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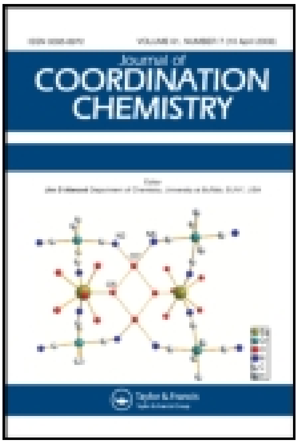

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Three new polyoxoniobates constructed from Lindqvist-type hexaniobate and copper–amine complexes

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Three new polyoxoniobates constructed from Lindqvist-type $[Nb_6O_{19}]^{8-}$ and copper–amine complexes, $[Cu(1,2\text{-dap})_2]\{[Cu(1,2\text{-dap})_2]_2[Nb_6O_{19}H_2]\}\cdot 10H_2O$ (**1**), $[Cu(1,3\text{-dap})_2]_2\{[Cu(1,3\text{-dap})]_2[Nb_6O_{19}]\}\cdot 10H_2O$ (**2**), and $[Cu(en)_2]_{0.5}\{[Cu(en)_2]_2[Nb_6O_{19}H_3]\}\cdot 12H_2O$ (**3**) (1,2-dap = 1,2-diaminopropane, 1,3-dap = 1,3-diaminopropane, and en = ethylenediamine), have been synthesized and characterized by elemental analyses, infrared, powder X-ray diffraction, thermogravimetric analysis, X-ray photoelectron spectrum, and single-crystal X-ray diffraction. Compounds **1–3** exhibit bisupporting hexaniobate cluster structure, each with a $[Nb_6O_{19}]^{8-}$ cluster decorated by two copper–amine complexes. In **1**, adjacent bisupporting clusters are connected with one $[Cu(1,2\text{-dap})_2]^{2+}$ fragment *via* $Cu\cdots O$ weak interactions to generate a 1-D supramolecular chain structure. In contrast to **1**, each bisupporting cluster in **2** is linked to another four neighboring ones through four $[Cu(1,3\text{-dap})_2]^{2+}$ fragments by $Cu\cdots O$ weak interactions to yield a 2-D supramolecular network. Different from **1** and **2**, no detected interaction was found between bisupporting cluster and $[Cu(en)_2]^{2+}$ in **3**, the $[Cu(en)_2]^{2+}$ fragment merely acts as an isolated countercation.

Keywords: Polyoxoniobate; Lindqvist-type; Bisupporting polyoxoanion

1. Introduction

There has been extensive interest in polyoxoniobates due to their unique structures and potential applications in virology, nuclear-waste treatment, and base-catalyzed decomposition of biocontaminants [1–5]. However, compared with a large number of reports on the chemistry of polyoxotungstates, -molybdates, and -vanadates, which can be easily obtained from a wide pH range, development of polyoxoniobate chemistry is still very limited because of the lack of soluble monomeric precursors and the low activity of Nb species [3–6]. In addition, polyoxoniobates are stable only in basic solutions, and their chemistry is still dominated by the Lindqvist-type $[Nb_6O_{19}]^{8-}$ anion [7–11]. As a notable subfamily in polyoxometalate chemistry, explorations of new polyoxoniobate series possessing novel structures and properties have been attracting extensive

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interest [12, 13]. Much attention has been focused on a combination of $[Nb_6O_{19}]^{8-}$ and transition metal ions, and some structurally characterized compounds have been obtained. For example, Pope *et al.* [14] synthesized several tricarbonyl metal derivatives of hexaniobate anions $[Nb_6O_{19}\{M(CO)_3\}_n]^{(8-n)-}$ (M = Re, Mn; $n = 1, 2$). Hegetschweiler *et al.* [15] reported two complexes $\{trans/cis-[H_xNb_6O_{19}][Ni(taci)]_2\}^{n-}$ [(taci = 1,3,5-triamino-1,3,5-trideoxy-cis-inositol), $x = 0$, $n = 4$ and $x = 2$, $n = 2$], in which two $[Ni(taci)]^{2+}$ entities are bonded to the surface oxygens of hexaniobate anion. Nyman and co-workers [16] prepared five polyoxoniobates based on linkage of $[Nb_6O_{19}]$ clusters and $[CuL_x]$ (L = ethylenediamine (en), NH_3, H_2O). Niu *et al.* [17] reported a new neutral polyoxoniobate $\{Nb_6O_{19}[Cu(2,2'\text{-bipy})]_2[Cu(2,2'\text{-bipy})_2]_2\} \cdot 19H_2O$ and three 2-D polyoxoniobates constructed from $[Nb_6O_{19}]^{8-}$ and mixed organic ligands [18].

