



Polyoxometalate cluster $[V_{12}B_{18}O_{60}H_6]$ functionalized with the copper(II) bis-ethylenediamine complex

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ARTICLE INFO

Article history:

Received 30 July 2010

Received in revised form 17 November 2010

Accepted 23 November 2010

Available online 4 December 2010

Keywords:

Oxovanadium borates

Copper(II) complexes

Functionalization

VBO

POM

ABSTRACT

Three compounds based on the polyoxometalate building block $[V_{12}B_{18}O_{60}H_6]$, $(Na)_{10}[(H_2O)V_{12}B_{18}O_{60}H_6] \cdot 18H_2O$ (**1**), $Na_8[Cu(en)_2]_2[V_{12}B_{18}O_{60}H_6](NO_3)_2 \cdot 14.7H_2O$ (**2**), $Na_7[Cu(en)_2]_2[V_{12}B_{18}O_{60}H_6](NO_3)_2 \cdot 15.5H_2O$ (**3**), (en = ethylenediamine), have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction analysis and TGA. Compound **1** consists of polyoxovanadium borate $[V_{12}B_{18}O_{60}H_6]$ clusters which are surrounded by sodium countercations in octahedral sites, stabilized by electrostatic interactions with the oxygen atoms of both vanadium and boron centres. However, compounds **2** and **3** correspond to more complicated structures, constructed from the same polyoxometalate clusters, which are interconnected by $[Cu(en)_2]^{2+}$ moieties via the terminal oxygen atoms of the polyoxoanions, generating one-dimensional structures. The functionalization of this polyoxovanadium borate cluster has been obtained by the use of $[Cu(en)_2]^{2+}$ complex ions, thus demonstrating the capacity of the terminal oxygen atoms of the cluster to bind transition metal centres. The structural stability of the $[V_{12}B_{18}O_{60}H_6]$ cluster permits the formation of functionalized polyoxometalate clusters, generating various crystalline lattices.

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1. Introduction

Transition metal oxide clusters, or polyoxometalates (POMs), represent an important class of molecular systems with wide ranging applications in several areas such as analytical chemistry, materials science and catalysis, nanotechnology, energy storage, sorption, and as optical and magnetic materials [1–16]. Polyoxovanadates, constitute an important but, as compared to polyoxomolybdates and polyoxotungstates, relatively less studied subclass of polyoxometalates. Among these both polyoxovanadium borophosphates [17–19] and polyoxovanadium borates remain

largely unexplored [20–27]. One challenging task in POM chemistry is to connect these with various organic and/or transition metal complex moieties, and in this way to link them up into one-, two-, and three-dimensional extended solid frameworks. The crucial requirement for the success of this approach is to find suitable POMs that can be readily assembled. Thus the introduction of a transition metal complex cannot only enrich the framework of polyoxometalates, but can also modify their electronic and magnetic properties [10,13,28–39].

In this paper we describe the hydrothermal synthesis and crystal structure of three polyoxovanadium borates frameworks, in which the negative charge is counterbalanced by alkaline cations and/or by copper(II) ethylenediamine complex cations; $(Na)_{10}[(H_2O)V_{12}B_{18}O_{60}H_6] \cdot 18H_2O$ (**1**), $Na_8[Cu(en)_2]_2[V_{12}B_{18}O_{60}H_6](NO_3)_2 \cdot 14.7H_2O$ (**2**), $Na_7[Cu(en)_2]_2[V_{12}B_{18}O_{60}H_6](NO_3)_2 \cdot 15.5H_2O$ (**3**). Even though other compounds based on the $[V_{12}B_{18}O_{60}H_6]$ cluster has been described before, in this work we are reporting a new framework for the polyoxovanadium borate cluster, and

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two novel chain structures for the functionalized polyoxovanadium borate cluster.

2. Experimental

All reagents were analytical grade products and were used without further purification.

2.1. Synthesis of compound $(\text{Na})_{10}[(\text{H}_2\text{O})_7\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6] \cdot 18\text{H}_2\text{O}$ (**1**)

The starting mixture: NH_4VO_3 (0.217 g, 1.85×10^{-3} mol), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (1.89 g, 4.94×10^{-3} mol), ethylenediamine (0.08 mL, 1.24×10^{-3} mol) and 2 mL H_2O was heated in a 23 mL Teflon lined Parr reactor at 170 °C for 72 h. After the autoclave had cooled down to room temperature, orange crystals of **1** were isolated and washed with water, and then dried at room temperature.

2.2. Synthesis of compounds $\text{Na}_8[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3)_2 \cdot 14.7\text{H}_2\text{O}$ (**2**), and $\text{Na}_7[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3) \cdot 15.5\text{H}_2\text{O}$ (**3**)

By hydrothermal treatment of the starting mixture: NH_4VO_3 (0.217 g, 1.85×10^{-3} mol), $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ (1.89 g, 4.94×10^{-3} mol), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.448 g, 1.85×10^{-3} mol), ethylenediamine (0.08 mL, 1.24×10^{-3} mol), 3,5-dicarboxypyridine (0.155 g, 9.27×10^{-4} mol) and H_2O (1.5 mL) was performed. The mixture was heated in a 23 mL Teflon lined Parr reactor at 170 °C for 72 h. After the autoclave had cooled down to room temperature, crystals of **1**, **2** and **3**, together with an unidentified bulk blue product, were isolated mechanically with the use of a microscope, washed with water, and then dried at room temperature.

