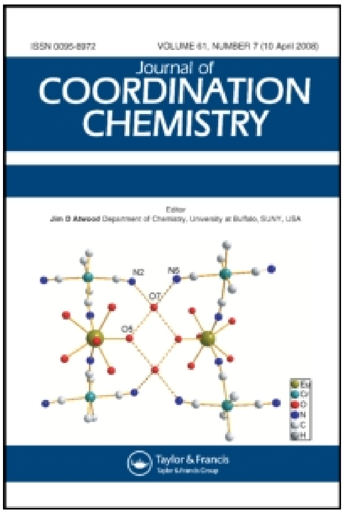

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A polyoxoniobate based on dimeric hexanionbate: $[Cu(en)_2]_4\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2\cdot(H_2en)\cdot 17H_2O$

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A polyoxoniobate, $[Cu(en)_2]_4\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2\cdot(H_2en)\cdot 17H_2O$ (en = ethylenediamine) (**1**), has been synthesized and characterized by elemental analysis, IR, XPS, TGA, and single-crystal X-ray diffraction. Compound **1** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 12.3533(16)$ Å, $b = 12.7188(16)$ Å, $c = 29.626(4)$ Å, $\alpha = 93.235(2)^\circ$, $\beta = 96.094(1)^\circ$, $\gamma = 106.098(2)^\circ$, $V = 4429.0(10)$ Å^3, $Z = 2$. The polyoxoanion is composed of a Lindqvist-type $[Nb_6O_{19}H_2]^{6-}$ dimer bi-bridged *via* two K^+. K^+ is 10-coordinate with 10 oxygens, three from one $[Nb_6O_{19}H_2]^{6-}$, one from a terminal oxygen of another $[Nb_6O_{19}H_2]^{6-}$ moiety, and the other six from water molecule. Adjacent dimeric polyoxoanions are linked to form an infinite 1-D chain *via* O–H $\cdots$ O hydrogen-bonding interactions which exist between the two water trimers and the dimeric polyoxoanions.

Keywords: Polyoxoniobate; Lindqvist type; Dimer; Trimer

1. Introduction

Polyoxoniobates have unique structures and potential applications in catalyses and virology [1–6]. However, in contrast to the extensive reports on the chemistry of polyoxotungstates, polyoxomolybdates, and polyoxovanadates, which can be easily obtained over a wide pH range, polyoxoniobate chemistry remains relatively undeveloped because polyoxoniobates can only be isolated from basic solutions [7]. Up to now, polyoxoniobate chemistry is dominated by the Lindqvist-type anion $[Nb_6O_{19}]^{8-}$ [8–12]. In 1969, the dimeric structure of $[Mn(Nb_6O_{19})_2]^{12-}$ and $[Ni(Nb_6O_{19})_2]^{12-}$ were determined by Flynn [13]. Recently, several polyoxoniobates built on $[Nb_6O_{19}]^{8-}$ have been reported, typical examples include $[Nb_6O_{19}\{M(CO)_3\}_n]^{(8-n)-}$ (M = Mn, Re; $n = 1$, 2) [14], $[Nb_6O_{19}\{Ru(p\text{-cym})\}_n]^{8-2n}$ ($n = 1$–4) (*p*-cym = *p*-cymene) [15], $[(Nb_6O_{19}H_2)_2Cu(en)_2]^{10-}$ [16], and $\{Nb_6O_{19}[Cu(2,2'\text{-bipy})]_2[Cu(2,2'\text{-bipy})_2]_2\}\cdot 19H_2O$ [17]. Besides the hexaniobate, the decaniobate $[Nb_{10}O_{28}]^{6-}$ [18, 19] and icosaniobate $[Nb_{20}O_{54}]^{8-}$ [20] have been isolated and structurally characterized. Hexaniobate as a precursor has been used to prepare several

