The New Vanadoborate-supported Hexanuclear Zinc Complex $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)\cdot 8H_2O$

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The new vanadoborate-supported zinc complex $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)\cdot 8H_2O$ (**1**, teta = triethylenetetramine) was synthesized hydrothermally and characterized by elemental and thermogravimetric analysis, and IR and UV/Vis spectroscopy. Complex **1** crystallizes in the trigonal system in space group $R\bar{3}$ and consists of the neutral $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)$ cage aggregate that is built up from a $[(VO)_{12}O_6B_{18}O_{36}(OH)_6]^{12-}$ cluster decorated with six $[Zn(teta)]^{2+}$ complex groups, and a water molecule occupying the center of the cluster cage.

Key words: Vanadium, Hydrothermal Synthesis, Crystal Structures, Borates

Introduction

Increasing interest in polyoxometalates (POMs) mainly stems from a fascinating variety of structures and applications including catalysis, medicine and magnetism [1], although the mechanisms of their formation are still not well understood and commonly described as self-assembly. A recent important advance in POMs chemistry is that POMs with transition metal complexes (TMCs) as decorating groups produce POM-supported TMCs by molecular assemblies, as exemplified by $[Mo_8V_7O_{42}][Cu(2,2'\text{-bpy})_2]_2[Cu(2,2'\text{-bpy})]\cdot 2H_3O$ [2], $[(BW_{12}O_{40})Cd(2,2'\text{-bpy})_2(H_2O)][Cd(2,2'\text{-bpy})_3]_{1.5}\cdot 0.5H_2O$ [3], $\{Mo_8V_8O_{40}(PO_4)[Co(phen)(en)(H_2O)]_2\}[Co(phen)_3]\cdot 1.5\ H_2O$ [4], and $[Cu_5(2,2'bpy)_6(H_2O)][GeW_8O_{31}]\cdot 9H_2O$ [5]. The use of TMCs as decorating group has several distinct features. Among them, the most important one is the integration of electronic, optical, and magnetic properties of TMCs with those of POMs, which helps to fine-tune the material properties and brings about novel synergistic effects.

Boron vanadium clusters, one of the most important subclasses of POMs, have been extensively studied. A number of vanadoborates with unprecedented structures, as exemplified by $[H_2en]_4[Hen]_2[V_6B_{22}O_{53}H_8]\cdot 5H_2O$ [6], $(enH)(enH_2)_4[(VO)_{12}B_{17}O_{38}(OH)_8]\cdot H_2O$ [7], $(enH_2)_5[(VO)_{12}O_6\{B_3O_6(OH)\}_6]\cdot H_2O$ [7], $(enH_2)_3[(VO)_{12}O_4\{B_8O_{17}(OH)_4\}_2\{Na(H_2O)\}_2]\cdot(H_3O)_2(H_2O)_{6.5}$ [8], and $Na_2(H_2en)_2\{(VO)_{10}[B_{14}O_{30}(OH)_2]_2\}\{Mn_4(C_2O_4)[B_2O_4(OH)_2]_2\}Mn(H_2O)_2(H_3O)_{12}(H_2O)_{19}$ [9], have been obtained from B-V-O systems under hydrothermal conditions, but vanadoborate-supported TMCs are less explored. There is only one example of vanadoborate-supported TMCs, $[Zn(en)_2]_6[(VO)_{12}O_6B_{18}O_{39}(OH)_3]\cdot 13\,H_2O$ [10], where a $[(VO)_{12}O_6B_{18}O_{39}(OH)_3]^{12-}$ cluster is decorated by six $[Zn(en)_2]^{2+}$ groups. To learn more about vanadoborate-supported TMC systems, we started to explore further the system $V_2O_5/TM^{2+}/H_3BO_3/$amine (amine = chelating organic amine) and obtained the compound $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)\cdot 8H_2O$ using hydrothermal conditions.