The use of 3,5-dicarboxypyridine permits to obtain the isolated crystalline compounds. If this reagent is not used, metallic copper is formed during the reaction, and the above mentioned species are not formed. The influence of reactants, not present in the products obtained from hydrothermal reactions, has previously been reported [20,22,28]. These reactants may influence the pH value of the reacting mixture, and thus the redox properties of the involved species defining the nature of the isolated products.

2.3. X-ray crystal structure determination

Data collection for **1** were performed at room temperature on a Nonius Kappa-CCD diffractometer, with graphite-monochroma-

tized Mo $K\alpha$ radiation ($\lambda = 0.71073$), while data collection for **2** and **3** were performed at room temperature on a Bruker-Kappa-CCD diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$). Intensities were collected by means of the program COLLECT [40]. Preliminary examination with X-ray showed reasonable crystal quality for (**1**), (**2**), and (**3**). More detailed exploration of the reciprocal space showed no sign of rotational twinning. Reflection indexing, Lorentz-polarization correction, peak integration and background determination were carried out with the DENZO program of the Kappa-CCD software package [41]. Unit-cell parameters refinement and frame scaling were performed with the program DIRAX/LSQ [42]. Data integration and scaling of the reflections were performed with the suite SCALEPACK [43]. Empirical multiscan absorption corrections using equivalent reflections were performed with the program SADABS [44]. The structure was solved and refined against F2 by full-matrix least-squares techniques using SIR-97 [45] and SHELX-L-97 [46] implemented in the WINGX software package [47]. Efforts for lowering the rather high residuals on (**1**) and (**2**) included the evaluation of different models of solvation and the use of squeeze (for the modelling of the remaining density), and were unsuccessful. The values may be considered as arising from the complexity of the model used for the solvation and counterbalancing. Crystallographic data and details on data collection are listed in Table 1. Structure drawings were carried out with DIAMOND-3.0e, supplied by Crystal Impact [48].

2.4. Thermogravimetric analysis

The thermogravimetric analyses were done on a TG 209 Fl Iris Netzsch analyzer. A microcrystalline sample of approximately 15 mg was used in each determination. The sample was heated under nitrogen with a heating speed of 10 °C/min, in the temperature range of 298–1300 K. The thermal behaviour of the clusters was recorded in the TGA and DTG modes.

3. Results and discussion

Large structurally complicated clusters, which present different number of boron and vanadium atoms, easily form in good yield from simple vanadium and boron sources by hydrothermal synthesis. Among these the anionic $[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]$ cluster is a molecular species that is easily formed with different synthetic conditions, and therefore can be considered as the precursor of a series of oxovanadium

Table 1
Crystal data and details of the data collection and refinement for complexes **1–3**.

Complex	1	2	3
Formula	$\text{H}_{44}\text{B}_{18}\text{Na}_{10}\text{O}_{79}\text{V}_{12}$	$\text{C}_8\text{H}_{67.4}\text{B}_{18}\text{Cu}_2\text{N}_{10}\text{Na}_8\text{O}_{80.7}\text{V}_{12}$	$\text{C}_8\text{H}_{69}\text{B}_{18}\text{Cu}_2\text{N}_9\text{Na}_7\text{O}_{78.5}\text{V}_{12}$
Moiety formula	$\text{Na}_{10}[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6] \cdot 19\text{H}_2\text{O}$	$\text{Na}_8[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3)_2 \cdot 14.7\text{H}_2\text{O}$	$\text{Na}_7[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3) \cdot 15.5\text{H}_2\text{O}$
Formula weight	2344.10	2712.15	2641.56
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	13.610(5)	13.175(3)	13.629(3)
<i>b</i> (Å)	16.992(5)	13.567(3)	15.591(3)
<i>c</i> (Å)	14.338(5)	13.768(3)	21.599(4)
α (°)	90.000(5)	85.49(3)	75.06(3)
β (°)	97.747(5)	70.45(3)	73.60(3)
γ (°)	90.000(5)	61.14(3)	70.24(3)
<i>V</i> (Å ³)	3285.6(2)	2020.8(7)	4075.8(14)
<i>Z</i>	2	1	2
<i>T</i> (K)	293(2)	293(2)	293(2)
<i>D_c</i> (g/cm ³)	2.346	2.207	2.167
μ (mm ⁻¹)	1.847	2.004	1.976
Independent reflections	9410	8724	18097
Parameters	556	679	1243
<i>R</i> ₁ [<i>I</i> > 2(<i>I</i>)]	0.0721	0.0820	0.0463
<i>wR</i> ₂ [<i>I</i> > 2(<i>I</i>)]	0.1914	0.2540	0.1254
<i>R</i> ₁ (all data)	0.1041	0.1296	0.0641
<i>wR</i> ₂ (all data)	0.2154	0.3403	0.1407

borates. This cluster can crystallize with different counteractions such as sodium (framework **1**), and sodium and $[\text{Cu}(\text{en})_2]^{2+}$ (frameworks **2–3**) reported in this work, or with sodium, potassium and enH^+ as published recently by Lu et al. [49] or with diprotonated ethylenediamine as reported by Rijssenbeek et al. [27].

