

Hydrothermal Synthesis and X-Ray Single Crystal Structure of $[\text{Zn}(\text{en})_2]_6[(\text{VO})_{12}\text{O}_6\text{B}_{18}\text{O}_{39}(\text{OH})_3] \cdot 13\text{H}_2\text{O}$

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A hydrothermal reaction of NaVO_3 , H_3BO_3 , $\text{Zn}(\text{CH}_3\text{COO})_2$, ethylenediamine, and H_2O gives a coordination cluster $[\text{Zn}(\text{en})_2]_6[(\text{VO})_{12}\text{O}_6\text{B}_{18}\text{O}_{39}(\text{OH})_3] \cdot 13\text{H}_2\text{O}$ (denoted on $\text{Zn}_6\text{V}_{12}\text{B}_{18}$). The $\text{Zn}_6\text{V}_{12}\text{B}_{18}$ crystallizes in a rhombohedral system with space group $R\bar{3}$ and unit cell parameters $a = 20.686(3) \text{ \AA}$, $c = 20.915(4) \text{ \AA}$, $V = 7751(2) \text{ \AA}^3$, $Z = 3$, and $R = 0.0689$. The structure consists of an 18-membered ring of $\text{B}_{18}\text{O}_{39}(\text{OH})_3$ sandwiched between two alternating edge-sharing vanadium–oxygen clusters V_6O_{15} by six $\text{B}-(\mu_3\text{-O})-\text{V}_2$ bonds and three $\text{B}_2-(\mu_3\text{-O})-\text{V}$ bonds. Each of the six zinc atoms coordinated with two ethylenediamine molecules and connected with the $\text{B}_{18}\text{O}_{39}(\text{OH})_3$ ring by one $\text{Zn}-(\mu_3\text{-O})-\text{B}$ bond. A water molecule occupied the center of the $\text{Zn}_6\text{V}_{12}\text{B}_{18}$ cluster. The oxidation states of vanadium in the compound are V(IV) and V(V) in a ratio of 3:1. Other characterizations by IR spectroscopy, TGA, and DTA are also described. © 1999 Academic Press

Key Words: hydrothermal synthesis; crystal structure; polyoxovanadium; borate compound; transition metal complex.

INTRODUCTION

Recently, the utilization of polar organic molecules as structural directors of the crystallization of inorganic frameworks has caused great interest in the structural design and rational synthesis of functional coordination clusters and polymers. In such systems, transition metal coordination complexes usually serve as binders of the main metal oxide framework, so that new polyoxometalates linked by the binder crystallize in a variety of structures with 1–3 dimensions (1–4). In those polyoxovanadiums, the structural motifs are usually based on edge- and corner-sharing VO_5 square pyramids and VO_4 tetrahedrals. Although some compounds of polyoxovanadium borate species possessing unprecedented structures such as $(\text{enH})(\text{enH}_2)_4[(\text{VO})_{12}\text{B}_{17}\text{O}_{38}(\text{OH})_8] \cdot \text{H}_2\text{O}$, $(\text{enH}_2)_2[(\text{VO})_5(\text{H}_2\text{O})\{\text{O}_3\text{PB}(\text{O})_2$

$\text{OPO}_3\}_{12}] \cdot 1.5\text{H}_2\text{O}$, $\text{Rb}_4[(\text{VO})_6\{\text{B}_{10}\text{O}_6(\text{OH})_6\}_2] \cdot 0.5\text{H}_2\text{O}$, and $[(\text{VO})_{12}\text{O}_4\{\text{B}_8\text{O}_{17}(\text{OH})_4\}\{\text{Mn}(\text{H}_2\text{O})_2\}_2]^{8-}$ were reported in B–V–O systems by hydrothermal synthesis (5–11), the preparation and characterization of B–V–O systems containing transition elements still remain challenging (12, 13). Here, we report the hydrothermal synthesis and X-ray single crystal structure of $[\text{Zn}(\text{en})_2]_6[(\text{VO})_{12}\text{O}_6\text{B}_{18}\text{O}_{39}(\text{OH})_3] \cdot 13\text{H}_2\text{O}$.