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giant polyoxoniobate clusters, such as $\{Nb_{24}O_{72}H_9\}^{15-}$ [7], $[H_{23}NaO_8Cu_{24}(Nb_7O_{22})_8]^{16-}$ [21], $[HNb_{27}O_{76}]^{16-}$, and $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$ [22]. In addition, Nyman *et al.* [23, 24] reported the heteropolyniobate clusters $[TNb_{12}O_{40}]^{16-}$ (T = Si, Ge) and $[H_2Si_4Nb_{16}O_{56}]^{14-}$, and the lacunary derivatives which were prepared under hydrothermal conditions [25]. However, despite some progress in polyoxoniobate chemistry, the systematic design and synthesis of polyoxoniobate clusters with unexpected structures and properties remain a challenge. Herein, we report a polyoxoniobate cluster isolated from cyclohexylamine/H_2O mixed-solution, $[Cu(en)_2]_4\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2 \cdot (H_2en) \cdot 17H_2O$.

2. Experimental

2.1. *Materials and methods*

$K_7HNb_6O_{19} \cdot 13H_2O$ was prepared according to the procedures in the literature [26] and confirmed by IR spectrum. Other reagents were purchased from commercial sources and used without purification. C, H, and N elemental 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 (TGA) was performed on a TGA Q50 instrument under nitrogen with a heating rate of 10°C min^{-1}. X-ray photoelectron spectrum (XPS) analysis was performed on a VG Escalabmkll spectrometer (UK) with a Al-Kα ($h\nu = 1486.7$ eV) achromatic X-ray source.

2.2. *Synthesis of* $[Cu(en)_2]_4\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2 \cdot (H_2en) \cdot 17H_2O$ *(1)*

$CuSO_4 \cdot 5H_2O$ (0.1 mmol) was added to 5 mL cyclohexylamine, the resulting solution was heated to 50°C with stirring, then 0.3 mL ethylenediamine (en) and a solution of $K_7HNb_6O_{19} \cdot 13H_2O$ (0.05 mmol) in water (5 mL) were added sequentially to the above solution. The reaction mixture was stirred at 50°C for 1 h and allowed to cool to room temperature, filtered, and left to evaporate slowly at ambient temperature (26% yield based on Nb). After 6 weeks, purple crystals of **1** were obtained. Elemental analysis, Calcd (%): C, 6.99; H, 4.27; N, 8.16. Found (%): C, 6.91; H, 4.21; N, 8.25.

2.3. *X-ray crystallography*

A purple single crystal of **1** with approximate dimensions 0.40 mm × 0.30 mm × 0.27 mm was mounted on a glass fiber capillary. The data were collected on a Rigaku RAXIS-RAPID CCD diffractometer with Mo-Kα radiation ($\lambda = 0.71073$ Å) at 93(2) K from $3.08 < \theta < 25.50°$. A total of 25,995 (15,963 unique, $R_{int} = 0.0196$) reflections were measured ($-12 \le h \le 14$, $-15 \le k \le 15$, $-34 \le l \le 35$). The structures were solved by direct methods and refined using full-matrix least-squares calculations with anistropic thermal parameters for all non-hydrogen atoms. The hydrogens were geometrically fixed to allow riding on the parent atoms to which they are attached. All calculations were

Table 1. Crystallographic data and structure refinement for **1**.

Empirical formula	$C_{18}H_{132}Cu_4K_2N_{18}Nb_{12}O_{65}$
Formula weight	3088.57
Temperature (K)	93(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	12.3533(16)
b	12.7188(16)
c	29.626(4)
α	93.235(2)
β	96.0940(10)
γ	106.098(2)
Volume (Å^3), Z	4429.0(10), 2
Density (calculated) (Mg m^{-3})	2.304
Absorption coefficient (mm^{-1})	2.634
$F(000)$	3032
θ range for data collection (°)	3.08–25.50
Limiting indices	$-12 \le h \le 14$, $-15 \le k \le 15$, $-34 \le l \le 35$
Reflections collected	25995
Independent reflections	15,963 ($R_{int} = 0.0196$)
Completeness to $\theta = 25.50$ (%)	96.7
Refinement method	Full-matrix least-squares on F^2
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.0892$
Largest diffraction peak and hole (e Å^{-3})	1.073 and −0.970

