_6(H_2O)]^{10-}$ clusters to form a distorted octahedron with a *cis*-configuration (Fig. 3d). The tepe molecule of **3** acts as a new bichelating coordination mode with three uncoordinated N atoms, because it usually displays a pentachelating ligand [9–12].

The solid-state reflectance spectrum of **3** was obtained at room temperature (Fig. S4). The absorption data were calculated from the reflectance using the Kubelka–Munk function [13]. The higher energy band at 345 nm (3.59 eV) can be assigned to the lowest possible electronic excitation located at $[V_{12}B_{18}O_{54}(OH)_6(H_2O)]^{10-}$ cluster. Compared with the crystal V_2O_5 (2.20 eV) [14], there is a noticeable blue shift of the absorption edge. The weak absorptions at about 552 nm (1.85 eV), 532 nm (2.33 eV) and 475 nm (2.61 eV) presumably arise from d–d electronic transition [2]. In the IR spectra of **1–3**, the bands at 1342–1399 cm^{-1} are due to the asymmetrical stretch of the $[BO_3]$ group, while the bands at 1023–1050 cm^{-1} are attributed to the asymmetrical stretch of the $[BO_4]$ tetrahedron [2–5]. The bands at 920–946 cm^{-1} are attributed to the asymmetrical stretching vibration of the terminal $V=O$ [2–5]. The variable-temperature magnetic susceptibility of **3** was measured between 2 and 300 K. Fig. 4 shows the magnetic behavior of **3** in the form of the product $\chi_M T$ versus temperature, where χ_M is the molar magnetic susceptibility. The $\chi_M T$ value of 1.54 $cm^3 \cdot K \cdot mol^{-1}$ at 300 K is much lower than the spin only value of 3.75 $cm^3 \cdot K \cdot mol^{-1}$ expected for ten uncoupled $S = 1/2 V^{4+}$ centers considering $g = 2$. The $\chi_M T$ value decreases smoothly from 1.54 $cm^3 \cdot K \cdot mol^{-1}$ at 300 K to 0.11 $cm^3 \cdot K \cdot mol^{-1}$ at 2 K. The temperature dependencies of $\chi_M T$ for **1** demonstrate the existence of a strong

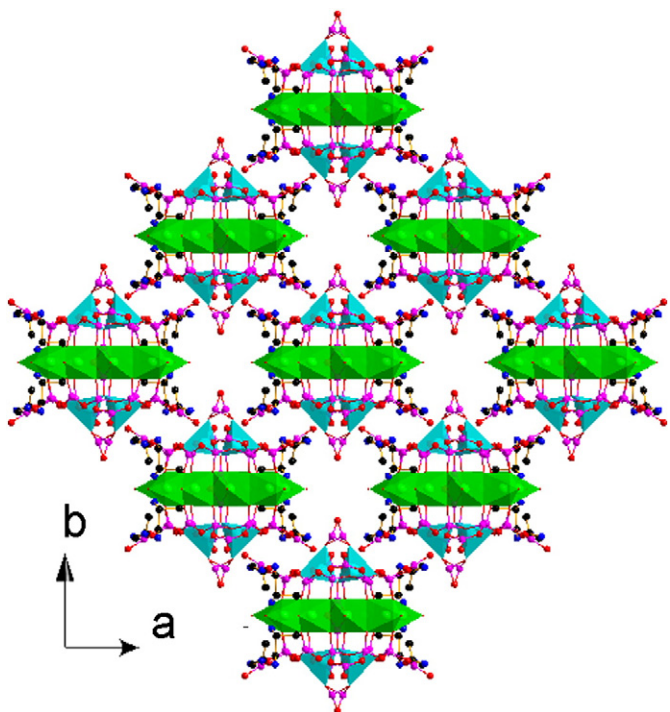


Fig. 2. Crystal packing of **1**.

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