EXPERIMENTAL

Preparation

Starting materials used in this study were NaVO_3 , H_3BO_3 , $\text{Zn}(\text{CH}_3\text{COO})_2$, and en (ethylenediamine). In a typical procedure for preparing single crystal $[\text{Zn}(\text{en})_2]_6[(\text{VO})_{12}\text{O}_6\text{B}_{18}\text{O}_{39}(\text{OH})_3] \cdot 13\text{H}_2\text{O}$, 0.17 g NaVO_3 , 2.47 g H_3BO_3 , and 1.08 g $\text{Zn}(\text{CH}_3\text{COO})_2$ were dissolved in 20 ml deionized water to form a solution, to which 1 ml ethylenediamine was added with stirring for 2 h at room temperature to form a reaction mixture. The mixture was heated in a 30-ml sealed Teflon-lined stainless steel autoclave at 160°C for 60 h. Black crystalline products were filtered, washed, and isolated.

Composition analysis was carried out on a Jarrzall-ash 800 Mark-II ICP instrument. The IR analysis was carried out on an Impact 410 using KBr pellets. The differential thermal analysis was conducted on a Perkin–Elmer DTA 1700 differential thermal analyzer, and the thermogravimetric analysis (TGA) was carried out on a Perkin–Elmer TGA 7 thermogravimetric analyzer in air with a heating rate of $20^\circ\text{C min}^{-1}$.

Crystal Structure Determination

Diffraction intensities for $\text{Zn}_6\text{V}_{12}\text{B}_{18}$ (size $0.50 \times 0.44 \times 0.40 \text{ mm}$) were collected at 22°C on a Siemens R3m diffractometer using the ω -scan technique at 293 K with graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$). Lp and

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absorption corrections were applied (14). The structures were solved with direct methods of SHELXTL-Plus (15) and refined with a full-matrix least-squares technique using the SHELXL-97 program (16). All water molecules were located from difference maps during refinement. O(3w) and O(5w) were located near a 3-fold axis, and the site occupation factors (SOF) were assigned to 1/3. The SOF of O(4w) was assigned to 1/3 according the elemental analysis. Non-hydrogen atoms were refined anisotropically. The alkyl hydrogen atoms were generated geometrically (C–H = 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated (17). The crystallographic data for Zn₆V₁₂B₁₈ are listed in Table 1. Atomic coordinates and equivalent isotropic displacement parameters and selected interatomic distances and angles for Zn₆V₁₂B₁₈ are given in Tables 2 and 3. Drawings were produced with SHELXTL-PC (15).

TABLE 1
Crystal Data and Structure Refinement for Zn₆V₁₂B₁₈

Empirical formula	C ₂₄ H ₁₂₅ B ₁₈ N ₂₄ O ₇₃ V ₁₂ Zn ₆
Formula weight	3116.56
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Rhombohedral
Space group	<i>R</i> -3
<i>a</i> (Å)	20.686(3)
<i>b</i> (Å)	20.686(3)
<i>c</i> (Å)	20.915(4)
Volume (Å ³)	7751(2)
<i>Z</i>	3
ρ_{calc} (g cm ⁻³)	2.003
μ (mm)	2.511
<i>F</i> (000)	4701
Crystal size (mm)	0.5 × 0.44 × 0.40
θ range (deg)	2.26–27.53
Index ranges	–17 ≤ <i>h</i> ≤ 26, –26 ≤ <i>k</i> ≤ 0, –27 ≤ <i>l</i> ≤ 17
Reflections collected	6266
Independent reflections	3948 (<i>R</i> _{int} = 0.0597)
Absorption correction	ψ -scan (Ref. (14))
Max. and min. transmission	0.756 and 0.651
Refinement method	full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	3948/55/256
Goodness-of-fit on <i>F</i> ²	1.057
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0689, <i>wR</i> ₂ = 0.1829
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0959, <i>wR</i> ₂ = 0.2005
Extinction coefficient	0.00032(5)
$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$ (e/Å ⁻³)	1.029 and –1.846

Note. $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. $wR = [\sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$.

TABLE 2
Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å²)