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

performed using the SHELXL-97 program [27, 28]. Crystallographic data are summarized in table 1. Selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Synthesis*

Compound **1** was obtained from the reaction of $CuSO_4 \cdot 5H_2O$, en, and $[Nb_6O_{19}]^{8-}$ in cyclohexylamine/H_2O mixed-solution. The conditions for the preparation of **1** are critical because the product is influenced by many factors, such as the starting materials and reaction time. Parallel experiments show that en is vital for the crystallization of **1**. We tried to synthesize isostructural compounds using other ligands, such as 2,2′-bipyridine, *N*-methylethylenediamine, 1,3-diaminopropane, 1,10-phenanthroline, and 4,4′-bipyridine under the same reaction conditions, but did not obtain the expected compounds. In order to investigate the influence of divalent transition metal on the products, we tried to replace $CuSO_4 \cdot 5H_2O$ with $CoSO_4 \cdot 7H_2O$ or $NiSO_4 \cdot 6H_2O$ under the same conditions, but no crystals were isolated. Furthermore, the presence of cyclohexylamine is necessary for the formation of **1**. In our experiments, if we use other solvent, for example diethylenetriamine, instead of cyclohexylamine, **1** could not be obtained. In addition, when the reaction time of the reaction mixture is longer than 1 h, no crystalline product was formed.

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

Nb(1)–O(6)	1.785(3)	Nb(1)–O(3)	1.894(3)
Nb(1)–O(4)	1.917(3)	Nb(1)–O(2)	2.108(3)
Nb(2)–O(10)	1.773(3)	Nb(2)–O(9)	1.974(3)
Nb(2)–O(2)	2.122(3)	Nb(2)–O(1)	2.359(3)
Nb(3)–O(11)	1.962(3)	Nb(3)–O(12)	1.980(3)
Nb(3)–O(13)	2.009(3)	Nb(3)–O(1)	2.429(3)
Nb(4)–O(11)	1.969(3)	Nb(4)–O(15)	1.992(3)
Nb(4)–O(16)	2.000(3)	Nb(4)–O(3)	2.033(3)
Nb(5)–O(15)	1.963(3)	Nb(5)–O(12)	1.981(3)
Nb(5)–O(8)	2.004(3)	Nb(5)–O(1)	2.368(3)
Nb(6)–O(19)	1.781(3)	Nb(6)–O(13)	1.924(3)
Nb(6)–O(16)	1.960(3)	Nb(6)–O(1)	2.376(3)
Nb(7)–O(25)	1.775(3)	Nb(7)–O(21)	1.955(3)
Nb(7)–O(24)	1.981(3)	Nb(7)–O(23)	2.005(3)
Nb(8)–O(29)	1.755(3)	Nb(8)–O(21)	1.975(3)
Nb(8)–O(27)	1.993(3)	Nb(8)–O(28)	2.014(3)
Nb(9)–O(26)	1.898(3)	Nb(9)–O(32)	1.925(3)
Nb(9)–O(30)	2.119(3)	Nb(9)–O(20)	2.365(3)
Nb(10)–O(22)	1.899(3)	Nb(10)–O(34)	1.946(3)
Nb(10)–O(35)	2.067(3)	Nb(10)–O(20)	2.344(3)
Nb(11)–O(23)	1.916(3)	Nb(11)–O(27)	1.960(3)
Nb(11)–O(34)	2.006(3)	Nb(11)–O(31)	2.154(3)
Nb(12)–O(28)	1.944(3)	Nb(12)–O(24)	1.967(3)
Nb(12)–O(35)	2.082(3)	Nb(12)–O(20)	2.370(3)
K(1)–O(42)	2.797(4)	K(1)–O(25)	2.862(3)
K(1)–O(39)	3.116(4)	K(1)–O(41)	3.212(4)
K(2)–O(22)	2.941(3)	K(2)–O(44)	2.975(4)
K(2)–O(24)	3.029(3)	K(2)–O(46)	3.378(4)
Cu(1)–N(1)	1.989(4)	Cu(1)–N(3)	1.997(4)
Cu(1)–N(2)	2.013(4)	Cu(1)–N(4)	2.024(4)
Cu(4)–N(13)	1.995(4)	Cu(4)–N(13)#1	1.995(4)
Cu(5)–N(15)#2	1.991(4)	Cu(5)–N(16)	2.014(4)
O(31)–Nb(11)–O(20)	75.05(11)	O(29)–Nb(8)–O(20)	179.38(13)
O(8)–K(1)–O(25)	162.46(10)	O(39)–K(1)–O(12)	51.00(9)
O(45)–K(2)–O(46)	52.96(12)	O(39)–K(2)–O(46)	163.66(10)
N(5)–Cu(2)–N(6)	84.77(16)	N(16)–Cu(5)–N(16)#2	180.0