Although some progress has been made in the investigation of polyoxoniobate chemistry, fewer endeavors were made on the deliberate design and synthesis of polyoxoniobates modified by different amine. As further exploration of the polyoxoniobate system, we employed different organoamines as templates and obtained three polyoxoniobates $[Cu(1,2\text{-dap})_2]\{[Cu(1,2\text{-dap})_2]_2[Nb_6O_{19}H_2]\} \cdot 10H_2O$ (**1**), $[Cu(1,3\text{-dap})_2]_2\{[Cu(1,3\text{-dap})]_2[Nb_6O_{19}]\} \cdot 10H_2O$ (**2**), and $[Cu(en)_2]_{0.5}\{[Cu(en)_2]_2[Nb_6O_{19}H_3]\} \cdot 12H_2O$ (**3**).

2. Experimental

2.1. *Materials and methods*

$K_7HNb_6O_{19} \cdot 13H_2O$ was prepared according to the procedures in the literature [19] and confirmed by infrared (IR) spectrum. Other reagents were purchased from commercial sources and used without purification. C, H, and N analyses were performed on a Perkin-Elmer 2400 element analyzer. IR spectra were recorded on a Nicolet 170SXFT/IR spectrometer using KBr pellets from 4000 to 400 cm^{-1}. Thermogravimetric analysis was performed on a SDT Q600 instrument under nitrogen with a heating rate of 10°C min^{-1}. X-ray photoelectron spectrum (XPS) analyses were performed on a VG Escalabmkll spectrometer (UK) with an Al-Kα ($h\nu = 1486.7$ eV) achromatic X-ray source.

2.2. *Synthesis of $[Cu(1,2\text{-dap})_2]\{[Cu(1,2\text{-dap})_2]_2[Nb_6O_{19}H_2]\} \cdot 10H_2O$ (1)*

Five milliliters dimethylsulfoxide (DMSO) solution containing $Cu(NO_3)_2 \cdot 3H_2O$ (1.0 mmol, 0.241 g) and 0.6 mL 1,2-dap, 3 mL 2 : 1 DMSO: H_2O mixed-solution, and 5 mL H_2O solution containing $K_7HNb_6O_{19} \cdot 13H_2O$ (0.15 mmol, 0.205 g) were dropped slowly in a 20 mL test tube in sequence. The test tube was sealed with film and left at room temperature. After 2 weeks, blue crystals of **1** were obtained (yield: 27.86% based on Nb). Elemental analysis for $C_{18}H_{82}Cu_3N_{12}Nb_6O_{29}$ (%). Calcd: C, 12.87; H, 4.88; N, 10.01. Found: C, 12.96; H, 4.75; N, 9.85.

2.3. *Synthesis of* $[Cu(1,3\text{-}dap)_2]_2\{[Cu(1,3\text{-}dap)]_2[Nb_6O_{19}]\} \cdot 10H_2O$ *(2)*

The synthetic method of **2** is similar to **1** except that 1,2-dap was replaced by 1,3-dap. After 2 weeks, blue crystals of **2** were obtained (yield: 18.91% based on Nb). Elemental analysis for $C_{18}H_{80}Cu_4N_{12}Nb_6O_{29}$ (%). Calcd: C, 12.41; H, 4.59; N, 9.65. Found: C, 12.56; H, 4.45; N, 9.56.

