A New 1D Polyoxovanadate $[Cu(en)_2V_{10}O_{28}][Cu(en)_2(H_2O)]_2 \cdot 2H_3BO_3 \cdot 2H_2O$ Containing the Rarely Non-condensed Boric acid

Litao An[a], Xing Liu[b], Jian Zhou[b,c], Feilong Hu[c], and Liuliu Zhu[c]

[a] College of Chemistry and Chemical Engineering, Huaiyin Normal University, Huaian, 223300, P. R. China

[b] College of Chemistry, Chongqing Normal University, Chongqing, 401331, P. R. China

[c] College of Chemistry and Material, Yulin Normal University, Yulin 537000, P. R. China

Reprint requests to Prof. Dr. Jian Zhou. E-mail: Jianzhou888888@163.com or Jianzhou888888@yahoo.com.cn

A new 1D polyoxovanadate containing boric acid $[Cu(en)_2V_{10}O_{28}][Cu(en)_2(H_2O)]_2 \cdot 2H_3BO_3 \cdot 2H_2O$ (**1**, en = ethylenediamine) has been hydrothermally synthesized and structurally characterized. Compound **1** consists of a polyoxovanadate chain $[Cu(en)_2V_{10}O_{28}^{4-}]_n$ based on the linkage of decavanadate clusters and $[Cu(en)_2]^{2+}$ groups, complex cations $[Cu(en)_2(H_2O)]^{2+}$, free H_3BO_3 and H_2O molecules. The polyoxovanadates and boric acid can undergo polycondensation into various B-O-V clusters under hydrothermal conditions, but **1** is the only example of the non-condensation of polyoxovanadate and boric acid. The IR spectrum and the thermal behavior of **1** were also studied.

Key words: Polyoxovanadate, Borate, Hydrothermal Synthesis, Crystal Structure, Boric Acid

Introduction

There has been continuous interest in preparing new polyoxometalates (POMs), because of their intriguing variety of architectures and potential applications in catalysis, medicine, and material science [1 – 4]. Such POMs are an outstanding class of inorganic building blocks for the construction of open-framework or supramolecular networks with unexpected properties. Polyoxovanadates (POVs) represent an important subset of POMs and have the capability of coordinating to various transition-metal complexes (TMCs) to form extended POV frameworks because of the large number of their surface O atoms [5 – 10]. However, extended POVs constructed by the combination of decavanadate anions and TMCs are very scarce [11 – 14], and most of them display discrete structural moieties [15 – 17].

Borates have been receiving particular attention because of their outstanding nonlinear optical properties and fascinating structural diversity [18, 19].

Boron is a unique element, which can be coordinated by oxygen with triangular $[BO_3]$ or tetrahedral $[BO_4]$ geometries. $[BO_x]$ (x = 3, 4) and VO_y (y = 4, 5, 6) groups favor polymerization through sharing corners or edges into a wide range of large B-O-V clusters [20 – 23]. These B-O-V clusters can be further bonded with TCMs or metal cations to form novel extended vanadoborates, as exemplified by the chains in $Na[V_{12}B_{16}O_{50}(OH)_7(en)]_2(enH_2)_6(enH)_2(OH)$ $(H_2O)_{19}$ [20], the layers in $[Zn(en)_2]_2[Zn(OH_2)(en)]_4$ $[Zn_4(B_2O_4H_2)(BO_2H)_2(V_{10}B_{28}O_{74}H_8)] \cdot 10H_2O$ [21] and $Na_2(H_2en)_2\{(VO)_{10}[B_{14}O_{30}(OH)_2]_2\}\{Mn_4(C_2O_4)$ $[B_2O_4(OH)_2]_2\}Mn(H_2O)_2 \cdot (H_3O)_{12}(H_2O)_{19}$ [22], and the network in $[Na(H_2O)]_2[Na(H_2O)_2]_2[Cu(en)_2][V_{12}$ $B_{18}O_{54}(OH)_6] \cdot (H_3O)_2 \cdot (H_2O)_{18}$ [23]. However, an example of non-condensation of polyoxovanadate and boric acid has not been observed to date. Here we report the synthesis and characterization of a new 1D polyoxovanadate-borate $[Cu(en)_2V_{10}O_{28}][Cu(en)_2(H_2O)]_2 \cdot 2H_3BO_3 \cdot 2H_2O$ (**1**), which represents a unique example.

