Journal of Coordination Chemistry

A polyoxoniobate constructed from Lindqvist-type hexaniobates and copper coordinated cations

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Published online: 09 Aug 2011.

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A polyoxoniobate constructed from Lindqvist-type hexaniobates and copper coordinated cations

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A new organic–inorganic hybrid polyoxoniobate $[Cu(1,3\text{-}dap)_2(H_2O)][(H_6Nb_6O_{19})_2Cu(1,3\text{-}dap)_2] \cdot 4(1,3\text{-}dap) \cdot 20H_2O$ (**1**) (1,3-dap = 1,3-diaminopropane) has been synthesized by the diffusion method and structurally characterized by elemental analyses, infrared spectrum, ultraviolet spectroscopy, and single crystal X-ray diffraction. Crystal structure analysis reveals that **1** consists of a dimeric dumbbell anion $[(H_6Nb_6O_{19})_2Cu(1,3\text{-}dap)_2]^{2-}$, a copper coordinated cation, four 1,3-dap ligands and 20 crystal water molecules. Neighboring units are combined *via* hydrogen bonds forming a 3-D supramolecular framework.

Keywords: Polyoxoniobate; Lindqvist-type; Synthesis; Crystal structure

1. Introduction

Investigation of polyoxometalate (POM) chemistry is a rapidly growing field because of their potential applications in magnetochemistry, catalysis, medicinal chemistry, materials science, and nanotechnology [1]. As one of the most important subfamilies of POM chemistry, polyoxoniobates (PONs) have applications in virology, nuclear-waste treatment, and the base-catalyzed decomposition of biocontaminants [2, 3].

Since the Lindqvist-type polyoxoanion $[Nb_6O_{19}]^{8-}$ was first structurally reported in 1953 [4], the development of PON chemistry is dominated by the hexaniobate anion [5]. PON chemistry progressed when the decaniobate ion $[Nb_{10}O_{28}]^{6-}$ was isolated by Graeber and Morosin [6]. Yagasaki *et al*. published an icosaniobate $[Nb_{20}O_{54}]^{8-}$, which can be considered as a fusion of two decaniobate anions [7]. Later, Hu and co-workers [8] illustrated two isostructural 1-D organic–inorganic hybrid decaniobates. Nyman's [9] group made great contributions, publishing a series of Keggin-type heteropolynio-bates $[TNb_{12}O_{40}]^{y-}$ (T = Si^{IV}, Ge^{IV}, P^V; y = 15, 16). Their derivatives $[H_2Si_4Nb_{16}O_{56}]^{14-}$ and $[(PO_2)_3PNb_9O_{34}]^{15-}$ were obtained under hydrothermal conditions [9]. Furthermore, the isopolyoxoniobates $[Nb_{24}O_{72}H_9]^{15-}$ and five copper-containing hexaniobates were communicated by routine aqueous solution methods [2c, 10]. In 2008, Casey *et al*. [11] prepared a supraoctahedral polyoxotitanoniobate $[Ti_{12}Nb_6O_{44}]^{10-}$ [11]. More recently, Cronin's [12] group separated two gigantic

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isopolyoxoniobates $[HNb_{27}O_{76}]^{16-}$ and $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$ built from pentagonal $\{Nb(Nb)_5\}$ units.

Our group has concentrated on investigation of PON systems since 2005. In 2007, we presented a family of giant PON clusters based on $[Nb_7O_{22}]^{9-}$ units by the conventional aqueous solution method [13]. Afterward, an organic–inorganic hybrid PON was produced by self-assembly [14]. Very recently, two copper-undecaniobates $[\{Cu(H_2O)L\}_2\{CuNb_{11}O_{35}H_4\}]^{5-}$ (L = phen, 2,2′-bipy) were synthesized through the diffusion approach [15]. Subsequently, by introducing mixed ligands to the reaction of hexaniobate system, three 2-D organic–inorganic hybrid PONs $[Cu(L_1)_2]_2$ $\{[Cu(L_2)][Cu(L_2)(H_2O)]Nb_6O_{19}\} \cdot nH_2O$ (L$_1$ = en or 1,2-dap, L$_2$ = phen or 2,2′-bipy) were reported through the same method [16]. Currently, we are making great efforts to explore the design and synthesis of PONs with attractive structures and properties using the diffusion technique. Fortunately, a new organic–inorganic hybrid PON $[Cu(1,3-dap)_2(H_2O)][(H_6Nb_6O_{19})_2Cu(1,3-dap)_2] \cdot 4(1,3-dap) \cdot 20H_2O$ (1) has been isolated using the diffusion method and fully characterized by elemental analyses, infrared (IR) spectrum, and ultraviolet (UV) spectroscopy. Crystal structure analysis reveals that **1** is constructed from two Lindqvist-type polyoxoanions linked by a copper complex, in which the neighboring units are combined together *via* hydrogen bonds forming a 3-D supramolecular framework. Due to steric hindrance, it is very difficult to graft 1,3-dap ligands to POMs. Therefore, **1** is a rare example of PON complexes containing 1,3-dap.