2.4. *Synthesis of* $[Cu(en)_2]_{0.5}\{[Cu(en)_2]_2[Nb_6O_{19}H_3]\} \cdot 12H_2O$ *(3)*

Five milliliters H_2O solution containing $K_7HNb_6O_{19} \cdot 13H_2O$ (0.15 mmol, 0.205 g) and $LiCl \cdot H_2O$ (1 mmol, 0.06 g), 3 mL 2 : 1 methanol: H_2O mixed-solution, and 5 mL methanol solution containing $Cu(CH_3COO)_2 \cdot H_2O$ (1 mmol, 0.20 g) and 0.6 mL en were dropped slowly in a 20 mL test tube in sequence. The test tube was sealed with film and left at room temperature. After 4 weeks, blue crystals of **3** were obtained (yield: 53.47% based on Nb). Elemental analysis for $C_{10}H_{40}Cu_{2.5}N_{10}Nb_6O_{31}$ (%). Calcd: C,7.39; H, 2.64; N, 9.25. Found: C, 7.28; H, 2.56; N, 9.37.

2.5. *X-ray crystallography*

Crystal data for **1–3** were collected at 296(2) K on a Bruker APEX–II CCD detector with graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). The three structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL-97 [20, 21]. All the active hydrogens were not incorporated in the refinement. Charge balance requires the presence of two protons in the structural unit of **1** and three protons in **3**. These protons may be delocalized in the Lindqvist cluster anion and have not been located in the crystal structure. Such phenomenon is common according to previous literature [4, 22]. The crystal data and structure refinement for **1–3** are summarized in table 1. Selected bond lengths (Å) and angles (°) for **1–3** are listed in table 2.

3. Results and discussion

3.1. *Synthesis*

Compounds **1–3** have been prepared by using the diffusion strategy. Compounds **1** and **2** were synthesized under the same reaction conditions (from the H_2O/DMSO system) except for using different organoamines, but the structures of **1** and **2** display some differences, which may result from the influence of geometric configuration of the organic ligands. In addition, by using the same preparation conditions for **1** (or **2**) except that 1,2-dap (or 1,3-dap) was replaced by en, a previously reported compound $[Cu(en)_2(H_2O)_2]_2[(Nb_6O_{19}H_2)Cu(en)_2] \cdot 14H_2O$ was afforded [16], in which the crystal structure is different from **1** and **2**. So it can be concluded that the organoamines play a role in the formation of crystal structures. After parallel experiments, we found that **3** could be isolated from the H_2O/methanol system. With other reaction conditions unchanged, we tried to synthesize **3** by replacing $Cu(CH_3COO)_2 \cdot H_2O$ with $Cu(NO_3)_2 \cdot 3H_2O$, but no desired crystal was observed. After further investigation on

Table 1. The crystal data and structure refinement for **1–3**.

	1	**2**	**3**
Empirical	$C_{18}H_{82}Cu_3N_{12}Nb_6O_{29}$	$C_{18}H_{80}Cu_4N_{12}Nb_6O_{29}$	$C_{10}H_{40}Cu_{2.5}N_{10}Nb_6O_{31}$
Formula weight	1678.41	1739.96	1512.53
Temperature (K)	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Crystal description	Blue, Block	Blue, Block	Blue, Block
Crystal size (mm^3)	0.18 × 0.11 × 0.13	0.13 × 0.10 × 0.09	0.15 × 0.11 × 0.09
Space group	*P2(1)/c*	*C2/m*	*P2(1)/n*
Unit cell dimensions (Å, °)			
a	11.6243(4)	14.950(7)	13.0902(4)
b	13.8337(5)	14.578(7)	20.2853(6)
c	16.0647(5)	13.624(7)	17.4200(5)
α	90	90	90
β	94.5440(10)	118.973(7)	100.7290(10)
γ	90	90	90
Z	4	8	2
Absorption coefficient, μ (mm^{-1})	2.587	2.963	2.700
θ range for data collections (°)	1.95–28.34	1.71–25.99	2.06–28.35
Limiting indices	$-15 \leq h \leq 14$; $-14 \leq k \leq 18$; $-21 \leq l \leq 21$	$-18 \leq h \leq 17$; $-17 \leq k \leq 17$; $-16 \leq l \leq 16$	$-16 \leq h \leq 17$; $-21 \leq k \leq 27$; $-23 \leq l \leq 22$
Reflection collected	19,664	11,867	31,690
Independent reflections	6225 [R(int) = 0.0172]	2657 [R(int) = 0.0644]	11300 [R(int) = 0.0204]
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0415$, $wR_2 = 0.1232$	$R_1 = 0.0560$, $wR_2 = 0.1456$	$R_1 = 0.0262$, $wR_2 = 0.0742$
R indices (all data)	$R_1 = 0.0490$, $wR_2 = 0.1321$	$R_1 = 0.0803$, $wR_2 = 0.1725$	$R_1 = 0.0310$, $wR_2 = 0.0767$
Largest difference peak and hole (e $Å^{-3}$)	1.027 and −0.948	1.892 and −1.071	1.007 and −0.810