3.1. Structural description of $(\text{Na})_{10}[(\text{H}_2\text{O})\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]\cdot 18\text{H}_2\text{O}$ (**1**)

The orange colour of the $(\text{Na})_{10}[(\text{H}_2\text{O})\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]\cdot 18\text{H}_2\text{O}$ (**1**) zero-dimensional cluster indicates a mixed V(IV)/V(V) species. The stoichiometry of the compound permits to propose 10 V(IV) and 2 V(V) centres in the cluster, in order to maintain the electro-neutrality of the compound. The vanadium oxidation states were determined by considering the other known charges present in the framework and confirmed by valence bond calculations [50], which show a mean valence of +4.24 for each vanadium atom. This value is close to the +4.17 expected for a vanadium (IV)/vanadium (V) ratio of 5:1. The individual calculated values permit to infer that each vanadium position has an equal probability of containing either type of oxidation state for vanadium.

The cluster shown in Fig. 1 has an approximate diameter of 8.739 Å when measured internally from a trigonal B1 atom to the B1 on the opposite side of the ring, while a height of 7.128 Å can be defined for the species when measuring from V2 from one ring to the V2 of the other ring. This $[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]$ cluster can be described as being formed by a puckered $\text{B}_{18}\text{O}_{42}\text{H}_6$ ring in between two rings of six alternating *cis* and *trans* edge-sharing vanadium atoms. A water molecule is confined in the middle of the cluster. The hexagonal vanadium rings are constituted by VO_5 square base pyramids, with the oxygen atoms of the vanadyl groups protruding

to the periphery of the ring, presenting V–O bond distances of 1.630 Å. The other V–O bond distances are in the range of 1.918–2.036 Å. The equatorial bond angles range from 77.51° to 96.80°, while the O–V–O apical angles are of the order 113°.

The $\text{B}_{18}\text{O}_{42}\text{H}_6$ ring can be described by six B_3O_7 building blocks, each one constituted by one planar trigonal boron atom and two boron atoms in tetrahedral geometry. The B–O bond distances for the trigonal boron atom are in the range of 1.362–1.388 Å and the O–B–O bond angles are in the range of 116.29–123.71°. The distances for the B–O bonds corresponding to boron in a tetrahedral geometry are in the range of 1.440–1.533 Å, with O–B–O bond angles in the range of 105.98–111.30°. The trigonal boron atoms present protonated terminal oxygen atoms.

With respect to the crystalline packing, the structure is formed by anionic clusters of $[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]$ that are surrounded by sodium counteractions, which are placed in octahedral sites, stabilized by electrostatic interactions with the oxygen atoms of both vanadium and boron atoms. The apical Na–O distances are 2.362 and 3.040 Å, and the equatorial ones range from 2.219 to 2.481 Å, thus describing a distorted octahedral environment around the sodium atoms. Besides, the sodium cations interact with each other through water molecules which are also part of the distorted octahedral coordination spheres.

3.2. Structural description of

$\text{Na}_8[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3)_2\cdot 14.7\text{H}_2\text{O}$ (**2**)

The crystal structure of $\text{Na}_8[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3)_2\cdot 14.7\text{H}_2\text{O}$ (**2**) is composed by the same cluster $[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]$ described for **1**. The negative charge of this cluster, together with that