Results and Discussion

Compound **1** crystallizes in the monoclinic centrosymmetric space group $C2/c$ with four formula units in the unit cell. It consists of polyoxovanadate chains [Cu(en)$_2$V$_{10}$O$_{28}^{4-}$]$_n$, complex cations [Cu(en)$_2$(H$_2$O)]$^{2+}$, free H$_3$BO$_3$, and H$_2$O molecules (Fig. 1a). The [V$_{10}$O$_{28}$]$^{6-}$ cluster, which is built up from ten VO$_6$ edge- and corner-sharing doctahedra, is a typical decavanadate. The V–O bond lengths vary from 1.600(3) to 2.296(2) Å, and the O–V–O bond angles are in the range of 74.05(8)–175.13(12)°, which are consistent with those found in previously reported structures of decavanadate salts [11–17]. Two crystallographically distinct copper sites display two different coordination environments: an elongated octahedron N$_4$Cu(1)O$_2$ owing to Jahn-Teller distortion and a square pyramid N$_4$Cu(2)O. The equatorial positions of the N$_4$Cu(1)O$_2$ octahedron are occupied by four N atoms of two en ligands, and the axial positions are occupied by two O atoms from two [V$_{10}$O$_{28}$]$^{6-}$ clusters. The distorted square pyramid N$_4$Cu(2)O is defined by four N atoms of two en ligands and one O atom of one H$_2$O molecule. The Cu–N bond lengths vary from 1.990(4) to 2.031(5) Å and are in the normal range [11–14]. The Cu–O bonds [2.523(5)–2.619(3) Å] can be compared with those of [Cu(en)$_2$H$_2$O]$_2$[H$_2$V$_{10}$O$_{28}$]·12H$_2$O (2.530–2.668 Å) [11].
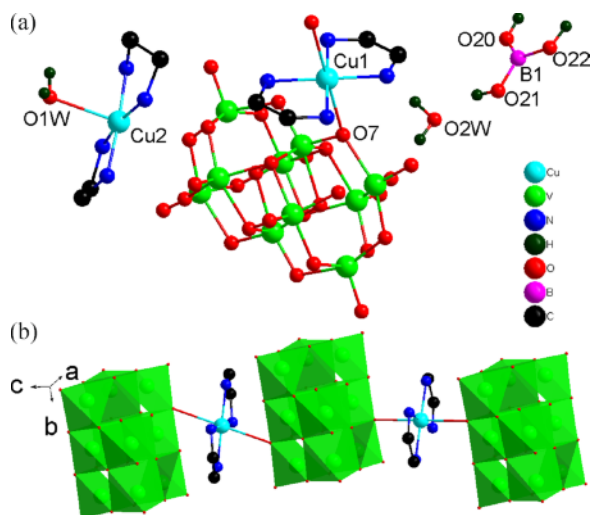

