A Novel Polyoxovanadium Borate Incorporating an Organicamine Ligand: Synthesis and Structure of $[V_{12}B_{16}O_{50}(OH)_7(en)]^{7-}$

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Electronic Supplementary Information:

physical measurements

All analytical regent grade chemicals were commercially purchased and used without purification. The elemental analyses of C, H, and N were performed with an Elementar Vario EL III elemental analyzer. The IR spectra were recorded with a Perkin-Elmer Spectrum 2000 FT-IR spectrometer in the range of 400-4000 cm^{-1} using the KBr pellet technique. Thermogravimetric(TG) analyses were conducted on a Perkin-Elmer TGA7 Thermal analyzer in an N_2 atmosphere with a heating rate of 10 °C/min from 25 °C to 800 °C.

In order to obtain the 2D IR correlation spectra, a series of dynamic IR spectra were recorded in the range 4000–400 cm^{-1} on a Perkin-Elmer FT–IR spectrum 2000 spectrometers using KBr pellets. The temperature variation was controlled by a Portable programmable temperature controller (Model 50–886, Love Control Corporation) from 50 to 120 °C at intervals of 10°C. The magnetic intensity variation was controlled by a homemade magnetic intensity controller from 5 to 50mT at intervals of 5mT. Before 2D calculation, each spectrum was smoothed

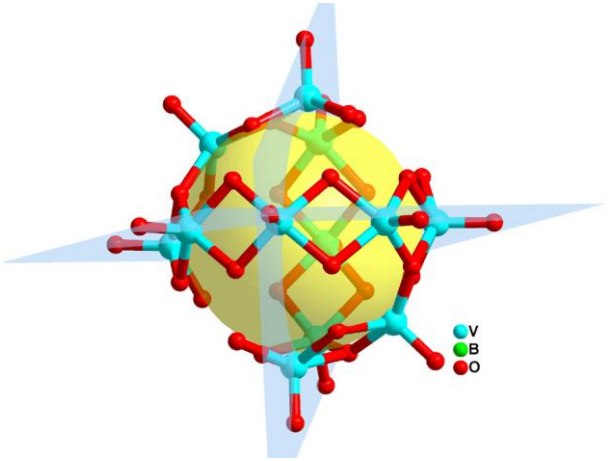
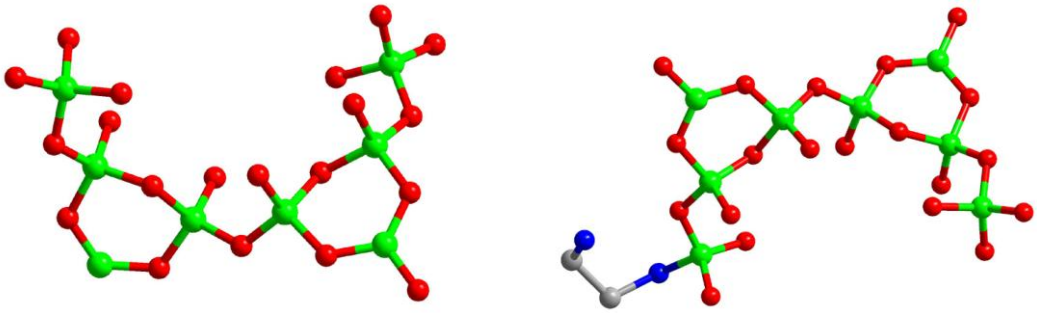


Figure S1. V_{12} cage cluster with two semi-circles of five *trans* edge-sharing VO_5 square pyramids bridged by two additional VO_5 units.

The contorted V_{12} ring is composed of two semi-circles of five *trans* edge-sharing VO_5 square pyramids bridged by two additional VO_5 units (Fig 2a). The dihedral angles between the planes of the two semi-circles is 84.58° . The dodecavanadate ring in **1** is a closed 12-membered vanadate

ring but not planar



(a) **(b)**

Figure S2. (a) Ball and stick presentation of $[B_8O_{17}(OH)_3(en)]^{13-}$ cluster. (b) Ball and stick presentation of $[B_8O_{17}(OH)_4]^{-14}$ cluster.

According to the classification of polyborate anions by Heller, Christ, and Clark, the shorthand notation for this oxo boron cluster is "8: [2Δ+6T]", where the specified number is the number of boron atoms in the isolate cluster, and the symbols Δ and T mean triangle and tetrahedron, respectively.