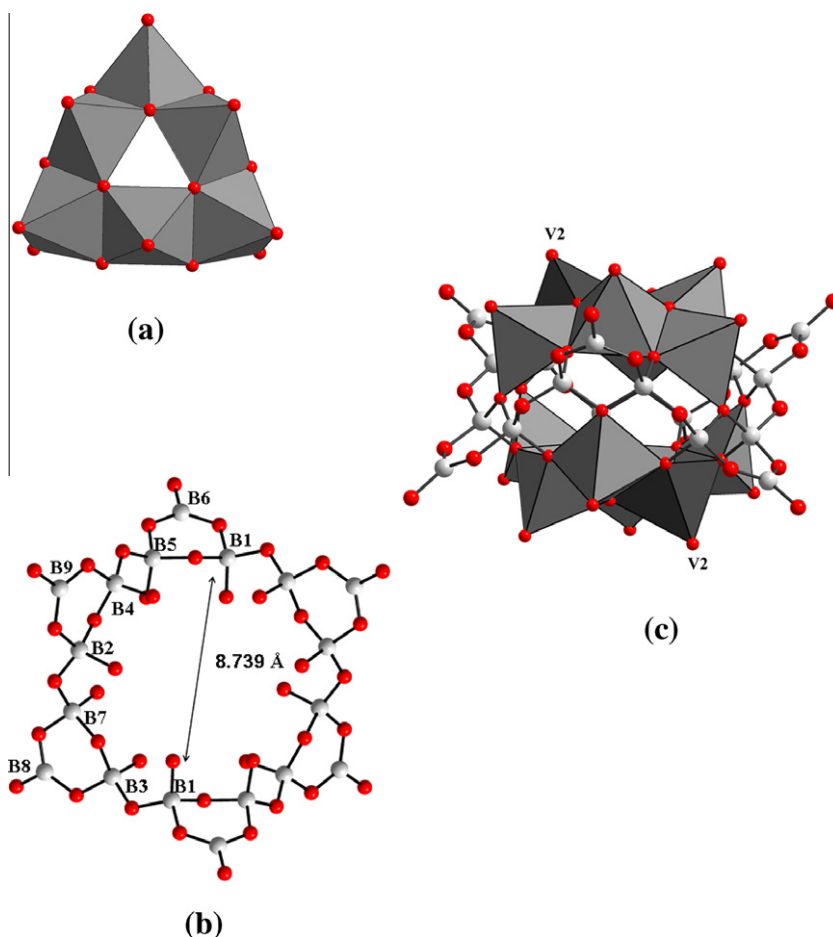


Fig. 1. (a) Polyhedral representation of the oxovanadium ring; (b) borate ring; (c) $[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]$ cluster.

of the nitrate ions present in the framework is compensated by sodium cations and $[\text{Cu}(\text{en})_2]^{2+}$ complex ions.

The crystalline packing shown in Fig. 2 is formed by the interlinking of the cluster moieties with $[\text{Cu}(\text{en})_2]^{2+}$ complex cations. There are two crystallographically independent copper atoms in compound **2**. The Cu1 atom is in a distorted octahedral coordination environment, built up from four nitrogen atoms from two ethylenediamine molecules and two oxygen atoms from the vanadyl group of the VO_5 square pyramids of the cluster (Cu1–O18 = 2.590 Å). The Cu1–N1 and Cu1–N2 bond distances are 2.027 and 2.018 Å, respectively (Table 2).

As the internal symmetry of the cluster anion is C_i , two vanadium atoms share oxygen with two crystallographically equivalent copper ions; being the copper(II) ion on a centre of symmetry. Consequently a one-dimensional chain along the *b* axis is formed by $[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]$ clusters interlinked with $[\text{Cu}(\text{en})_2]^{2+}$ complexes in an alternated fashion.

The Cu2 atom is also coordinated to two ethylenediamine ligands at bond lengths of Cu2–N3 = 1.989 Å and Cu2–N4 = 1.986 Å in a square planar geometry (Table 2). Contrary to Cu1, Cu2 remains isolated as a compensating charge complex cation. Sodium ions are also found in the three-dimensional arrangement, close to the cluster anions. Nitrate ions from the copper precursor are also observed in the intercluster space.

3.3. Structural description of $\text{Na}_7[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3) \cdot 15.5\text{H}_2\text{O}$ (**3**)

This compound presents a cluster with the same structural and valence features described for **2**. The crystalline framework is built

Table 2
Copper coordination distances for complexes **2** and **3**.

Distance (Å)	2	3
Cu1–N1	2.027(7)	2.025(4)
Cu1–N2	2.018(7)	1.996(4)
Cu2–N3	1.989(8)	2.005(4)
Cu2–N4	1.986(7)	2.017(4)
Cu3–N5		2.014(4)
Cu3–N6		2.026(4)
Cu4–N7		2.011(5)
Cu4–N8		2.003(4)
Cu1–O18	2.590(6)	
Cu1–O18 ⁱ	2.590(6)	
Cu2–O25	2.987(6)	
Cu2–O25 ⁱⁱ	2.987(6)	
Cu1–O41		2.543(6)
Cu1–O41 ⁱⁱⁱ		2.543(6)
Cu2··O26 ^{iv}		3.051(6)
Cu2··O26 ⁱⁱ		3.051(6)
Cu3–O30		2.621(6)
Cu3–O30 ^v		2.621(6)
Cu4··O55		2.960(6)
Cu4··O55 ^{vi}		2.960(6)

(i) $-x, 2-y, 2-z$; (ii) $1-x, 1-y, 1-z$; (iii) $3-x, 1-y, 1-z$; (iv) $x, y, z-1$; (v) $2-x, -y, 2-z$; (vi) $2-x, -y, 1-z$.

up by the interconnection of the $[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]$ clusters bonded to $[\text{Cu}(\text{en})_2]^{2+}$ complex ions, forming infinite chains running along the *a* axis (Fig. 3). The metal ligand atom distances are similar as the ones informed for **2**. The difference with the packing observed for **2** is associated with the amount of sodium and nitrate ions in the crystal lattice. Besides, the nitrate ion in **3** is occupying an