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

the experimental conditions, we found that $LiCl \cdot H_2O$ was important for the synthesis of **3**. When the reaction was carried out without $LiCl \cdot H_2O$, no crystal could be found except for some colorless flakes. We surmise that the role of $LiCl \cdot H_2O$ might be as a mineralizer, which is also found in previous work [22].

3.2. *Description of the structures*

The structures of **1–3** are built on $[Nb_6O_{19}]^{8-}$ and copper–amine complexes. The anion $[Nb_6O_{19}]^{8-}$ exhibits the well-known Lindqvist-type structure, formed by six edge-sharing NbO_6 octahedra. For **1–3**, Nb–O distances are in the range of 1.766(3)–2.4269(4) (av. 2.028 Å), 1.772(6)–2.3820(14) Å (av. 2.023 Å), and 1.750(2)–2.465(2) (av. 2.031 Å), respectively. All the Nb–O bond lengths fall in the normal ranges and agree with those described in the literature [16–18]. Bond valence sum calculations [23] indicate all Cu is in the +2 oxidation state, further confirmed by XPS spectra (figures S1–S3). The XPS spectra of **1–3** are similar and each gives two peaks: 934.5 and 954.2 eV for **1**, 934.2 and 955.0 eV for **2**, and 934.5 and 954.8 eV for **3**, ascribed to $Cu2p_{3/2}$ and $Cu2p_{1/2}$ [24], respectively.

Single-crystal X-ray analysis reveals that **1** consists of one bisupporting polyoxoanion $\{[Cu(1,2\text{-dap})_2]_2[Nb_6O_{19}H_2]\}^{2-}$, one $[Cu(1,2\text{-dap})_2]^{2+}$, and 10 lattice waters.

Table 2. Selected bond lengths (Å) and angles (°) for **1–3**.

1					
Nb(1)–O(1)	1.766(3)	Nb(1)–O(5)	1.971(3)	Nb(1)–O(10)	2.3878(4)
Nb(2)–O(2)	1.781(3)	Nb(2)–O(6)	1.964(3)	Nb(2)–O(10)	2.4269(4)
Nb(3)–O(3)	1.785(3)	Nb(3)–O(6)#1	2.001(3)	Nb(3)–O(10)	2.3400(4)
Cu(1)–O(9	2.402(3)	Cu(1)–N(2)	1.999(4)	Cu(1)–N(1)	2.008(5)
Cu(2)–N(5)	2.014(4)	Cu(2)–N(5)#2	2.014(4)	Cu(2)–N(6)#2	2.037(4)
N(5)–Cu(2)–N(6)	85.01(18)	N(5)–Cu(2)–N(6)#2	94.99(18)	N(6)–Cu(2)–N(6)#2	180
2					
Nb(1)–O(1)	1.790(7)	Nb(1)–O(3)#1	1.933(5)	Nb(1)–O(7)	2.3820(14)
Nb(2)–O(2)	1.772(6)	Nb(2)–O(6)#2	2.041(5)	Nb(2)–O(7)	2.3574(10)
Cu(1)–O(6)	2.012(5)	Cu(1)–O(4)#2	2.331(7)	Cu(1)–O(6)	2.012(5)
Cu(1)–N(1)	2.017(8)	Cu(2)–N(2)	2.038(8)	N(3)–Cu(2)	2.039(7)
N(2)#3–Cu(2)–N(3)	87.3(3)	N(2)–Cu(2)–N(3)	92.7(3)	N(2)–Cu(2)–N(2)#3	180
3					
Nb(1)–O(1)	1.779(2)	Nb(1)–O(18)	2.015(2)	Nb(1)–O(19)	2.363(2)
Nb(2)–O(2)	1.764(2)	Nb(2)–O(9)	2.163(2)	Nb(2)–O(19)	2.415(2)
Nb(3)–O(3)	1.764(2)	Nb(3)–O(17)	1.918(2)	Nb(3)–O(19)	2.361(2)
Nb(4)–O(4)	1.756(2)	Nb(4)–O(7)	1.966(2)	Nb(4)–O(19)	2.465(2)
Nb(5)–O(5)	1.766(2)	Nb(5)–O(10)	2.023(2)	Nb(5)–O(19)	2.422(2)
Nb(6)–O(6)	1.750(2)	Nb(6)–O(18)	1.934(2)	Nb(6)–O(19)	2.335(2)
Cu(1)–O(6)	2.222(2)	Cu(1)–N(3)	2.033(3)	Cu(1)–N(1)	2.029(3)
Cu(2)–O(12)	2.356(2)	Cu(2)–N(7)	2.009(3)	Cu(2)–N(8)	2.023(3)
Cu(3)–N(9)	2.013(3)	Cu(3)–N(9)#1	2.013(3)	Cu(3)–N(10)#1	2.028(3)
N(9)#1–Cu(3)–N(10)	85.21(13)	N(9)–Cu(3)–N(10)	94.79(13)	N(9)#1–Cu(3)–N(9)	180