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

3.2. *Description of structure*

Single-crystal X-ray diffraction analysis reveals that **1** consists of one $\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2^{10-}$, four $[Cu(en)_2]^{2+}$, one diprotonated en, and 17 lattice waters (figure S1). As shown in figure 1, two Lindqvist-type anions $[Nb_6O_{19}]^{8-}$ are linked by two K^+ ions giving the dimeric polyoxoanion. The $[Nb_6O_{19}]^{8-}$ cluster anion can be described as a super octahedron of six edge-sharing NbO_6 octahedra [29]. In the Lindqvist cluster, the Nb–O distances can be divided into three groups: 1.755(3)–1.793(3) Å for the terminal oxygens ($Nb–O_t$), 1.894(3)–2.154(3) Å for bridging ($Nb–O_b$), and 2.344(3)–2.431(3) Å for central oxygens ($Nb–O_c$). The O–Nb–O bond angles are in the range of 75.05(11)–179.38(13)°. All bond lengths and angles are comparable to the corresponding ones in $Rb_4[Cu(en)_2(H_2O)_2]_3[(Nb_6O_{19}H_2)_2Cu(en)_2]\cdot 24H_2O$ [16] and $Na[Cu(1,3\text{-pda})_2]_3[HNb_6O_{19}]\cdot 3H_2O$ [30].

Bond-valence calculations suggest that all Nb's and Cu's are in the +5 and +2 oxidation state, respectively [31, 32]. Bond-valence sum calculations [31] also indicate that two adjacent bridging oxygens are protonated in each $[Nb_6O_{19}]^{8-}$ cluster anion

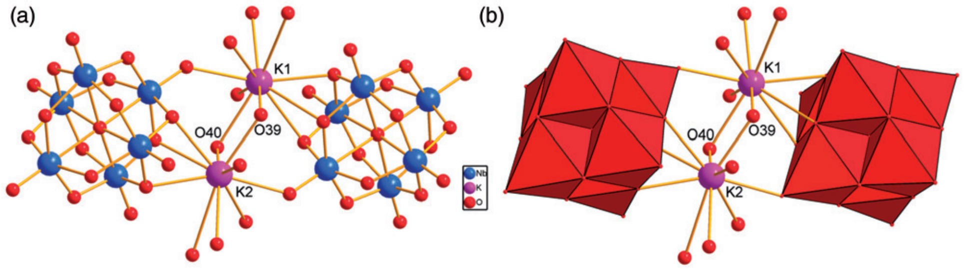

Figure 1. Ball-and-stick (a) and combined polyhedral/ball-and-stick (b) representation of the polyoxoanion $\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2^{10-}$ in **1**.

(the protonated oxygens are shown as yellow spheres in figure S2). This observation is also in accord with the conclusion that the bridging oxygens of the Lindqvist ions $[Nb_6O_{19}]^{8-}$ are less stable than the terminal oxygens and are probably protonated [7, 16].