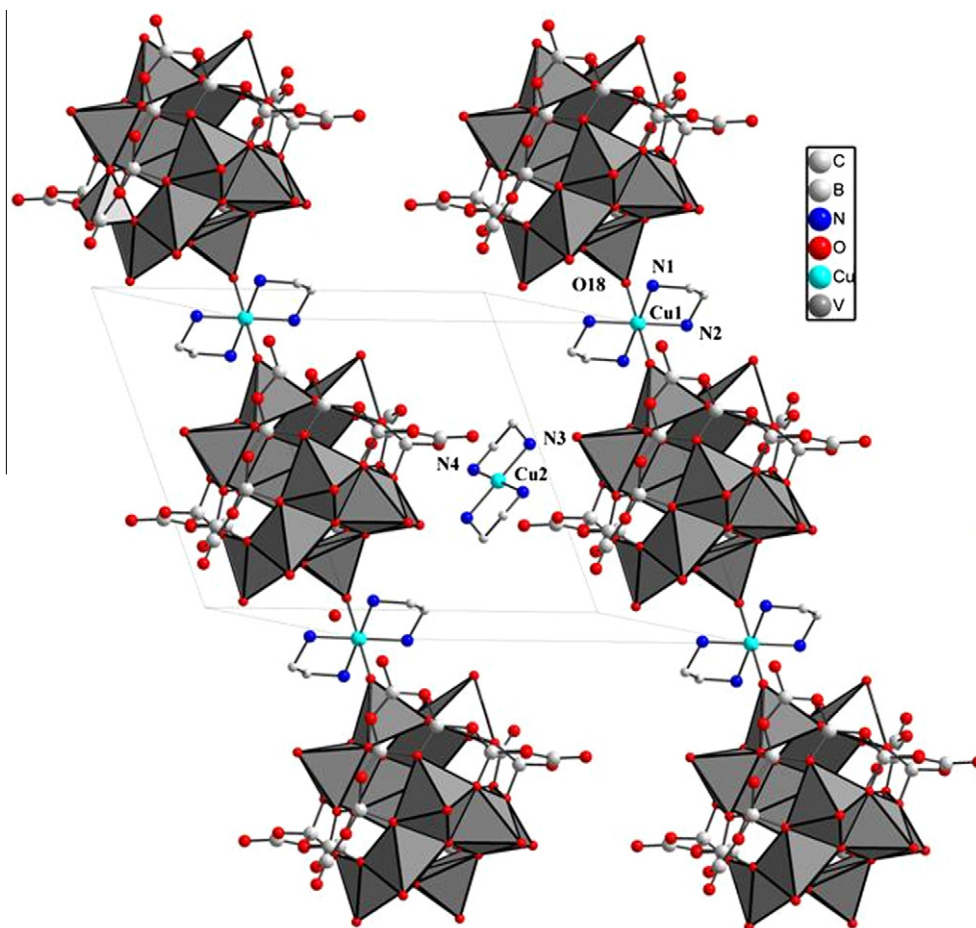


Fig. 2. Framework of compound **2**. Chains running along *b* axis.

apical position in the distorted octahedral environment around the sodium ion, while in **2** this anion presents a non-bonded position in the interstitial space between the cluster units. For the interstitial $[\text{Cu}(\text{en})_2]^{2+}$ complexes, the four Cu–N bond distances, which define the square planar geometry, are in the range 2.003–2.017 Å (Table 2).

3.4. Thermogravimetric analysis

The thermogravimetric analysis of compound **1** presents a 13% of mass loss around 101 °C. This experimental percentage can be associated with the loss of the solvation water molecules, which are present in the framework of $(\text{Na})_{10}[(\text{H}_2\text{O})\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6] \cdot 18\text{H}_2\text{O}$, since the calculated percentage for the loss of 18 water molecules is 13.8%. The loss of the occluded water molecule in the structure of the cluster should take place at a higher temperature, and induce the structure of the cluster to collapse.

For the cluster functionalized with the ethylenediamine copper(II) complexes, $\text{Na}_8[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3)_2 \cdot 14.7\text{H}_2\text{O}$ (**2**), the thermogram presents several mass losses in the temperature range of 30–164 °C. These are due to the dehydration process, in which the solvate water molecules are lost, together with the decomposition of the two nitrate ions. The experimental mass loss

is 14%, which compares well with the calculated value of 14.3%. The second process from 164 to 275 °C can be associated with the loss of the ethylenediamine ligands, which are coordinated to the copper(II) ions.

For the second cluster functionalized with the ethylenediamine copper(II) complexes, $\text{Na}_7[\text{Cu}(\text{en})_2]_2[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6](\text{NO}_3) \cdot 15.5\text{H}_2\text{O}$ (**3**), two processes which can be attributed to the joint loss of the water molecules and nitrate ion, are observed in the 30–150 °C temperature range. The experimental mass loss is 12%, which compares well with the calculated value of 12.9%. The following mass loss, which ends at 275 °C corresponds to the release of the ethylenediamine molecules coordinated to the copper(II) ions.

4. Discussion

Vanadium based polyoxometalates are good candidates for functionalization, as the oxygen atoms of the vanadyl group remain generally unshared within the cluster. Polyoxometalate heteronuclear clusters containing Mo(VI) or W(V)/W(VI) centres with V(IV)/V(V) atoms are known to covalently bind coordination compounds due to the fact that their surface contain sufficient charge density, thus producing one-, two-, and three-dimensional