Atom	10 ⁴ <i>x</i>	10 ⁴ <i>y</i>	10 ⁴ <i>z</i>	10 ³ <i>U</i> _{eq} ^a
V(1)	6629(1)	1750(1)	9229(1)	18(1)
V(2)	5636(1)	2329(1)	9675(1)	18(1)
Zn(1)	8460(1)	1292(1)	8184(1)	76(1)
N(1)	8409(3)	360(3)	7751(3)	108(2)
N(2)	7765(4)	483(3)	8851(3)	124(2)
N(3)	9417(3)	1699(3)	8742(3)	97(2)
N(4)	9153(2)	2012(3)	7488(3)	110(2)
C(1)	7970(6)	–271(5)	8090(4)	183(6)
C(2)	7646(6)	–234(5)	8652(5)	208(6)
C(3)	10061(4)	2183(4)	8341(4)	133(3)
C(4)	9836(4)	2584(4)	7860(3)	118(2)
B(1)	8249(2)	2599(2)	8726(2)	21(1)
B(2)	7333(2)	1694(2)	7961(2)	22(1)
O(3)	7393(1)	2291(1)	7555(1)	22(1)
O(5)	6630(1)	1386(1)	8339(1)	19(1)
O(7)	7989(1)	1941(1)	8343(1)	21(1)
O(8)	7297(1)	1078(1)	7554(1)	26(1)
B(3)	6634(2)	535(2)	7342(2)	25(1)
O(1)	6624(1)	1128(1)	9704(1)	31(1)
O(2)	6643(1)	2541(1)	9727(1)	22(1)
O(4)	5240(1)	1949(1)	10336(1)	35(1)
O(6)	7637(1)	2553(1)	9099(1)	21(1)
O(9)	5980(1)	478(1)	7510(1)	25(1)
O(10)	6586(1)	–24(1)	6948(1)	36(1)
O(1w)	6667	3333	8333	148(7)
O(2w)	8244(3)	1610(3)	10173(2)	112(2)
O(3w) ^b	6967(14)	3692(11)	11166(7)	147(9)
O(4w) ^b	8899(13)	669(12)	10061(9)	167(10)
O(5w) ^b	9889(13)	507(12)	9122(14)	237(11)

^aEquivalent isotropic *U* defined as one-third of the trace of the orthogonalized *U*_{*ij*} tensor.

^bThe s.o.f = 1/3.

RESULTS AND DISCUSSION

Hydrothermal synthesis is a relatively complex process. Many factors can effect the reaction, such as initial reactants, concentration, pH, and crystallization temperature. In the synthesis of Zn₆V₁₂B₁₈, the initial reactants and pH value of the reaction system were very important for the formation of product. The en molecule acts as both an organic ligand and a reductive agent for adjusting the pH value of the reaction system. When the pH value was about 8, the pure crystallized product was prepared; when the pH was below or above 8, no product was obtained, and there was no other crystal obtained.

The structure was determined by single crystal X-ray diffraction. The asymmetric unit of [Zn(en)₂]₆[(VO)₁₂O₆B₁₈O₃₉(OH)₃] · 13H₂O with a content [Zn(en)₂]₃V₂O₁₃ is shown in Fig. 1. The unit includes two V atoms, three B atoms, ten oxygen atoms, and one Zn(en)₂ complex. The

TABLE 3
Bond Lengths (Å) and Angles (deg)