Results and Discussion

As shown in Fig. 1, the smallest formula unit of **1** contains two V atoms, three B atoms, ten O atoms, one Zn(teta) complex and three water molecules. Each V atom adopts a square-pyramidal environment (VO_5) with the V–O distances ranging from 1.619(2) to 2.019(2) Å and O–V–O angles from 77.60(7) to 145.09(7)°. The B atoms adopt two modes of coordination with B–O bond lengths varying from 1.351(4) to 1.378(4) Å for the BO_3 triangles and 1.456(3) to 1.511(3) Å for the BO_4 tetrahedra. The O–B–O bond angles are distributed in the range of 115.1(3) – 122.9(2)° for the triangles and 105.6(2) – 112.3(2)° for the tetrahedra. These data are in agreement with those of other vanadoborates [6–10]. The Zn^{2+} ion is coordinated to four N atoms of one teta ligand and one O atom, forming a distorted square pyramid with

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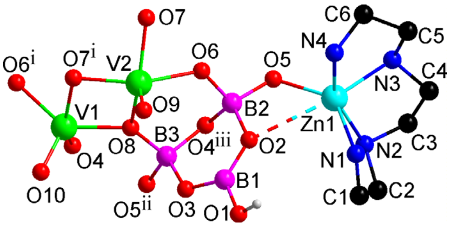

Fig. 1 (color online). Part of the molecular structure of **1** in the crystal showing the $B_3O_6(OH)^{4-}$ unit and the coordination spheres of the Zn and V atoms. H atoms bonded to C/N atoms, uncoordinated water molecules and disordered C/N atoms are omitted for clarity. Symmetry operations: (i) $-x+y, -x, z$; (ii) $y, x+y, -z$; (iii) $x-y, x, -z$.

Zn–N bond lengths of 2.067(10) – 2.231(9) Å and a Zn1–O5 bond length of 1.979(2) Å. Besides a regular Zn–O bond, the Zn atom also has weak but significant Zn···O interactions at the longer distance of 2.831 Å for Zn1–O2, shorter than the sum of the van der Waals' radii of Zn and O (3.19 Å) [11]. As a result, the Zn atom completes its coordination sphere *via* weak bonds to O atoms forming a distorted octahedron (ZnN_4O_2). On the basis of valence sum ($\sum_s$) calculations [12], the oxidation state of the V atoms in **1** is +4 ($\sum_s$ = 4.01 – 4.12, average value 4.07), and that of the B atoms is +3 ($\sum_s$ = 2.98 – 3.06).

As shown in Fig. 2, the $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)$ cluster shell is built up from twelve VO_5 square pyramids, six $[Zn(teta)]^{2+}$ complex groups, six $BO_2(OH)$ triangles, and twelve BO_4 tetrahedra, with one H_2O molecule at the center. Two BO_4 tetrahedra and one $BO_2(OH)$ triangle form a $B_3O_6(OH)^{4-}$ unit. Six $B_3O_6(OH)^{4-}$ units share their corners to give a puckered $B_{18}O_{36}(OH)_6$ ring. The $B_{18}O_{36}(OH)_6$ ring is sandwiched between two triangles of vanadium atoms comprising six alternating *cis* and *trans* edge-sharing VO_5 square pyramids to give a ball-like structure $\{[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)\}^{12-}$, which is covalently linked to six $[Zn(teta)]^{2+}$ complex groups through the bond type Zn–(μ_3-O)–B_2 to form a novel B-V-O cluster complex $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)$. All the vanadyl groups radiate away from the cluster surface. In addition, taking into account strong hydrogen bonding interactions between $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)$ clusters and water molecules, a 3-D supramolecular structure (Fig. 3) is generated by the combination of N–H···O (2.975 – 3.278 Å for N···O) and O–H···O (2.804 Å for O1···O10) hydrogen bonds.

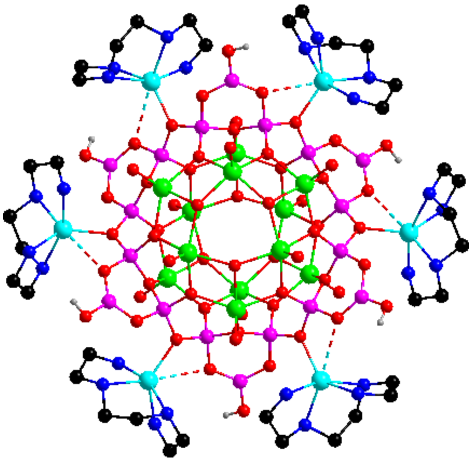

Fig. 2 (color online). The structure of the entire $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6](H_2O)$ cluster.