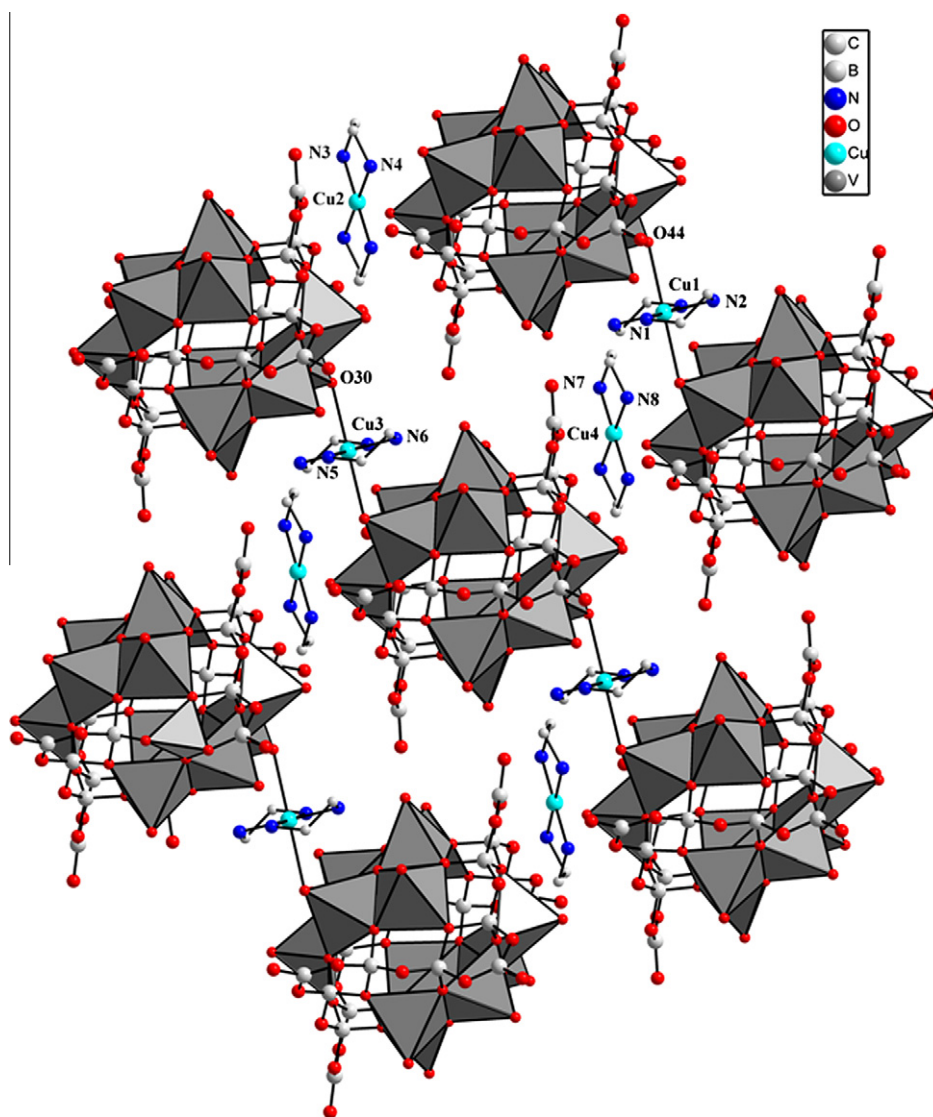


Fig. 3. Framework of compound **3**. Chains running along *a* axis.

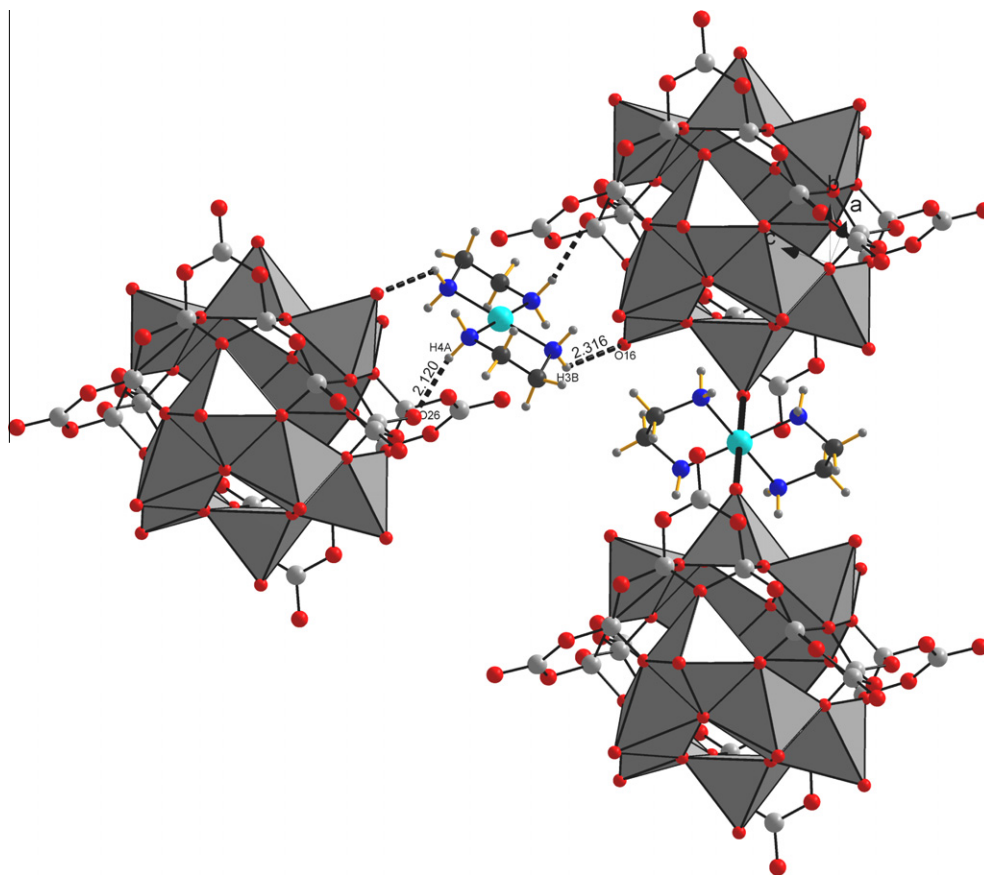


Fig. 4. Hydrogen bonding in compound 2.