In the polyoxoanion of **1**, the two K^+ (K1 and K2) are not strictly symmetrical, and the $K \cdots K$ separation distance is 4.205(17) Å. The two K^+ ions are bridged by two waters (Ow: O39 and O40) to form a K_2O_2 dimer; the four atoms (K1, K2, O39, O40) are almost coplanar with average deviation from ideal plane 0.0224 Å. In addition, each K^+ is 10 coordinate with three bridging oxygens from one $[Nb_6O_{19}H_2]^{6-}$, one terminal oxygen from another $[Nb_6O_{19}H_2]^{6-}$, and six oxygens from waters. The K–O distances are within the range of 2.797(4)–3.4598(36) Å (mean value 3.022 Å) and 2.794(4)–3.4931(35) Å (mean value 3.014 Å) for K1 and K2, respectively. The O–K–O bond angles are in the range of 51.00(9)–162.46(10)° and 52.96(12)–163.66(10)° for K1 and K2, respectively. The rather long K–O distances may result from these high coordination numbers [33].

Detailed analysis of the structure reveals that two water trimers (O_{51}, O_{62}, and O_{63}; O_{50}, O_{59}, and O_{60}) exist in **1**; each water trimer has a "V"-like shape. Such type of three-membered water cluster is notable because most water trimer clusters exhibit cyclic structures [34]. In one water trimer, the $O_{51} \cdots O_{63}$ and $O_{62} \cdots O_{63}$ distances are 2.7722(63) and 2.7493(79) Å, respectively, and the $O_{51} \cdots O_{63} \cdots O_{62}$ angle is 99.489(207)°. In the other water trimer, the $O_{50} \cdots O_{59}$ and $O_{59} \cdots O_{60}$ distances are 2.7825(54) and 2.6580(59) Å, respectively, and the $O_{50} \cdots O_{59} \cdots O_{60}$ angle is 95.839(161)°. The two water trimers are identical except for slight differences in $O \cdots O$ distances and $O \cdots O \cdots O$ angle. Furthermore, there exists extensive hydrogen-bonding interactions between the two water trimers and the dimeric $\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2^{10-}$ polyoxoanion. As shown in figure 2a, the two water trimers link the neighboring dimeric polyoxoanions into an infinite 1-D chain through six pairs of hydrogen bonds ($O_{50} \cdots O_{16} = 2.6953(48)$ Å, $O_{50} \cdots O_{43} = 2.7561(56)$ Å, $O_{19} \cdots O_{60} = 2.6909(47)$ Å, $O_{51} \cdots O_{44} = 2.7567(58)$ Å, $O_{51} \cdots O_{27} = 2.7109(47)$ Å, and $O_{62} \cdots O_{37} = 2.6717(52)$ Å). O_{44}, O_{16}, and O_{19} belong to one polyoxoanion, while O_{43}, O_{27}, and O_{37} belong to the other polyoxoanion. Here O_{44} is a water coordinated to K2, while O_{43} is a water coordinated to K1. In addition, O_{16} and O_{27} are bridging oxygens, while O_{19} and O_{37} are terminal oxygens. The prominent feature in the structure of **1** is that the 1-D chains are arranged in layers parallel to the *ac* plane (figure 2b). The spaces between the layers are occupied by $[Cu(en)_2]^{2+}$ cations, H_2en^{2+}, and the remaining waters which are not involved in hydrogen bonding.