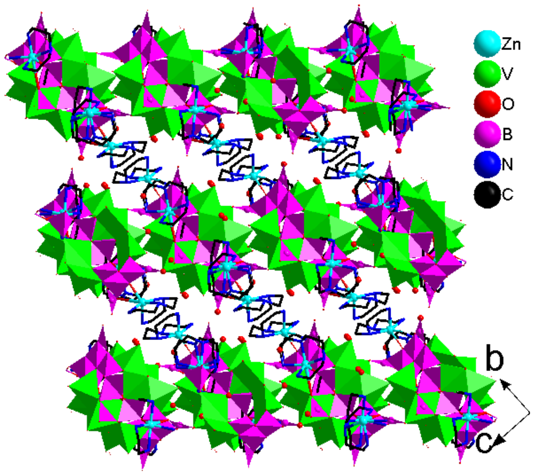

Fig. 3 (color online). Polyhedron and wire representation of the 3-D supramolecular structure of **1**. All H atoms are omitted for clarity.

Compared with the known vanadoborate decorated by $[Zn(en)_2]^{2+}$ complex cations $[Zn(en)_2]_6[(VO)_{12}O_6B_{18}O_{39}(OH)_3]\cdot 13H_2O$ (**2**) [10], several noteworthy features were found in **1**. First, the $[Zn(amine)_x]^{2+}$ fragments display different geometrical conformations: ZnN_4O_2 in **1** is an octahedron, while ZnN_4O in **2** exhibits a square pyramid. Second, with regard to the bonds, the number of Zn–(μ_3-O)–B bonds in **1** is 2, and in **2** it is 1. Finally, the number of -OH groups in **1** is 6, and in **2** it is 3. Clearly, the different chelating amines have a significant effect on the structures of **1** and **2**.

The UV/Vis absorption spectrum of **1** (Fig. 4) was calculated from the data of diffuse reflectance by using the Kubelka-Munk function [13]. The weak

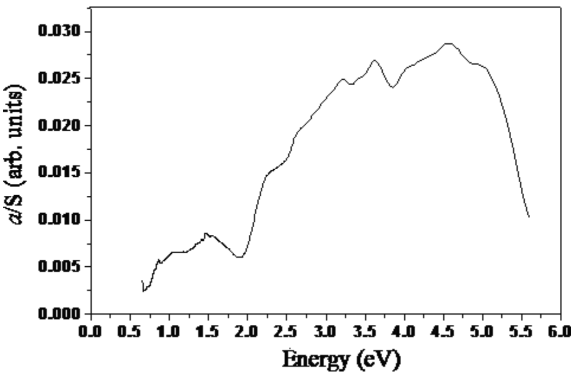

Fig. 4. Solid-state optical absorption spectrum of **1**.

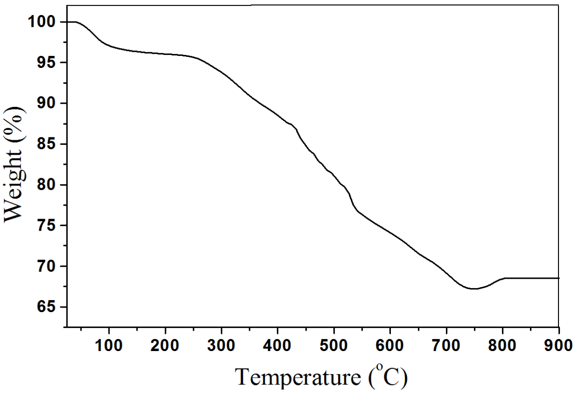

Fig. 5. TG curve of **1**.

absorptions at 0.85 and 1.45 eV presumably arise from d_ε(V)→ d_γ(V) electronic transitions of the V^{4+} ($3d^1$) ion. The onset of the main absorption is observed at 2.00 eV. We assign this onset to the lowest possible electronic excitation located at the vanadoborate cluster.

The TGA study of **1** was carried out in flowing air from room temperature to 900 °C (Fig. 5). A weight loss of 5.0 % from 25 to 220 °C is in agreement with the calculated amount of water molecules (5.1 %). The successive weight loss of 27.8 % from 220 to 750 °C can be ascribed to the removal of -OH groups and teta ligands, but it is slightly less than the sum of the calculated value (29.1 %) and may also be attributed to a concomitant the partial oxidation of the V^{4+} to V^{5+} [14]. The weight increase in the temperature range of 750 – 810 °C further confirms the oxidation of V^{4+}. Up to 810 °C, all of the vanadium is fully oxidized to V_2O_5. The residual material might be a complex mixture of ZnO, V_2O_5 and B_2O_3, for which the observed total weight loss (68.5 %) is in good agreement with the calculated value (68.9 %).