Fig. 1 (color online). a) Crystal structure of **1**; b) polyoxovanadate chain [Cu(en)$_2$V$_{10}$O$_{28}^{4-}$]$_n$.
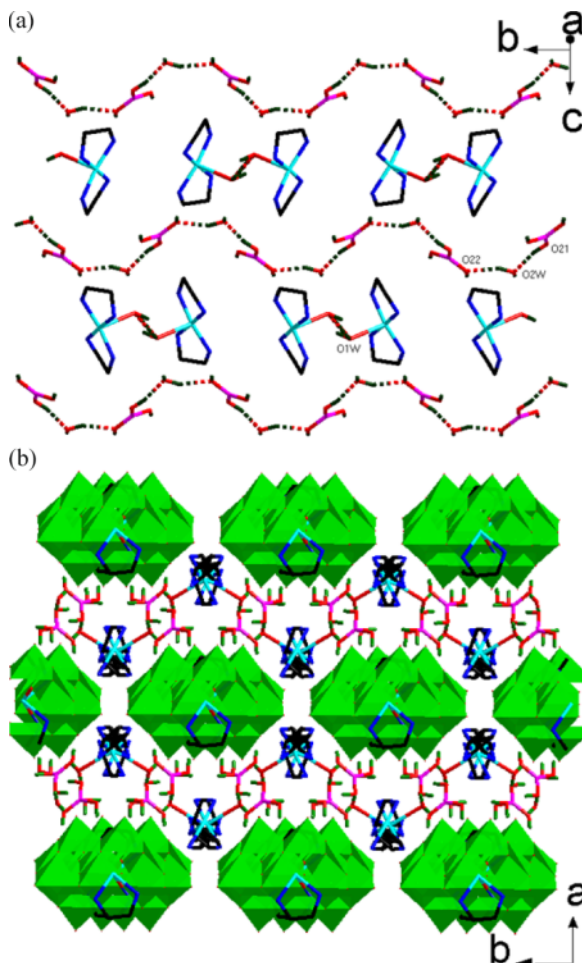

Fig. 2 (color online). a) The pseudo-layer in **1**; b) the 3D H-bonding network of **1**.

Adjacent [Cu(en)$_2$]$^{2+}$ complex cations are connected by [V$_{10}$O$_{28}$]$^{6-}$ clusters as bridging ligands into polyoxovanadate chains [Cu(en)$_2$V$_{10}$O$_{28}^{4-}$]$_n$ along [001] (Fig. 1b). The negative charge of the chain is neutralized by complex cations [Cu(en)$_2$(H$_2$O)]$^{2+}$. The [V$_{10}$O$_{28}$]$^{6-}$ cluster and Cu1 lie on independent inversion centers. There are several interesting hydrogen bonding interactions in **1**. The alternating connectivity between free H$_2$O and H$_3$BO$_3$ molecules by O–H$\cdots$O hydrogen bonding interactions gives rise to a sinusoidal chain along [010]. These sinusoidal chains are aligned in an antiparallel fashion. The water molecule in [Cu(en)$_2$(H$_2$O)]$^{2+}$ (at x, y, z) acts as H bond donor to another [Cu(en)$_2$(H$_2$O)]$^{2+}$ cation (at $1/2-x$, $-1/2-y$, $-z$) thereby generating by inver-
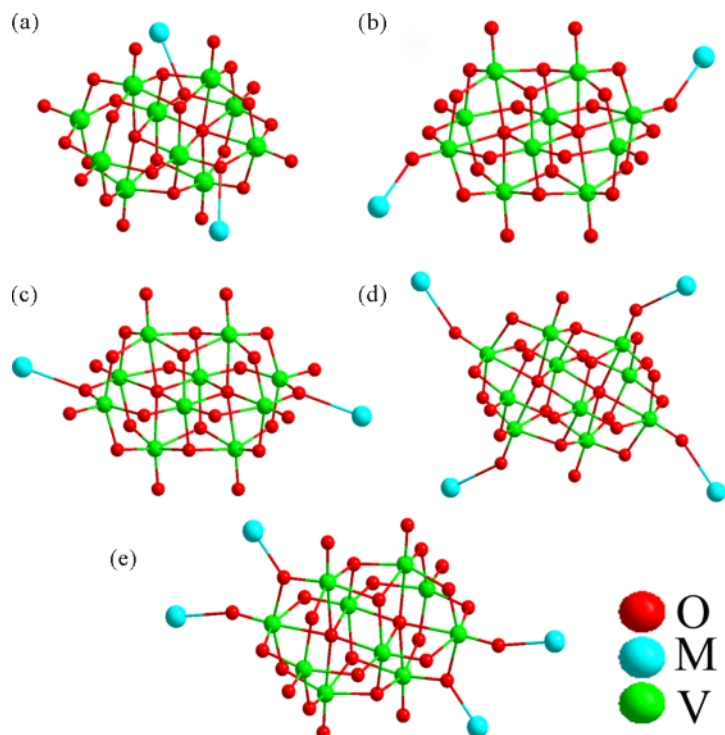
Fig. 3 (color online). Coordination modes of the [V$_{10}$O$_{28}$]$^{6-}$ cluster.