Symmetry codes: **1**: #1 $-x+2$, $-y+1$, $-z+2$, #2 $-x+1$, $-y+1$, $-z+2$; **2**: #1 x, $-y+1$, z, #2 $-x$, $-y+1$, $-z$, #3 $-x+1/2$, $-y+1/2$, $-z+2$; **3**: #1 $-x+1$, $-y$, $-z+2$.

There are two crystallographic independent Cu atoms exhibiting different coordination geometry. The Cu1 lies in a distorted square-pyramidal coordination geometry, defined by four nitrogens from two 1,2-dap molecules (Cu–N = 1.999(4)–2.008(5) Å) and one terminal oxygen from Lindqvist-type anion. Cu2 displays a nearly square-planar coordination geometry and is coordinated by four nitrogens from two 1,2-dap molecules (Cu–N = 2.014(4) and 2.037(4) Å).

As shown in figure 1a, two symmetry-related $[Cu(1)(1,2\text{-dap})_2]^{2+}$ fragments are bound to one $[Nb_6O_{19}H_2]^{6-}$ *via* covalent interactions to form a bisupporting polyoxoanion $\{[Cu(1,2\text{-dap})_2]_2[Nb_6O_{19}H_2]\}^{2-}$ with Cu1–O9 (and Cu1A–O9A, symmetry code A: −x + 2, −y + 1, −z + 2) distance of 2.402(3) Å. The Cu–O distance is similar to those of the previously reported compounds $\{Nb_6O_{19}[Cu(2,2'\text{-bipy})]_2[Cu(2,2'\text{-bipy})_2]_2\}\cdot 19H_2O$ [17] and $K_3Na_2[\{Cu(H_2O)(phen)\}_2\{CuNb_{11}O_{35}H_4\}]\cdot 22H_2O$ [5]. $[Cu(2)(1,2\text{-dap})_2]^{2+}$ fragments are bridges linking adjacent bisupporting polyoxoanions $\{[Cu(1,2\text{-dap})_2]_2[Nb_6O_{19}H_2]\}^{2-}$ through Cu···O weak interactions (Cu2···O1 = 2.546(2) Å) to generate a 1-D infinite chain parallel to the *a*-axis (figure 2).