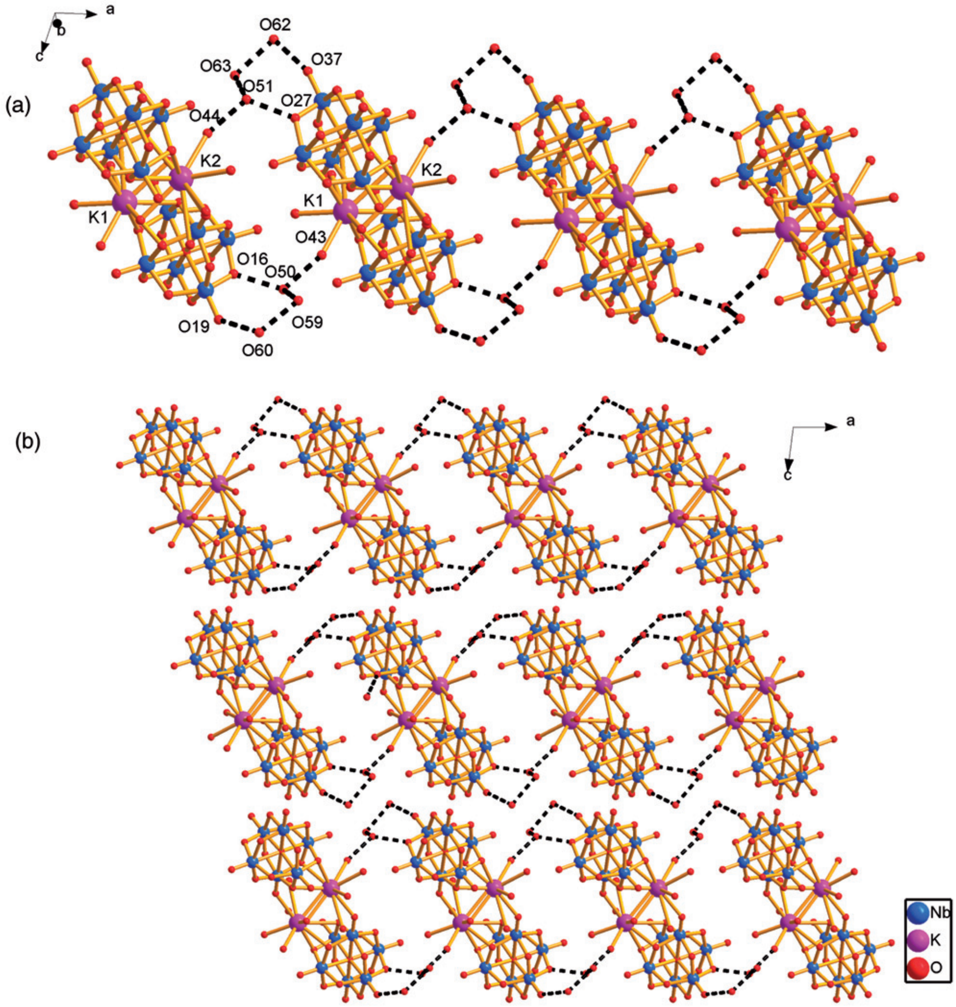

Figure 2. (a) The 1-D chain structure constructed from the two water trimers and dimeric polyoxoanion $\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2^{10-}$. (b) The packing arrangement of 1-D chains along the *b*-axis. The hydrogens are omitted for clarity.

In the discrete cation $[Cu(en)_2]^{2+}$, Cu exhibits a slightly distorted square-planar geometry, being coordinated by four nitrogens from two en molecules with Cu–N distance of 1.989(4)–2.031(4) Å, comparable to the Cu–N distance in $[Cu(en)_2]^{2+}$ [7, 35] and $[Cu(1,3\text{-pda})_2]^{2+}$ [30]. A strong interaction exists between $[Cu1(en)_2]^{2+}$ and one $[Nb_6O_{19}H_2]^{6-}$ with the $Cu1 \cdots O11$ distance of 2.5215(34) Å (figure S3). The Cu4 and Cu5 in **1** are disordered with an occupancy of 0.5.

3.3. *IR, XPS, and TG analysis*

The IR spectrum of **1** shows vibration patterns in the low-wavenumber regions similar to those of the Lindqvist-type $[HNb_6O_{19}]^{7-}$ anion (figure S4) [14]. The characteristic