extended frameworks. $[\text{Cu}(\text{en})_2]^{2+}$ complex ions are known to act as linkers between polyoxometalate heteronuclear clusters and are reported in the literature [10,28–33]. For example, the compounds $\text{H}_3\{\text{V}^{\text{V}}\text{Mo}^{\text{VI}}_8\text{V}^{\text{IV}}_6\text{O}_{42}\}[\text{Cu}(\text{en})_2]_4[\text{MoO}_4]_2 \cdot 14\text{H}_2\text{O}^{10}$ and $[\text{Cu}(\text{en})_2(\text{H}_2\text{O})_2]_2[\text{Cu}(\text{en})_2][\text{AsW}^{\text{VI}}_2\text{W}^{\text{V}}_7\text{V}^{\text{IV}}_7\text{O}_{44}] \cdot 2\text{H}_2\text{O}^{29}$ present mixed valence species which are linked by the $[\text{Cu}(\text{en})_2]^{2+}$ cations.

The studied cluster $[\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6]$ is potentially able to share the 12 oxygen atoms from the vanadyl groups. Owing to the ellipsoidal form of this cluster zero-, one-, two- or three-dimensional frameworks can be formed. As attempts to dissolve the isolated cluster in various solvents were unsuccessful, direct syntheses of the functionalized cluster were performed. The resulting compounds show $[\text{Cu}(\text{en})_2]^{2+}$ complexes coordinated to the cluster by the oxygen atom of the vanadyl groups as expected. However, while 12 oxygen atoms are potential candidates for coordination, only two of them are bonded for compounds 2 and 3. One of the remarkable features is that for the two reported chain like structures, functionalized with $[\text{Cu}(\text{en})_2]^{2+}$ complexes, the same vanadyl groups are involved in the formation of the chain.

The importance of the used synthetic conditions can be summarized by the products isolated in this work. Dark orange rectangular crystals of 1 were obtained with the use of a more basic medium than the previously reported one, in which an acidic medium generated by H_3BO_3 was used [27]. It is important to point out that compounds 2 and 3 are also obtained in this same medium together with cluster 1, thus showing the high structural stability of the above mentioned cluster.

In the two reported frameworks functionalized with copper complexes, extensive hydrogen bonding is present, mainly between the ethylenediamine complex cations and the anionic clusters. In compound 2 the free copper complex presents hydrogen

bonding with two adjacent clusters. Two different hydrogen bonds are observed: N3–B3H...O16 ($d_{\text{B3H-O16}} = 2.316 \text{ \AA}$) and N4–H4A...O26 ($d_{\text{H4A-O26}} = 2.130 \text{ \AA}$). In compound 3 the four copper complexes present hydrogen bonding. Cu1 and Cu3 complexes, located between two clusters, present hydrogen bonding with the clusters they are connected to; Cu1 complex through H2A with O41 shared between three vanadium atoms ($d_{\text{H2A-O41}} = 2.337 \text{ \AA}$) and Cu3 complex through H5A with O14 ($d_{\text{H5A-O14}} = 2.246 \text{ \AA}$). Cu2 and Cu4 isolated complexes are involved each in hydrogen bonding with two adjacent clusters in a very similar manner. Two hydrogen atoms from the same nitrogen (N4 for Cu2 complex and N7 for Cu4 complex) are involved in hydrogen bonding with two oxygen atoms from vanadyl groups ($d_{\text{H4A-O6}} = 2.396 \text{ \AA}$, $d_{\text{H4B-O2}} = 2.259 \text{ \AA}$, and $d_{\text{H7A-O31}} = 2.358 \text{ \AA}$, $d_{\text{H7B-O47}} = 2.319 \text{ \AA}$). The second nitrogen atom of the complex (N3 for Cu2 complex and N8 for Cu4 complex) share one hydrogen with an oxygen atom from a B–O–B bridge ($d_{\text{H3A-O25}} = 2.137 \text{ \AA}$ and $d_{\text{H8B-O54}} = 2.141 \text{ \AA}$). Consequently six hydrogen bonds are observed between Cu2 and Cu4 complexes and the corresponding adjacent cluster. Hydrogen bonding interactions are shown in Figs. 4 and 5.

Thus it is possible to conclude that all the copper complexes, which do not act as linkers for the one-dimensional frameworks, form hydrogen bonds with adjacent clusters, which strongly reinforce the crystalline lattices.