Under similar synthesis method, we obtained **2** by replacing 1,2-dap with 1,3-dap. Similar to **1**, a symmetry-related bisupporting polyoxoanion $\{[Cu(1,3\text{-dap})]_2[Nb_6O_{19}]\}^{4-}$ is found in **2**. But the linkage between $[Cu(1)(1,3\text{-dap})]^{2+}$ fragments and $[Nb_6O_{19}]^{8-}$ in **2** seems stronger than that in **1**, with three bridging oxygens of O6, O6A, and O4 to form three pairs of coordination interactions with Cu–O distance being 2.331(7) and 2.012(5) Å (symmetry code A: x, $-y+1$, z) (figure 1b). Such linking mode between $[Cu(1)(1,3\text{-dap})]^{2+}$ and the $[Nb_6O_{19}]^{8-}$ cluster is similar to that in

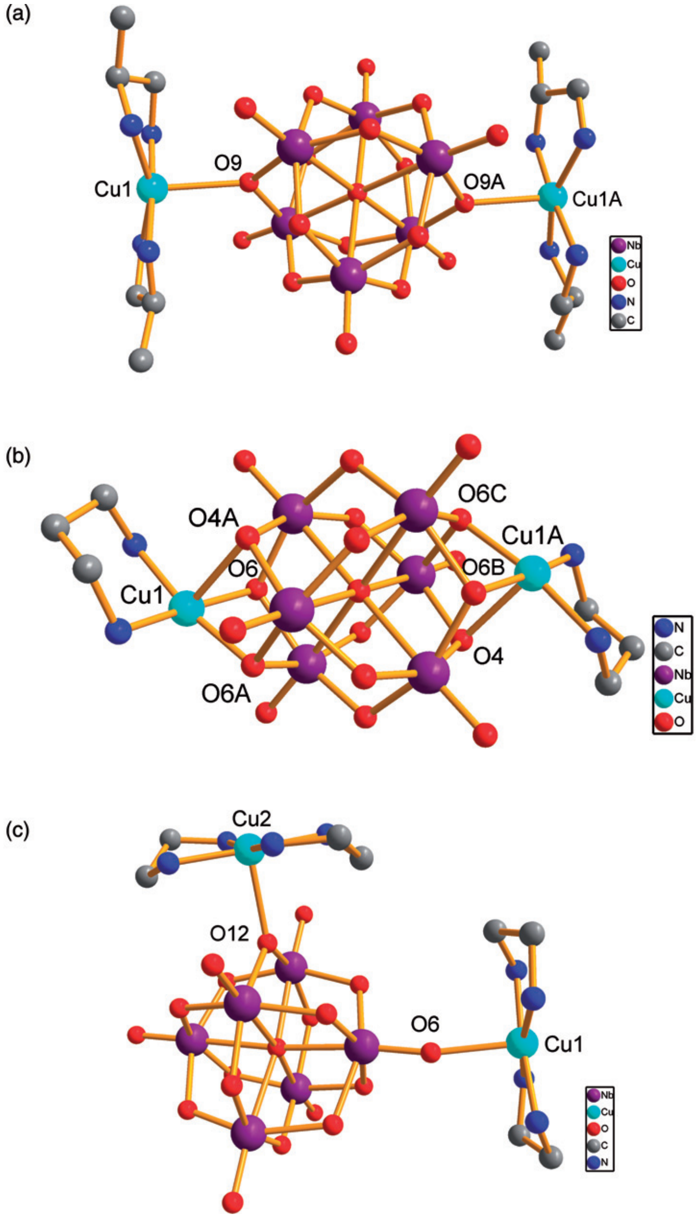

Figure 1. Ball/stick view of the bisupporting polyoxoanion: (a) $\{[Cu(1,2\text{-}dap)_2]_2[Nb_6O_{19}H_2]\}^{2-}$ for **1** (Cu1–O9 = 2.402(3) Å, A: $-x+2$, $-y+1$, $-z+2$); (b) $\{[Cu(1,3\text{-}dap)]_2[Nb_6O_{19}]\}^{4-}$ for **2** (Cu1–O4 = 2.331(7) Å, Cu1–O6 = 2.012(5) Å, A: x, $-y+1$, z; B: $-x$, y, $-z$; C: $-x$, $-y+1$, $-z$); $\{[Cu(en)_2]_2[Nb_6O_{19}H_3]\}^{1-}$ for **3** (Cu1–O6 = 2.222(2) Å, Cu2–O12 = 2.356(2) Å).