2. Experimental

2.1. *Materials and physical measurements*

All reagents were used as purchased. $K_7HNb_6O_{19} \cdot 13H_2O$ was synthesized according to the reference and identified by IR spectrum [17]. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400-II CHNS/O analyzer. IR spectra were recorded on a Nicolet 360 FT-IR spectrometer using KBr pellets from 4000 to 400 cm^{-1}. UV spectra were obtained on a HITACHI U-4100 UV-Vis-NIR spectrometer (distilled water as solvent) from 400 to 190 nm.

2.2. *Preparations of compound*

2.2.1. $[Cu(1,3-dap)_2(H_2O)][(H_6Nb_6O_{19})_2Cu(1,3-dap)_2] \cdot 4(1,3-dap) \cdot 20H_2O$ (1). 1,3-dap (10 mL, 118.71 mmol) was added to a stirred solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2.00 mmol) which was dissolved in 10 mL water. Then the light blue solution was added dropwise to a stirred aqueous solution (10 mL) containing $K_7HNb_6O_{19} \cdot 13H_2O$ (0.62 g, 0.45 mmol). Finally, the resulting mixture was kept at 65°C with stirring for 24 h, mixed with water (1 : 3, volume ratio) and then transferred to a straight glass tube. Another ethanol/water solvent (1 : 1, volume ratio) was carefully layered onto the resulting light purple solution and the mixed solvent of acetonitrile/N,N-dimethylformamide (1 : 2, volume ratio) was layered onto the ethanol/water solvent. Block-shaped light blue crystals of **1** appeared at the interface after 30 days. Yield: 20% based on $K_7HNb_6O_{19} \cdot 13H_2O$. Anal. Calcd for **1** (%): C, 10.22; H, 4.36; N, 7.94. Found: C, 10.35; H, 4.51; N, 7.69.

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

Empirical formula	$C_{24}H_{134}Cu_2N_{16}Nb_{12}O_{59}$
Formula weight	2833.36
Crystal system	Monoclinic
Space group	$P2(1)/c$
Temperature (K)	296(2)
Unit cell dimensions (Å, °)	
λ	0.71073
a	19.476(4)
b	15.305(3)
c	30.178(6)
β	95.622(3)
Volume (Å^3), Z	8952(3), 4
Crystal size (mm^3)	$0.28 \times 0.21 \times 0.18$
Calculated density (Mg cm^{-3})	2.093
Absorption coefficient (mm^{-1})	2.042
Reflections collected	45,002
Independent reflections	15,722 [$R_{(int)} = 0.0300$]
Data/restraints/parameters	15,722/6/1054
Goodness-of-fit on F^2	1.053
Completeness (%)	99.7
$F(000)$	5600
Index range	$-23 \leq h \leq 20;\ -18 \leq k \leq 16;\ -28 \leq l \leq 35$
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0356,\ wR_2 = 0.0929$
R indices (all data)	$R_1 = 0.0502,\ wR_2 = 0.0995$
Largest difference peak and hole (e Å^{-3})	1.107 and -0.675

2.3. *X-ray structure determination*

A crystal with dimensions $0.28 \times 0.21 \times 0.18\,\text{mm}^3$ for **1** was stuck on a glass fiber and intensity data were collected on a Bruker Apex-II CCD detector using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073\,\text{Å}$) at room temperature. Routine Lorentz and polarization corrections were applied. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set by using SADABS. The structures were solved by direct methods and refined using full-matrix least-square on F^2. All calculations were performed using the SHELXTL-97 program package [18]. No hydrogens associated with the molecules were located from the difference Fourier map. Positions of hydrogens attached to carbon and nitrogen were geometrically placed. All hydrogens were refined isotropically as a riding mode using the default SHELXTL parameters. All non-hydrogen atoms were refined anisotropically except for some carbons and water molecules. A summary of crystal data and structure refinement for **1** is provided in table 1; selected bond lengths and angles are listed in table 2.