V(1)–O(1)	1.622(3)	C(1)–C(2)	1.374(12)
V(1)–O(6)	1.9282(17)	C(3)–C(4)	1.519(12)
V(1)–O(2)	1.928(2)	B(1)–O(7)	1.433(4)
V(1)–O(3a)	1.9315(18)	B(1)–O(6)	1.448(4)
V(1)–O(5)	2.007(2)	B(1)–O(9d)	1.473(4)
V(1)–V(2b)	2.9911(8)	B(1)–O(5d)	1.505(4)
V(1)–V(2)	2.9983(9)	B(2)–O(7)	1.429(4)
V(2)–O(4)	1.599(2)	B(2)–O(3)	1.452(4)
V(2)–O(2)	1.906(2)	B(2)–O(5)	1.491(4)
V(2)–O(2c)	1.9161(18)	B(2)–O(8)	1.502(4)
V(2)–O(6c)	1.944(2)	O(3)–V(1d)	1.9315(18)
V(2)–O(3a)	1.963(2)	O(3)–V(2d)	1.963(2)
V(2)–V(1c)	2.9911(8)	O(5)–B(1a)	1.505(4)
Zn(1)–O(7)	2.042(2)	O(8)–B(3)	1.340(4)
Zn(1)–N(4)	2.064(5)	B(3)–O(9)	1.346(5)
Zn(1)–N(3)	2.080(5)	B(3)–O(10)	1.382(5)
Zn(1)–N(1)	2.084(6)	O(2)–V(2b)	1.9161(18)
Zn(1)–N(2)	2.100(6)	O(6)–V(2b)	1.944(2)
N(1)–C(1)	1.359(10)	O(9)–B(1a)	1.473(4)
N(2)–C(2)	1.439(11)	O(3w)–O(3wc)	1.19(3)
N(3)–C(3)	1.465(8)	O(3w)–O(3wb)	1.19(3)
N(4)–C(4)	1.526(8)		
O(1)–V(1)–O(6)	110.22(11)	N(4)–Zn(1)–N(2)	174.8(2)
O(1)–V(1)–O(2)	109.43(12)	N(3)–Zn(1)–N(2)	94.8(2)
O(6)–V(1)–O(2)	78.10(9)	N(1)–Zn(1)–N(2)	81.6(2)
O(1)–V(1)–O(3a)	109.87(11)	C(1)–N(1)–Zn(1)	111.3(6)
O(6)–V(1)–O(3a)	138.26(10)	C(2)–N(2)–Zn(1)	109.0(6)
O(2)–V(1)–O(3a)	78.19(9)	C(3)–N(3)–Zn(1)	108.2(4)
O(1)–V(1)–O(5)	105.78(11)	C(4)–N(4)–Zn(1)	103.8(4)
O(6)–V(1)–O(5)	89.37(8)	N(1)–C(1)–C(2)	120.2(9)
O(2)–V(1)–O(5)	144.78(9)	C(1)–C(2)–N(2)	117.9(8)
O(3a)–V(1)–O(5)	90.63(9)	N(3)–C(3)–C(4)	109.3(6)
O(1)–V(1)–V(2b)	112.23(8)	C(3)–C(4)–N(4)	109.5(6)
O(6)–V(1)–V(2b)	39.62(7)	O(7)–B(1)–O(6)	109.8(2)
O(2)–V(1)–V(2b)	38.77(5)	O(7)–B(1)–O(9d)	108.1(3)
O(3a)–V(1)–V(2b)	112.20(7)	O(6)–B(1)–O(9d)	109.8(3)
O(5)–V(1)–V(2b)	123.89(5)	O(7)–B(1)–O(9d)	108.1(3)
O(1)–V(1)–V(2)	113.06(10)	O(6)–B(1)–O(9d)	109.8(3)
O(6)–V(1)–V(2)	111.18(7)	O(9d)–B(1)–O(9d)	0.0(3)
O(2)–V(1)–V(2)	38.30(6)	O(7)–B(1)–O(5d)	112.1(3)
O(3a)–V(1)–V(2)	40.04(7)	O(6)–B(1)–O(5d)	108.7(3)
O(5)–V(1)–V(2)	124.60(7)	O(9d)–B(1)–O(5d)	108.2(2)
V(2b)–V(1)–V(2)	75.00(2)	O(7)–B(2)–O(3)	111.1(2)
O(4)–V(2)–O(2)	107.25(12)	O(7)–B(2)–O(5)	113.8(3)
O(4)–V(2)–O(2c)	106.65(12)	O(3)–B(2)–O(5)	108.9(3)
O(2)–V(2)–O(2c)	94.12(14)	O(7)–B(2)–O(8)	104.9(3)
O(4)–V(2)–O(6c)	109.84(12)	O(3)–B(2)–O(8)	109.7(3)
O(2)–V(2)–O(6c)	142.80(10)	O(5)–B(2)–O(8)	108.3(2)
O(2c)–V(2)–O(6c)	78.01(9)	B(2)–O(3)–V(1d)	130.18(17)
O(4)–V(2)–O(3a)	109.03(12)	B(2)–O(3)–V(2d)	129.10(16)
O(2)–V(2)–O(3a)	77.95(9)	V(1d)–O(3)–V(2d)	100.69(10)
O(2c)–V(2)–O(3a)	144.22(10)	B(2)–O(5)–B(1a)	114.0(2)
O(6c)–V(2)–O(3a)	87.48(8)	B(2)–O(5)–V(1)	121.09(16)
O(4)–V(2)–V(1c)	110.10(11)	B(1a)–O(5)–V(1)	121.59(17)
O(2)–V(2)–V(1c)	126.50(7)	B(2)–O(7)–B(1)	119.4(3)
O(2c)–V(2)–V(1c)	39.06(7)	B(2)–O(7)–Zn(1)	110.68(19)
O(6c)–V(2)–V(1c)	39.23(5)	B(1)–O(7)–Zn(1)	129.74(19)
O(3a)–V(2)–V(1c)	121.88(6)	B(3)–O(8)–B(2)	119.7(3)
O(4)–V(2)–V(1)	111.00(11)	B(3)–O(8)–Zn(1)	141.9(2)
O(2)–V(2)–V(1)	38.83(7)	B(2)–O(8)–Zn(1)	85.24(16)