Table 1. Crystal structure data for **1**.

	1
Formula	$C_{36}H_{132}B_{18}N_{24}O_{69}V_{12}Zn_6$
M_r	3203.72
Crystal system	trigonal
Space group	$R\bar{3}$
a, Å	20.693(3)
c, Å	21.101(4)
V, Å^3	7825(3)
Z	3
T, K	293(2)
Calcd. density, g cm^{-3}	2.03
μ (MoK_α), mm^{-1}	2.5
F(000), e	4788
$2\theta_{\max}$, deg	56.72
Refls. collected / unique / R_{int}	19054 / 4163 / 0.034
No. of ref. param.	340
$R1$ [$I \ge 2\sigma(I)$]	0.0383
$wR2$ (all data)	0.1140
GOF on F^2	1.019
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.59 / −1.36

Table 2. Selected bond lengths (Å) and angles (deg) for **1**.

Zn1–O5	1.979(2)	Zn1–N	2.067(10) – 2.231(9)
V1–O	1.635(2) – 2.019(2)	V2–O	1.619(2) – 1.976(3)
B1–O	1.351(4) – 1.378(4)	B2–O	1.456(3) – 1.511(3)
B3–O	1.465(3) – 1.507(3)		
O/N–Zn1–N1	81.2(4) – 156.8(3)	O–V1–O	77.96(7) – 145.09(7)
O–V2–O	77.60(7) – 144.28(8)	O–B1–O	115.1(3) – 122.9(2)
O–B2–O	105.6(2) – 112.0(2)	O–B3–O	106.7(2) – 112.3(2)

Experimental Section

General: All purchased starting materials were analytically pure and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer from dry KBr pellets. Elemental analysis was carried out on an EA-1110 elemental analyzer. The UV/Vis spectra were recorded at room temperature using a computer-controlled PE Lambda 900 UV/Vis spectrometer equipped with an integrating sphere in the wavelength range of 250 – 1800 nm. Thermogravimetric analyses (TGA) were performed using a Mettler TGA/SDTA851 thermal analyzer in air with a heating rate of 10 °C min^{-1} in the temperature range of 25 – 900 °C.

Synthesis of $[Zn(teta)]_6[(VO)_{12}O_6B_{18}O_{36}(OH)_6]$-$(H_2O) \cdot 8H_2O$ *(**1**)*

A mixture of V_2O_5 (0.1848 g, 1.01 mmol), $ZnSO_4 \cdot 7H_2O$ (0.2820 g, 1.00 mmol), H_3BO_3 (0.2445 g, 3.95 mmol), teta (1.5 mL), pyridine (3 mL), and H_2O (2 mL) was stirred for 1 h, sealed in a Teflon-lined steel autoclave (20 mL), kept at 145 °C for 6 d, and then cooled to r. t. Red block-shaped crystals were obtained by filtration, washed with distilled water, and dried in air. Yield: *ca.* 73 % (based on

V_2O_5). Anal. (%): calcd. C 13.50, H 4.15, N 10.49; found C 13.46, H 4.21, N 10.51. – IR (KBr pellet, cm^{-1}): ν = 3322(m), 3264(m), 2930(w), 2877(w), 1644(m), 1593(m), 1395(s), 1337(s), 1066(vs), 955(s), 787(m), 724(m), 671(w), 619(w), 561(w), 521(m), 463(m), 417(w).

X-Ray structure determination

The data collection was performed on a Rigaku Mercury CCD diffractometer with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at 293(2) K with a maximum 2θ value of 56.72°. The intensities were corrected for Lorentz and polarization effects. The structure was solved with Direct Methods using the program SHELXS-97 [15], and the refinement was performed against F^2 using SHELXL-97 [16]. All the non-hydrogen atoms were refined anisotropically. The H atoms located at C and N atoms were refined using the riding model, while H atoms associated with water molecules were not located from the difference Fourier map. The teta ligand is disordered with the occupancies of the disordered C and N atoms being 0.6/0.4. Relevant crystal and collection data and refinement results can be found in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

CCDC 794951 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data request/cif.

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