3. Results and discussion

3.1. *Synthesis*

Although the diffusion technique is rarely utilized in the synthesis of POMs, our group has proved that it is an effective and feasible method for crystal growth of

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

Nb1–O1	1.781(3)	Nb1–O8	1.954(3)
Nb1–O19	2.341(3)	Nb2–O2	1.765(3)
Nb2–O7	2.052(3)	Nb2–O9	1.974(3)
Nb2–O19	2.458(3)	Nb5–O5	1.790(3)
Nb6–O6	1.766(3)	Nb8–O21	1.785(3)
Nb9–O22	1.787(3)	Nb9–O33	1.972(3)
Nb9–O38	2.428(3)	Nb10–O23	1.790(4)
Nb12–O25	1.790(4)	Nb12–O29	1.907(3)
Nb12–O38	2.384(3)	Cu1–O9	2.646(7)
Cu1–O33	2.696(3)	Cu2–O1W	2.593(5)
Cu1–N1	2.038(4)	Cu1–N2	2.033(4)
Cu2–N6	2.004(6)	Cu2–N8	2.026(5)
O1–Nb1–O7	103.68(16)	O7–Nb1–O8	92.24(14)
O7–Nb1–O10	88.29(13)	O7–Nb1–O11	157.35(13)
O2–Nb2–O19	177.79(14)	O13–Nb2–O19	77.32(12)
O3–Nb3–O19	176.86(14)	O15–Nb4–O17	88.07(13)
O16–Nb5–O17	157.42(13)	O6–Nb6–O13	102.85(16)
O35–Nb7–O38	80.92(13)	O34–Nb8–O26	89.85(14)
O22–Nb9–O29	101.10(15)	O32–Nb10–O30	153.59(14)
O36–Nb11–O35	88.19(14)	O25–Nb12–O28	99.68(15)

PONs [15, 16, 19]. In this work, a number of parallel experiments were performed, indicating that good quality crystals of **1** were prepared when the concentration of the reaction mixture was diluted four times. Moreover, when the water–ethanol solvent was employed alone, microcrystallines were obtained. Therefore, the concentration of the reaction mixture and the categories of solvent are key factors for the formation of **1**.

To further investigate the structural diversity that can be tuned by the molar ratio of ligands, varying amounts of 1,3-dap were employed. When 20 mL (237.42 mmol) 1,3-dap was used, a reported 3-D network architecture built by $[H_2Nb_6O_{19}]^{6-}$ and $[Cu_3(1,3\text{-dap})_6]^{6+}$ was prepared [20]. More interestingly, in comparison with the reported synthesis method using $[N(CH_3)_4]_6[Nb_{10}O_{28}]\cdot 6H_2O$ as precursor [20], we explored a new way to obtain $[Cu(dap)_2]_3[H_2Nb_6O_{19}]\cdot 6H_2O$ by $K_7HNb_6O_{19}\cdot 13H_2O$ precursor through diffusion.

3.2. *Crystal structure of 1*

Single-crystal X-ray diffraction reveals that the molecular structural unit of **1** consists of one dumbbell dimer polyoxoanion $[(H_6Nb_6O_{19})_2Cu(1,3\text{-dap})_2]^{2-}$, one copper complex $[Cu(1,3\text{-dap})_2(H_2O)]^{2+}$, four 1,3-dap ligands, and 20 crystal water molecules (figure 1a). As a polyoxoanion, $[(H_6Nb_6O_{19})_2Cu(1,3\text{-dap})_2]^{2-}$ can be described as two $[H_6Nb_6O_{19}]^{2-}$ polyoxoanions linked by a $[Cu(1,3\text{-dap})_2]^{2+}$. In the polyoxoanion of **1**, the oxygens can be divided into four groups: O_t (terminal oxygens connected with one Nb), μ_2–O_b (bridging oxygens connecting two adjoining Nb's), μ_3–O_b (bridging oxygen connecting two adjoining Nb's and a Cu) and O_c (center oxygen connecting six NbO_6 octahedra). The corresponding Nb–O distances can be grouped into four sets: Nb–O_t: 1.765(3)–1.797(3) Å; Nb–μ_2–O_b: 1.904(3)–2.147(3) Å; Nb–μ_3–O_b: 1.964(3)–1.974(3) Å, and Nb–O_c: 2.337(3)–2.458(3) Å. The O–Nb–O bond angles vary from 74.89(12)° to 177.91(16)°, indicating that the NbO_6 octahedra are slightly distorted. Bond valence
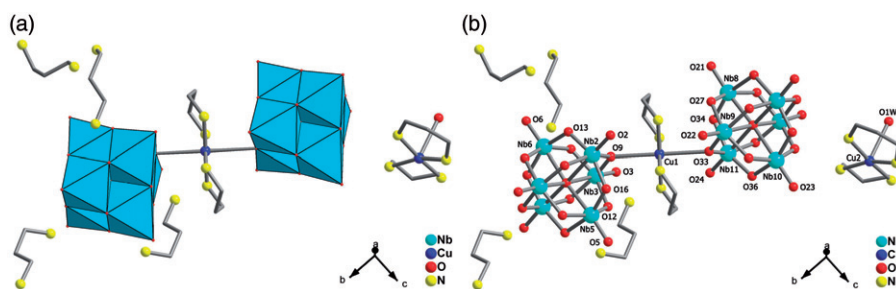
Figure 1.   (a), (b) Polyhedral/ball-and-stick view of **1**. All hydrogens and crystal water molecules are omitted for clarity.