TABLE 3—Continued

O(2c)–V(2)–V(1)	126.25(7)	O(8)–B(3)–O(9)	123.3(3)
O(6c)–V(2)–V(1)	120.78(7)	O(8)–B(3)–O(10)	121.0(3)
O(3a)–V(2)–V(1)	39.27(5)	O(9)–B(3)–O(10)	115.7(3)
V(1c)–V(2)–V(1)	138.85(3)	V(2)–O(2)–V(2b)	145.07(13)
O(7)–Zn(1)–N(4)	91.61(17)	V(2)–O(2)–V(1)	102.88(9)
O(7)–Zn(1)–N(3)	108.28(17)	V(2b)–O(2)–V(1)	102.17(10)
N(4)–Zn(1)–N(3)	85.8(2)	B(1)–O(6)–V(1)	131.67(18)
O(7)–Zn(1)–N(1)	149.12(18)	B(1)–O(6)–V(2b)	126.99(16)
N(4)–Zn(1)–N(1)	93.2(2)	V(1)–O(6)–V(2b)	101.15(10)
N(3)–Zn(1)–N(1)	102.5(2)	B(3)–O(9)–B(1a)	122.6(2)
O(7)–Zn(1)–N(2)	93.1(2)		

Note. Symmetry codes: (a) $y + 1/3$, $-x + y + 2/3$, $-z + 5/3$; (b) $-y + 1$, $x - y$, z ; (c) $-x + y + 1$, $-x + 1$, z ; (d) $x - y + 1/3$, $x - 1/3$, $-z + 5/3$.

environments of the two V sites are topologically different but chemically similar, and each coordinates with five O atoms to make a VO_5 square pyramid with the V–O distances ranging from 1.599 to 2.007 Å and O–V–O angles from 77.95° to 144.78° . Two VO_5 square pyramids are edge-sharing. For the three different B atoms, B(1) and B(2) are tetrahedrally coordinated by four O atoms with the B–O distances 1.429–1.505 Å with O–B–O angles 104.9° – 113.8° . B(3) connects with three O atoms in a triangle with B–O lengths from 1.340 to 1.382 Å. These atomic coordinations and connections are similar to those in the compound $(\text{enH}_2)_5[(\text{VO})_{12}\text{O}_6\{\text{B}_3\text{O}_6(\text{OH})\}_6] \cdot \text{H}_2\text{O}$ (5). The zinc atom is coordinated by four nitrogen atoms and one oxygen atom, providing a distorted trigonal bipyramidal geometry. The atomic coordination and equivalent isotropic displacement parameters, bond lengths, and bond angles are listed in Tables 2, 3, and 4, respectively.

Figure 2 shows the whole framework structure of $[\text{Zn}(\text{en})_2]_6[(\text{VO})_{12}\text{O}_6\text{B}_{18}\text{O}_{39}(\text{OH})_3] \cdot 13\text{H}_2\text{O}$. Inside the framework, twelve VO_5 square pyramids construct two

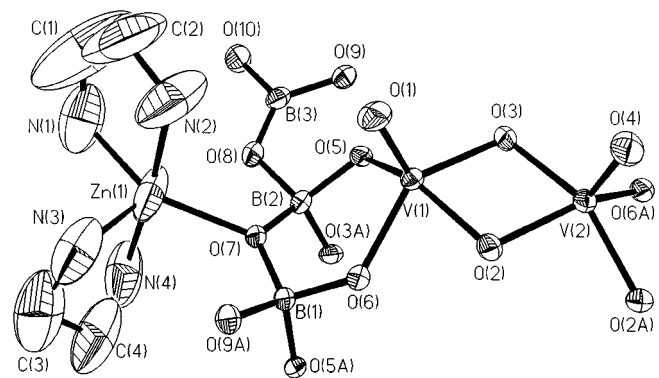


FIG. 1. An asymmetric unit of $\text{Zn}_6\text{V}_{12}\text{B}_{18}$.

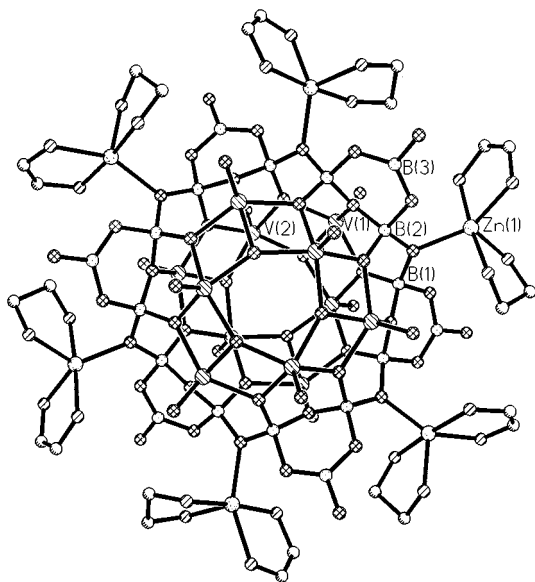


FIG. 2. View of the whole structural arrangement of the framework $Zn_6V_{12}B_{18}$ showing the situation of six $Zn(en)_2$ connected with the $B_{18}V_{12}$ cluster. A water molecule occupied the center of the cluster.