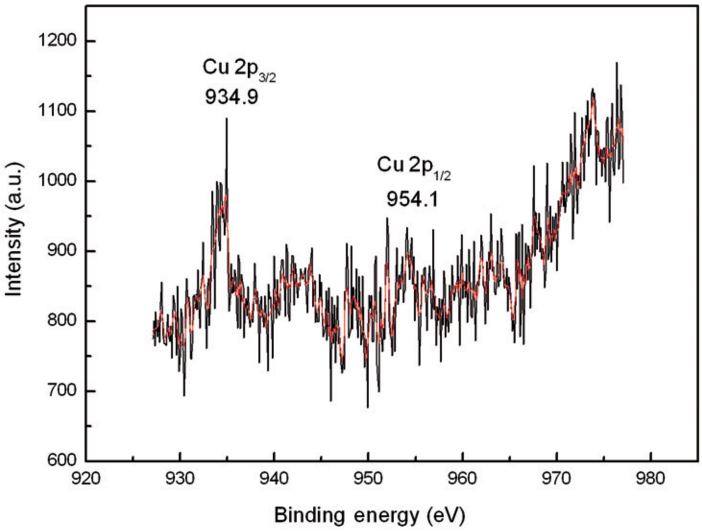

Figure 3. XPS spectra of **1** for Cu $2p_{3/2}$ and Cu $2p_{1/2}$.

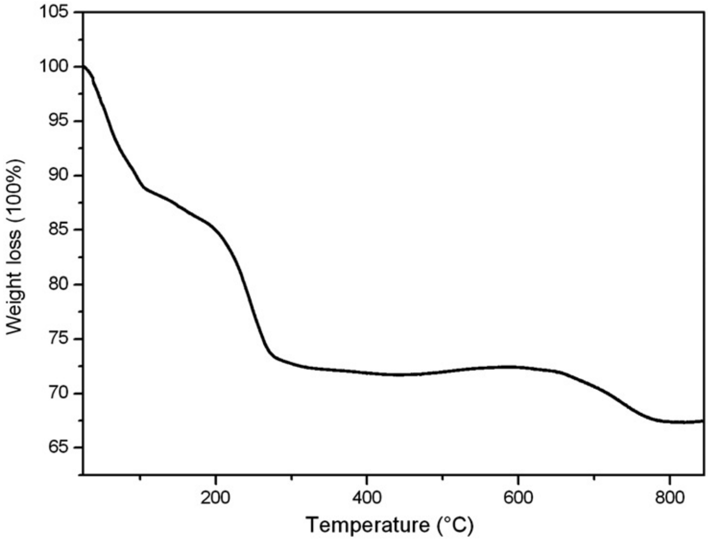

Figure 4. The TG curve of **1**.

vibration of the terminal Nb–O_t vibrations appears at $850\,cm^{-1}$. The peaks at 700, 621, and $525\,cm^{-1}$ are attributed to bridging Nb–O_b–Nb vibrations and have red shifts compared with $[HNb_6O_{19}]^{7-}$ [14] from the coordination of K^+ with the bridging oxygens of $[Nb_6O_{19}H_2]^{6-}$. Bands in the range $1050–1600\,cm^{-1}$ are attributed to characteristic vibrations of en. Absorptions at 3230 and $3140\,cm^{-1}$ can be assigned to water.

The XPS spectrum of **1** (figure 3) gives two peaks at 934.9 and 954.1 eV, attributable to $Cu^{2+}(2p_{3/2})$ and $Cu^{2+}(2p_{1/2})$, respectively [36, 37], confirming the composition of **1**.

The thermogravimetric (TG) curve of **1** exhibits two weight losses at 25–850°C (figure 4), giving a total weight loss of 32.60%, which agrees with the calculated value of 33.18%. The first weight loss of 27.57% at 25–600°C corresponds to the loss of 17 lattice water molecules, one diprotonated en, and eight en molecules (Calcd 27.38%). The second weight loss of 5.03% between 600 and 850°C is attributed to the loss of 10 coordination water molecules (Calcd 5.8%).

4. Conclusion

$[Cu(en)_2]_4\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2\cdot(H_2en)\cdot17H_2O$ has been prepared with $\{[Nb_6O_{19}H_2]K(H_2O)_5\}_2^{10-}$ as two Lindqvist-type anion $[Nb_6O_{19}H_2]^{6-}$ linked by two K^+ ions. Adjacent dimeric polyoxoanions are connected to form an infinite 1-D chain through hydrogen bonding interactions between the two water trimers and the dimeric polyoxoanions. This work shows that mixed solutions can be exploited to prepare polyoxoniobate clusters with intriguing 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 number 762260. 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; Email: deposit@ccdc.cam.ac.uk).

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