$[Nb_6O_{19}\{M(CO)_3\}_n]^{(8-n)-}$ (M = Mn, Re; $n = 1, 2$) [14] and $\{trans\text{-}[Nb_6O_{19}][Ni(taci)]_2\}^{4-}$ [15]. Furthermore, each bisupporting polyoxoanion $\{[Cu(1,3\text{-}dap)]_2[Nb_6O_{19}]\}^{4-}$ connects with four neighboring units by another discrete $[Cu(2)(1,3\text{-}dap)_2]^{2+}$ fragment through Cu···O weak interactions with Cu2···O3 distance of 2.636(2) Å to form a 2-D supramolecular network (figure 3).

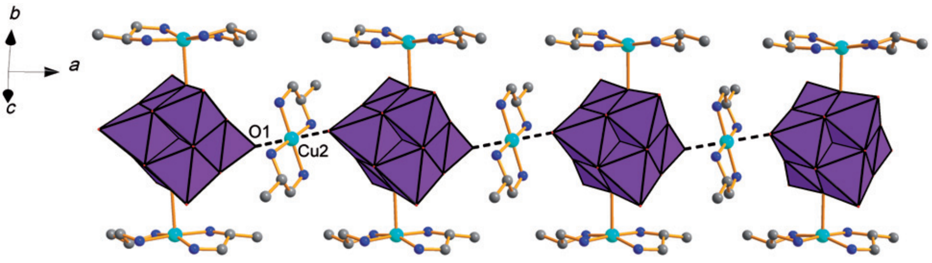

Figure 2. Polyhedral and ball/stick representation of the 1-D chain structure in **1**. The dashed lines indicate the Cu···O weak interactions.

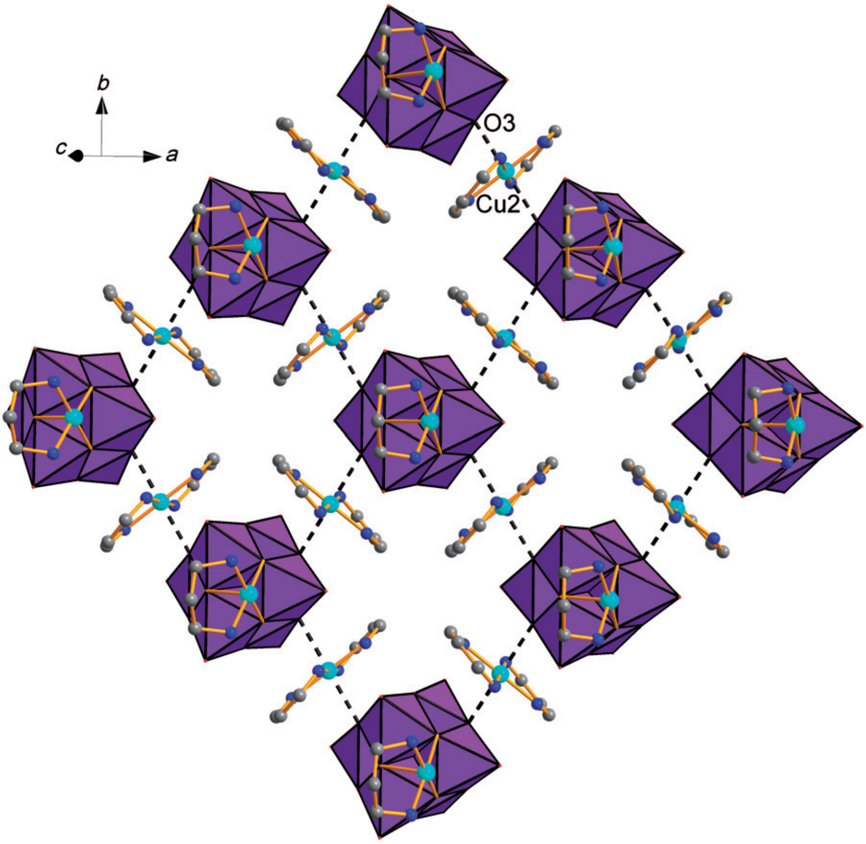

Figure 3. Polyhedral and ball/stick representation of the 2-D network in **2**. The dashed lines denote the Cu···O weak interactions.