novel triangles, and each triangle includes six alternating *cis* and *trans* edge-sharing vanadium atoms; the vertex of the triangular is a *cis* edge-sharing VO_5 , and the midpoint of

each edge contains a *trans* edge-sharing VO_5 polyhedron. All the vanadyl groups radiate away from the cluster surface (Figs. 3a and 3b). Outside the V_{12} cluster there is a B_{18} ring which is sandwiched between the two vanadium triangles through six $B-(\mu_3-O)-V_2$ bonds and three $B_2-(\mu_3-O)-V$ bonds. One water molecule occupies the center of the cluster. Six $Zn(en)_2$ units connect with the B_{18} ring through one $Zn-(\mu_3-O)-B_2$ bond.

In the compound, three of the twelve vanadium atoms are V(V) and nine are V(IV). These V oxidation states were determined by the charge balance in the unit cell and confirmed by empirical bond length/valence sum calculation (18, 19), which shows a valence of +4.29 for each V atom; this is close to the +4.25 for $V^{IV}:V^V = 3:1$. The existence of V(IV) accounts for the black color of the crystal.

In the IR spectrum of the compound, the strong bands at 950 and 902 cm^{-1} are due to terminal V–O stretching. The 792, 727, and 663 cm^{-1} bands are attributed to symmetrical and asymmetrical V–O–V stretching. The strong bands at about 1350 and 1400 cm^{-1} are due to B–O stretching. Other bands at 1650–1600 cm^{-1} are the stretch of δ_{N-H} . Bands at 2955 and 2892 cm^{-1} are assigned to the symmetric and asymmetric stretching of C–H. TGA and DTA curves are shown in Fig. 4. The TGA curve can be divided into two steps of mass loss ranging from 100 to 170°C and from 325