5. Conclusions

Direct syntheses of the functionalized clusters $\text{V}_{12}\text{B}_{18}\text{O}_{60}\text{H}_6$ with $[\text{Cu}(\text{en})_2]^{2+}$ complex ions were done, resulting in monodimensional frameworks. The obtained compounds reveal that the above

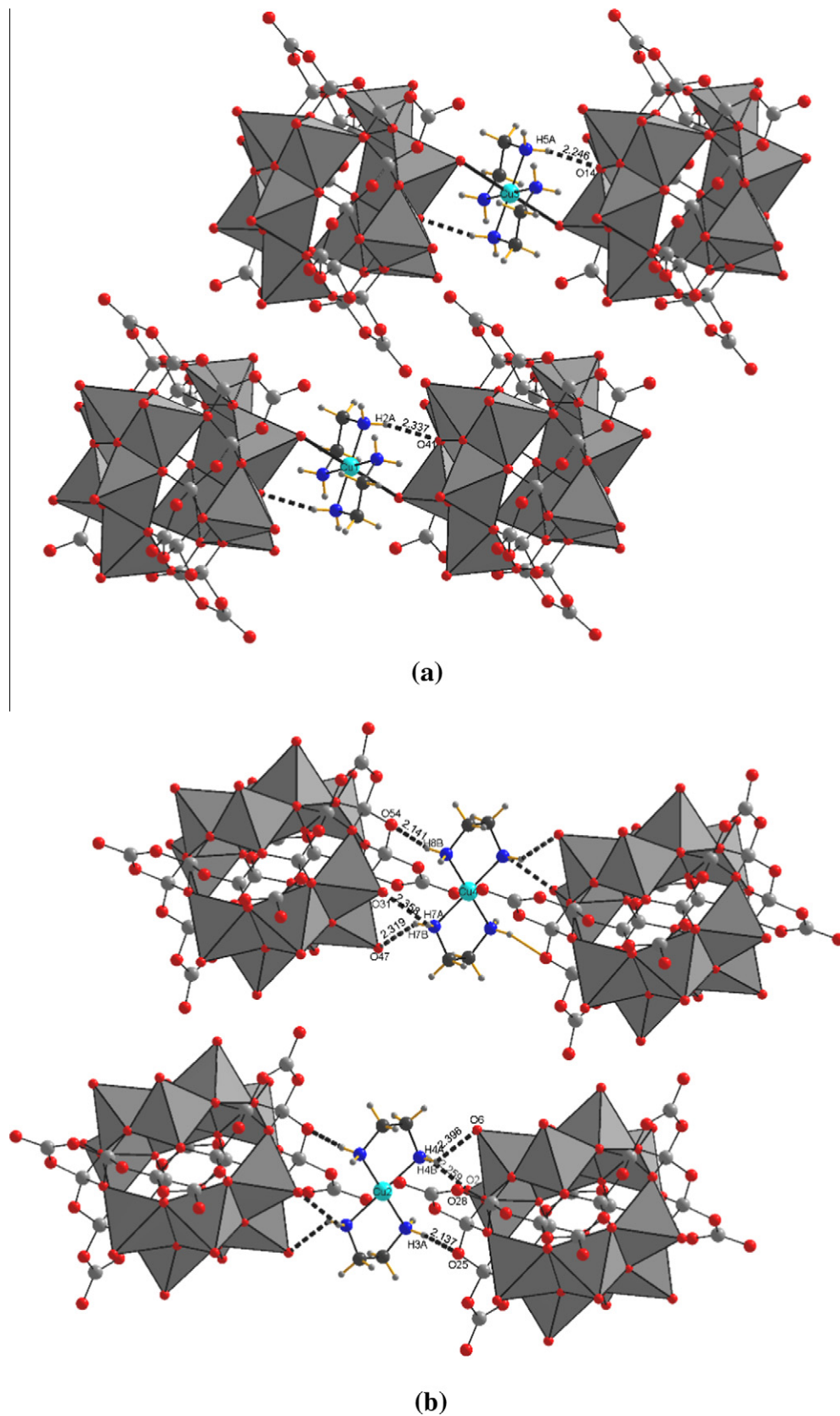


Fig. 5. Hydrogen bonding in compound 3: (a) copper connected to the clusters and (b) isolated copper complexes.

mentioned species can share twelve oxygen atoms of the vanadyl groups, suggesting that three-dimensional frameworks can also be obtained using this cluster.

The structural stability of the $[V_{12}B_{18}O_{60}H_6]$ cluster permits the formation of polyoxometalate species with different crystalline lattices, depending on the cations present in the synthesis.

Acknowledgments

Authors acknowledge ECOS-CONICYT C08E02 International Project. The authors also thank Financiamiento Basal Program FB0807 and FONDECYT 1080316 for partial financial support. This work was done under the LIA-MIF CNRS 836 Collaborative Program. KBA thanks CONICYT for the 21050162 and AT-24071044 doctoral scholarships, and the University of Chile AVV-5 grant. M.G.F.V. and R.A.A. acknowledge LDRX-UFF, and partial financial support from CAPES, FAPERJ and CNPq.

Appendix A. Supplementary material

Crystallographic data for structures of **1**, **2** and **3** reported in this paper, have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC-727716, 727718, 727719. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road Cambridge CB21EZ, UK (fax: +44 (123) 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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