We found that **3** could be isolated from the H_2O/methanol system. As shown in figure 1c, the bisupporting polyoxoanion $\{[Cu(en)_2]_2[Nb_6O_{19}H_3]\}^{1-}$ consists of one $[Nb_6O_{19}H_3]^{5-}$ and two $[Cu(en)_2]^{2+}$-decorated fragments. The protonated anion $[Nb_6O_{19}H_3]^{5-}$ is a bidentate ligand coordinating to two $[Cu(en)_2]^{2+}$ fragments *via* one terminal oxygen (O6) and one bridging oxygen (O12) with Cu1–O6 distance of 2.222(2) Å and Cu2–O12 distance of 2.356(2) Å. Different from **1** and **2**, there is no obvious interaction between bisupporting cluster and discrete $[Cu(en)_2]^{2+}$ fragments. The discrete $[Cu(en)_2]^{2+}$ fragment acts only as an isolated countercation.

3.3. *IR spectra*

IR spectra of **1–3** (figure S4) display strong characteristic vibration bands in the low-wavenumber regions. Terminal $Nb–O_t$ vibrations of the Lindqvist-type structures appear at 852 (**1**), 843 (**2**), and 850 cm^{-1} (**3**). The peaks at 717 and 543 cm^{-1} for **1**, at 719, 681, and 536 cm^{-1} for **2**, and at 746, 669, and 526 cm^{-1} for **3** are attributed to bridging $Nb–O_b–Nb$ vibrations. Comparing with the precursor $[HNb_6O_{19}]^{7-}$ [14], the vibration frequencies of **1–3** show different shifts, indicating that the anions in **1–3** still retain the Lindqvist-type structure but are distorted due to the coordination of transition metal fragments with the surface oxygens [4, 5, 16, 18, 25]. In addition, features at 1056–1596 cm^{-1} (**1**), 1030–1590 cm^{-1} (**2**), and 1050–1590 cm^{-1} (**3**) can be assigned to the vibrations of 1,2-dap, 1,3-dap and en, respectively.

3.4. *TG–DTA analyses*

For **1** (Supplementary material), the weight loss of 10.61% between 20°C and 110°C corresponds to the loss of 10 lattice waters (Calcd 10.72%), whereas the weight loss of 26.03% between 110°C and 700°C arises from release of six 1,2-dap molecules (Calcd 26.45%). Two endothermal peaks at 85°C and 251°C are observed in the corresponding DTA curve. The whole weight loss of 36.64% is consistent with the calculated value of 37.17%. Two continuous weight losses were found in **2**. The first of 10.12% at 20–120°C is attributed to the removal of 10 lattice waters (Calcd 10.34%). The subsequent second weight loss of 26.05% at 120–700°C is ascribed to the release of six 1,3-dap molecules (Calcd 25.52%). There are two endothermal peaks at 130°C and 202°C in the corresponding DTA curve. The whole weight loss of 36.17% is in agreement with the calculated value of 35.86%. For **3**, the first weight loss of 7.29% at 20–110°C corresponds to the removal of six lattice waters (Calcd 7.14%). The second weight loss of 27.20% at 110–700°C arises from the release of six lattice waters and five en molecules (Calcd 26.97%). Two endothermal peaks appear at 67°C and 267°C in the corresponding DTA curve. The whole weight loss of 34.49% is in agreement with the calculated value of 34.11%.

4. Conclusion

Three new polyoxoniobates based on Lindqvist-type hexaniobate and copper–amine complexes have been synthesized and structurally characterized. Despite the fact that **1–3** all contain bisupporting polyoxoanion, the linking mode between the hexaniobate and the decorated copper–amine complexes are different, due to the influence of the geometric configuration of organic ligands. Compounds **1** and **2** exhibit novel 1-D and 2-D supramolecular structures through weak $Cu\cdots O$ interactions between bisupporting polyoxoanions and discrete copper complexes. The successful preparation of **1–3** demonstrates that the hexaniobate can be used as a building block for the construction of polyoxoniobate clusters with unique structures.

Supplementary material

Crystallographic data for the structural analyses reported in this article has been deposited with the Cambridge Crystallographic Data Centre with the deposited CCDC numbers 796930–796932. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

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