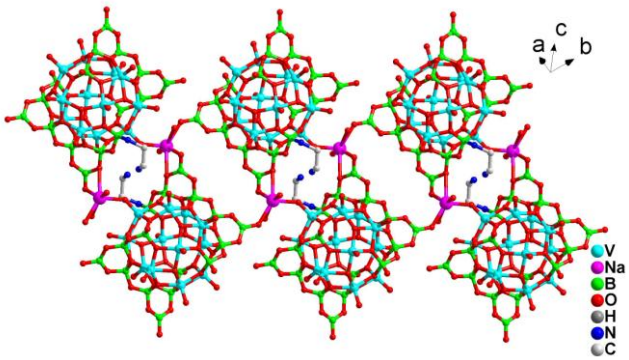


Figure S3. Ball and stick presentation of 1D anion dual chain bridged by Na^+ ions running along the [1-10] direction.

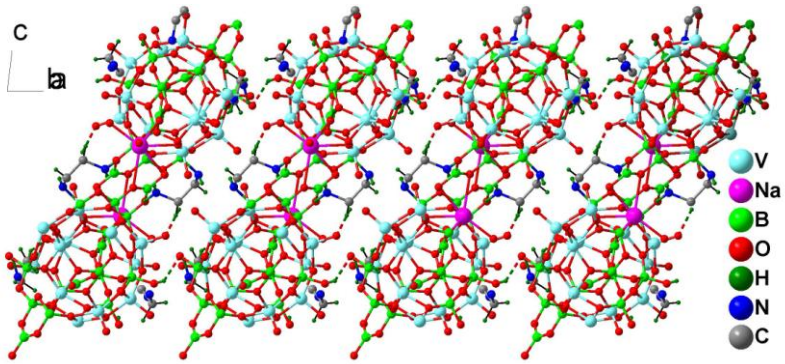


Figure S4. 2D supramolecular layer constructed by O-H···O hydrogen bonds.

The uncoordinated en molecules as structure-directing agents are accommodated in the free voids of **1** and are interacted to the $V_{12}B_{16}$ clusters by O-H···O H-bonds, then the 1D dual chains are further linked to 2D layer

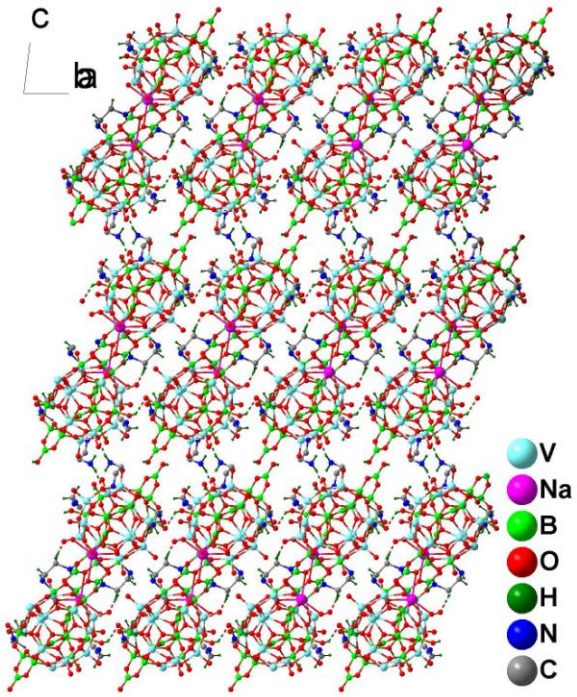


Figure S5. The dinuclear cluster (Dy_2) units containing two Dy atoms and two SO_4^{2-} anions. Atoms having "A" in their labels are symmetry-generated. A: -x, -y, -z.

A pair of central-symmetry Dy ions are bridged by two μ_2-O bridges of two SO_4^{2-} anions, forming a $[Dy_2O_2]$ rhombic dimeric cluster unit.

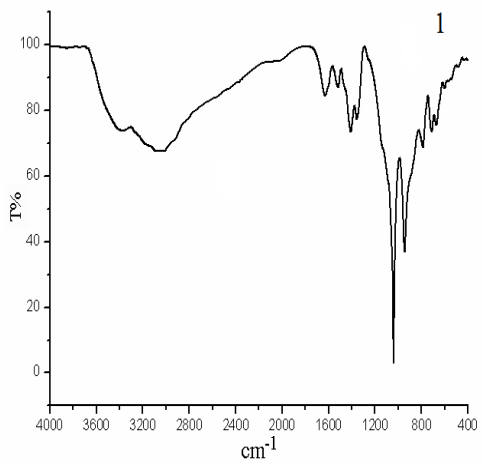


Figure S6. IR spectra of **1**.