sion a dimer characterized by the usual R$_2^2$(4) motif [24]. These dimers are located between the sinusoidal chains to form a pseudo-layer within the (100) plane (Fig. 2a). These layers are further stacked in an -ABA- fashion along the cyrstallographic *a* axis. The [Cu(en)$_2$V$_{10}$O$_{28}^{4-}$]$_n$ chains are located between the pseudo-layers *via* O–H···O and N–H···O hydrogen bonding interactions to give a 3D H-bonding network (Fig. 2b).

Interestingly, the [V$_{10}$O$_{28}$]$^{6-}$ cluster in **1** is coordinated to the copper centers *via* the bridging O atoms of two adjacent [VO$_6$] octahedra and has *C$_{2v}$* symmetry (Fig. 3a). This bridging mode is unfamiliar. Usually the [V$_{10}$O$_{28}$]$^{6-}$ clustering adopts the bridging/terminal O atoms of two/four opposite [VO$_6$] octahedra and has *D$_{2h}$* symmetry (Fig. 3b–e) [11 – 14]. Moreover, protonated [V$_{10}$O$_{28}$]$^{6-}$ clusters generally provide the bridging O atoms to link the metal centers [11, 12], and the bonding in unprotonated [V$_{10}$O$_{28}$]$^{6-}$ clusters takes place through the terminal O atoms [13, 14], but the unprotonated [V$_{10}$O$_{28}$]$^{6-}$ cluster in **1** provides the bridging O atoms. Hence this bonding mode in **1** is of a new type.

The IR spectrum of **1** is shown in Fig. 4. The band at 3444 cm^{-1} is the stretching vibration of the -OH groups in water molecules. The broad bands at 3311 – 2890 cm^{-1} correspond to the stretching bands of the -NH$_2$ and -CH$_2$ groups. The strong bands at 1428 and 1375 cm^{-1} are consistent with the existence of trigonally coordinated boron in boric acid. The strong bands near 948 cm^{-1} can be assigned to the stretching vibrations of V=O bonds.
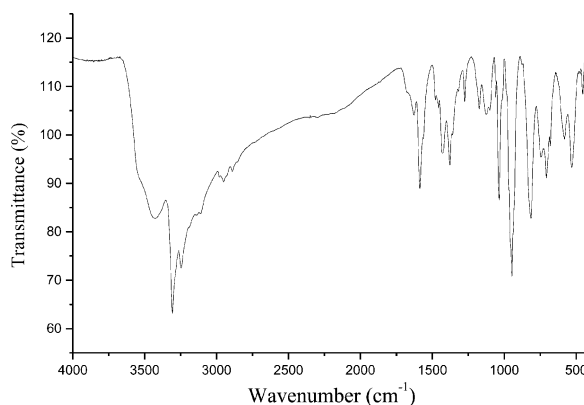

Fig. 4. IR spectrum of **1**.

The TG analysis of **1** was performed in the temperature range of 25–500 °C under N_2 atmosphere. Three steps of weight loss between 50 and 485 °C (29.2 %) correspond to the loss of water molecules and en ligands (calculated 28.6 %).