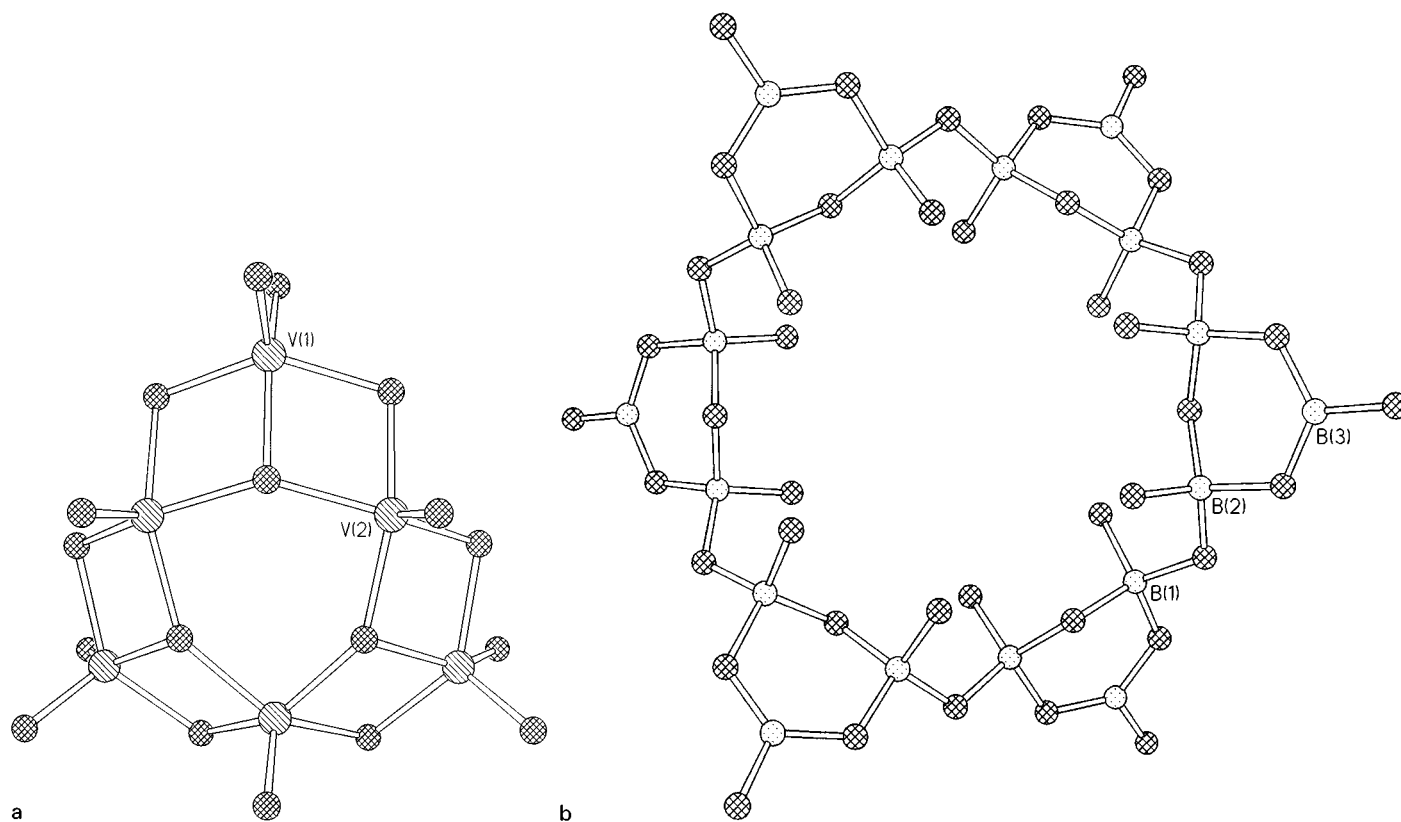


FIG. 3. (a) View of the V_6 ring. (b) View of the B_{18} ring along the pseudo-threefold axis.

TABLE 4
Anisotropic Displacement Parameters (\AA^2)

Atom	10^3U_{11}	10^3U_{22}	10^3U_{33}	10^3U_{23}	10^3U_{13}	10^3U_{12}
V(1)	17(1)	16(1)	22(1)	3(1)	0(1)	8(1)
V(2)	18(1)	17(1)	21(1)	2(1)	2(1)	9(1)
Zn(1)	111(1)	90(1)	74(1)	22(1)	29(1)	86(1)
N(1)	141(3)	141(3)	89(4)	-28(3)	-26(3)	106(2)
N(2)	208(5)	86(3)	103(4)	30(3)	37(4)	92(3)
N(3)	160(3)	111(2)	75(3)	2(2)	10(3)	109(2)
N(4)	141(2)	155(2)	106(3)	61(2)	71(2)	129(2)
C(1)	305(12)	106(5)	117(7)	-31(5)	-36(8)	87(6)
C(2)	251(9)	86(4)	300(14)	54(7)	89(10)	93(5)
C(3)	185(4)	194(4)	94(5)	-32(4)	14(4)	151(3)
C(4)	175(4)	139(4)	93(4)	38(3)	71(3)	119(3)
B(1)	18(1)	17(1)	30(2)	-1(1)	-3(1)	10(1)
B(2)	23(1)	19(1)	29(2)	0(1)	-1(1)	14(1)
O(3)	19(1)	14(1)	30(1)	2(1)	-1(1)	7(1)
O(5)	15(1)	15(1)	25(1)	-1(1)	-3(1)	6(1)
O(7)	16(1)	17(1)	32(1)	-2(1)	-2(1)	9(1)
O(8)	23(1)	21(1)	37(1)	-5(1)	2(1)	13(1)
B(3)	29(1)	19(1)	27(2)	2(1)	1(1)	12(1)
O(1)	36(1)	25(1)	35(1)	9(1)	0(1)	16(1)
O(2)	16(1)	23(1)	27(1)	0(1)	-2(1)	10(1)
O(4)	39(1)	37(1)	33(1)	13(1)	14(1)	21(1)
O(6)	18(1)	19(1)	28(1)	-2(1)	1(1)	10(1)
O(9)	25(1)	20(1)	32(1)	-6(1)	-2(1)	12(1)
O(10)	29(1)	28(1)	49(1)	-17(1)	1(1)	13(1)
O(1w)	149(8)	149(8)	146(13)	0	0	75(4)
O(2w)	90(3)	111(3)	98(3)	45(3)	-5(3)	23(3)
O(3w)	173(13)	191(17)	79(8)	21(10)	8(12)	92(9)
O(4w)	221(17)	166(15)	97(12)	21(11)	7(13)	85(12)
O(5w)	235(16)	203(14)	290(2)	86(13)	-70(16)	119(11)

to 600°C. The corresponding mass losses are 11.5 and 10.4%, respectively. The former is attributed to the loss of physical water in the crystal, and the latter is attributed to the decomposition of organic ligand. The DTA curve has