Table 1.The IR vibration frequences(cm^{-1}) of compound **1**

Vibration assignment	Vibration frequences(cm^{-1})
vas(V=O_t)	953
vas(V-O_μ)	787, 711
vs(V-O_μ)	672
vas(B^a-O)	1039
vas(B^b-O)	1356
δ(CH_2)	1458
δ(NH_3)	1518
δ(OH)	1629
v(N-H)	3081

v(O-H)	3395

a: tetrahedron coordinated B; b: triangle coordinated B.

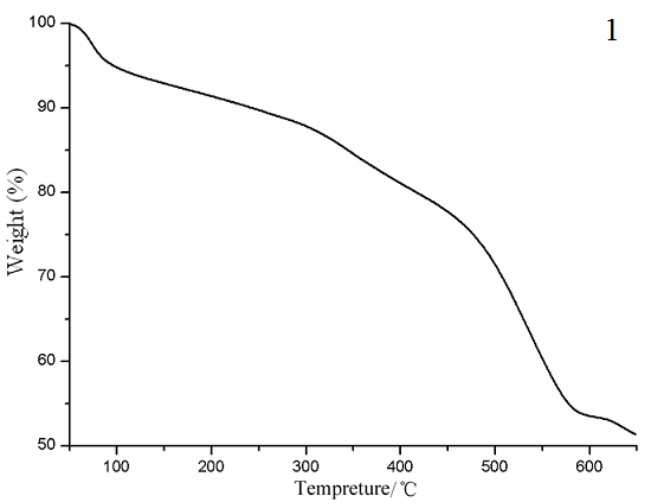


Figure S7 TG curves for **1**.

The thermal stability of **1** was examined by TGA in a dry nitrogen atmosphere from 40 to 700℃. The TG curves of **1** exhibit two-step primary weight loss processes for a crystalline sample. The initial weight loss of 5.86% in the range of 50– 90℃ corresponds to the release of sixteen lattice water molecules (calc. 6.57%). The second weight loss of 31.32% is observed from 90 to 570℃, and is attributed to the removal of four coordinated water molecules, eight en molecules, two B_8O_{20}(en) per formula unit (calc. 32.40%).

Table 2 The BVS of Vanadium and Oxygen for 1.

Atoms	V1	V2	V3	V4	V5	V6	V7	V8	V9	V10
BVS	4.272	4.314	4.396	4.354	4.271	4.377	4.269	4.358	4.347	4.413
Atoms	V11	V12	O37	O40	O44	O47	O48	O51	O55	
BVS	4.32	4.376	0.777	0.962	0.974	0.721	0.783	1.199	1.057	

Table 3 Parameters of hydrogen bonds for 1.

D-H⋯ A	d(D-H) (Å)	d(H⋯A) (Å)	d(D⋯A) (Å)	<DHA(°)
O37-H1⋯O47[a]	0.882	1.902	2.762	164.48
O40-H2⋯O50 [b]	0.878	1.811	2.685	173.78
O44-H3⋯O43[c]	0.881	1.996	2.724	139.03
O51-H6⋯O39[d]	0.883	1.940	2.780	158.39
O61-H7⋯O54	0.850	2.035	2.793	148.09
O62-H9⋯O52[e]	0.850	1.979	2.782	157.24
O62-H10⋯O55	0.850	1.931	2.770	168.73
O64-H13⋯O60[d]	0.850	1.936	2.720	152.75
O65-H15⋯O36[f]	0.850	2.028	2.831	157.18
O65-H16⋯O8	0.850	1.978	2.816	168.46
O66-H18⋯O41[c]	0.850	2.047	2.888	169.91
O67-H20⋯O8	0.850	2.032	2.866	166.77
O68-H21⋯O44[c]	0.850	2.150	2.959	158.87
O69-H23⋯O42	0.850	1.977	2.779	157.19
O70-H25⋯O37	0.850	1.976	2.700	142.40

O70-H26···N8[b]	0.850	2.198	2.875	136.56
N2-H30···O29[g]	1.110	1.911	2.870	142.14
N3-H31···O37	0.886	2.282	2.880	124.66
N3-H31···O32	0.886	2.341	2.997	130.82
N7-H35···O69[h]	0.881	1.944	2.799	163.31
N8-H36···O38[i]	0.886	1.796	2.677	172.41
N9-H37···O2[f]	0.917	1.913	2.819	169.10
N9-H38···O48	0.924	1.782	2.699	170.93

a [x+1, y, z]; b [x+1, y-1,z]; c [-x, -y, -z]; d [x-1, y+1, z]; e [-x, -y+1, -z+1]; f [-x, -y+1, -z]; g [-x+1, -y, -z+1]; h [x, y+1, z]; i [x-1, y+1, z].