Conclusion

We have synthesized a new 1D polyoxovanadate containing non-condensed boric acid. The $[V_{10}O_{28}]^{6-}$ cluster in **1** adopts the bridging O atoms to link with the copper complexes in rare C_{2v} symmetry. The array is further extended to a 3D supramolecular framework *via* hydrogen bonds. The results demonstrate that the decavanadates can provide various bridging O functions for constructing novel extended POV frameworks. Further investigations are in progress.

Experimental Section

General: All starting materials were analytically pure and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. Elemental analysis was carried out on an EA-1110 elemental analyzer. Thermogravimetric analyses (TGA) were performed using a Mettler TGA/SDTA851 thermal analyzer under a N_2 flow atmosphere with a heating rate of 10 °C·min⁻¹ in the temperature range of 25–500 °C.

Synthesis of [Cu(en)₂V₁₀O₂₈][Cu(en)₂(H₂O)]₂·2H₃BO₃·2H₂O (1)

A mixture of NH_4VO_3 (0.1175 g, 1.0 mmol), $CuCl_2·6H_2O$ (0.0930 g, 0.4 mmol), H_3BO_3 (0.1852 g, 3.0 mmol), en (0.5 mL), and water (2.0 mL) was stirred for 1 h, then the solution was sealed in a 25 mL Teflon-lined autoclave and heated at 110 °C for 5 d. After cooling slowly to room temperature, brown block-shaped crystals were isolated. The crystals were filtered and dried at room temperature. – Analysis: calcd. C 8.46, H 3.67, N 9.86; found C 8.43, H 3.70, N 9.83.

Crystal structure determination

The data collection was performed on a Rigaku Mercury CCD diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.71073$ Å) at 296(2) K with a maximum 2θ value of 50.20°. The intensities were corrected for Lorentz and polarization effects. The structures were solved with Direct Methods using the program SHELXS-97 [25, 26], and the refinement was performed against F^2 using SHELXL-97 [27, 28]. All non-hydrogen atoms were refined anisotropically. The H atoms of the en ligands were positioned with idealized geometry and refined with fixed isotropic displace-

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

	1
Formula	$C_{12}H_{62}B_2Cu_3N_{12}O_{38}V_{10}$
M_r	1704.41
Crystal system	monoclinic
Space group	$C2/c$
a, Å	26.504(5)
b, Å	11.639(2)
c, Å	19.836(4)
β, deg	124.02(3)
V, Å³	5072(2)
Z	4
D_{calcd}, g cm⁻³	2.23
$\mu(MoK_\alpha)$, cm⁻¹	30.9
$F(000)$, e	3396
Refl. measured / unique / R_{int}	14076 /4504 / 0.021
Param. refined	417
$R(F)/wR(F^2)$ (all refls.)	0.0409/0.1079
GoF (F^2)	1.044
$\Delta\rho_{fin}$ (max / min), e Å⁻³	2.07 / −1.07

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

Cu1–N	1.960(5) – 2.012(5)	Cu2–N	1.990(4) – 2.031(5)
V1–O	1.600(3) – 2.326(3)	V2–O	1.613(3) – 2.2527(13)
V3–O	1.603(2) – 2.296(2)	V4–O	1.609(3) – 2.2509(13)
V5–O	1.692(2) – 2.114(2)		
N–Cu1–N	85.3(2) – 180.00(3)	N–Cu2–N	84.2(2) – 176.13(19)
O–V1–O	74.05(8) – 153.85(11)	O–V2–O	75.17(9) – 174.41(12)
O–V3–O	74.66(9) – 172.73(11)	O–V4–O	75.62(9) – 175.13(12)
O–V5–O	78.90(10) – 167.16(10)		

ment parameters. The C1, C2, C5, and C6 atoms were disordered over two positions with the occupation factors of 0.76/0.24, 0.76/0.24, 0.20/0.80, and 0.80/0.20, respectively. Relevant crystal data collection and refinement results can be found in Table 1. Selected bond lengths and angles for **1** are listed in Table 2.

CCDC 885804 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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