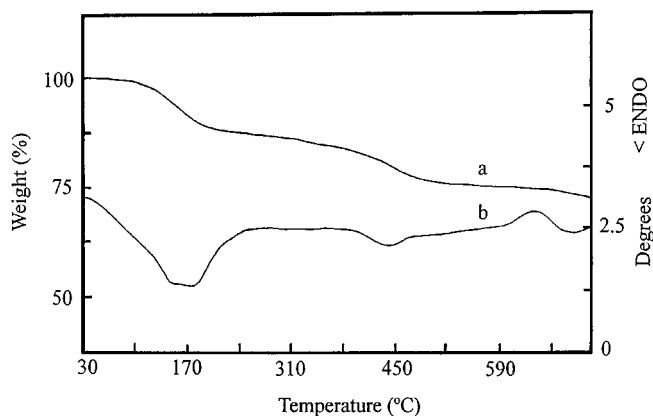


FIG. 4. TGA and DTA curves of $\text{Zn}_6\text{V}_{12}\text{B}_{18}$ in air.

two endothermic peaks corresponding to the TGA curve. The exothermal peak at 620–650°C is due to the oxidation of V(IV) to V(V); this also confirms the presence of V(IV).

In summary, we have introduced the transition metal complex into the polyoxovanadium borate cluster, producing the novel coordination cluster $[\text{Zn}(\text{en})_2]_6 [(\text{VO})_{12}\text{O}_6\text{B}_{18}\text{O}_{39}(\text{OH})_3] \cdot 13\text{H}_2\text{O}$ by hydrothermal reaction. This study shows that hydrothermal synthesis is a handy method for obtaining new coordination clusters. Combining the transition metals and main group oxide in polyoxo anions with the organic ligands imprinting the structural information of the framework will generate novel structures.

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REFERENCES

- P. J. Zapf, C. J. Warren, R. C. Haushalter, and J. Zubieta, *Chem. Commun.*, 1543 (1997).
- J. R. D. Debord, R. C. Haushalter, L. M. Meyer, D. J. Rose, P. J. Zapf, and J. Zubieta, *Inorg. Chim. Acta* **256**, 165 (1997).
- J. R. D. DeBord, Y. Zhang, R. C. Haushalter, J. Zubieta, and C. J. O. Connor, *J. Solid State Chem.* **122**, 251 (1996).
- D. Hagrman, C. Zubieta, D. J. Rose, J. Zubieta, and R. C. Haushalter, *Angew. Chem. Int. Ed. Engl.* **36**, 873 (1997).
- J. T. Rijssenbeek, D. J. Rose, R. C. Haushalter, and J. Zubieta, *Angew. Chem. Int. Ed. Engl.* **36**, 1008 (1997).
- C. J. Warren, R. C. Haushalter, D. J. Rose, and J. Zubieta, *Chem. Mater.* **9**(12), 2694 (1997).
- C. J. Warren, D. J. Rose, R. C. Haushalter, and J. Zubieta, *Inorg. Chem.* **37**, 1140 (1998).
- C. J. Warren, R. C. Haushalter, D. J. Rose, and J. Zubieta, *Inorg. Chim. Acta* **282**, 123 (1998).
- C. J. Warren, J. T. Rijssenbeek, D. J. Rose, R. C. Haushalter, and J. Zubieta, *Polyhedron* **17**, 2599 (1998).
- T. Yamase, M. Suzuki, and K. Ohtaka, *J. Chem. Soc. Dalton. Trans.*, 2463 (1997).
- J. Zubieta, P. C. Burns, J. D. Grice, and F. C. Hawthorne, *Can. Mineral.* **33**, 1331 (1995). [And references therein]
- S. C. Sevov, *Angew. Chem. Int. Ed. Engl.* **35**, 2630 (1996).
- R. Kniep, H. G. Will, I. Boy, and C. Rohr, *Angew. Chem. Int. Ed. Engl.* **36**, 1013 (1997). [And references therein]
- A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr. Sect. A* **24**, 351 (1968).
- G. M. Sheldrick, "SHELXTL-PC, User's Manual." Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
- G. M. Sheldrick, SHELXL-97, Program for X-Ray Crystal Structure Refinement. University of Göttingen, Germany, 1997.
- "International Tables for X-ray Crystallography," Vol. C, Tables 4.2.6.8 and 6.1.1.4. Kluwer Academic, Dordrecht, 1992.
- I. D. Brown and D. Altermatt, *Acta Crystallogr.* **B41**, 244 (1985).
- I. D. Brown and Kang Kun Wu, *Acta Crystallogr.* **B32**, 1950 (1976).