sum (BVS) [21] calculations give values of 1.16, 1.13, 1.15, and 1.12 for O11, O17, O28, and O31 atoms, respectively, suggesting monoprotonation. BVS calculations on the other oxygens in the polyoxoanion give values of 1.36–1.42 for O1, O3–O5, O20–O23, and O25, indicating eight of these positions for binding protons. Although these protons cannot be accurately located by BVS calculations and X-ray diffraction, the protons must be delocalized in the $[Nb_6O_{19}]^{8-}$ units [2c, 13].

As depicted in figure 1(b), there are two crystallographically independent Cu^{II} centers. Cu1 displays octahedral geometry defined by four nitrogens from two 1,3-dap ligands [Cu–N: 2.031(4)–2.038(4) Å, N–Cu–N: 89.54(18)–179.51(19)°] and two μ_3-O_b from polyoxoanions [Cu–O: 2.646(7)–2.696(3) Å]. $[Cu2(1,3-dap)_2(H_2O)]^{2+}$ is a five-coordinate square pyramid achieved by four nitrogens from two 1,3-dap ligands [Cu–N: 2.002(5)–2.026(5) Å] and one oxygen from a coordinated water molecule [Cu–O: 2.593(5) Å]. Cu–O weak interactions are considered because the evident Jahn–Teller distortion of CuII ion in the crystal field leads to elongation of the Cu–O distance [22].

There exist some moderately strong N–H···O contacts with nitrogens of organic groups as hydrogen donors and oxygens of PON anions as acceptors [N···O: 2.714–3.461 Å]. Table 3 shows the bond lengths and angles for **1**. As depicted in figure 2, the free 1,3-dap ligands and $[Cu(1,3-dap)_2(H_2O)]^{2+}$ cations act as a "glue" to assemble the adjacent "dumbbells" forming a 1-D zigzag chain. Each chain is connected to four surrounding chains *via* hydrogen-bonding resulting in a 3-D supramolecular architecture (figure 3). Such supramolecular interactions contribute to the structural stabilization and chemical stability of these compounds.

3.3. *FT-IR and UV spectroscopy*

IR spectrum of **1** (figure 4) were recorded between 400 and 4000 cm^{-1} as a KBr pellet to identify characteristic vibrations of PONs and organic components. The IR spectrum of **1** exhibits five characteristic vibrations resulting from $[Nb_6O_{19}]^{8-}$. The peak at 850 cm^{-1} is attributed to the terminal Nb–O_t and peaks at 685 and 530 cm^{-1} to bridging Nb–O_b–Nb vibration. Compared with the IR spectrum of $K_7HNb_6O_{19} \cdot 13H_2O$ (852, 669, 519, 413 cm^{-1}) [2b], the vibration bands of **1** are slightly shifted from coordination interactions between $[Nb_6O_{19}]^{8-}$ and $[Cu(1,3-dap)_2]^{2+}$. Stretching bands of –OH and –NH_2 are observed at 3410–3250 cm^{-1} and 3120 cm^{-1}, respectively, and bending

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

D–H$\cdots$A	d(D–H)	d(H$\cdots$A)	d(D$\cdots$A)	$\angle$(DHA)
N(1)–H(1A)$\cdots$O(2)	0.900	2.482	3.105	126.72
N(1)–H(1B)$\cdots$O(27)	0.900	2.144	3.040	173.72
N(2)–H(2A)$\cdots$O(34)	0.900	2.210	3.081	162.73
N(2)–H(2B)$\cdots$O(4W)	0.900	2.391	3.080	133.47
N(2)–H(2B)$\cdots$O(3)	0.900	2.531	3.242	136.24
N(3)–H(3A)$\cdots$O(22)	0.900	2.513	3.253	139.88
N(3)–H(3B)$\cdots$O(16)	0.900	2.205	3.067	160.24
N(4)–H(4A)$\cdots$O(12)	0.900	2.147	3.043	173.91
N(4)–H(4B)$\cdots$O(24)	0.900	2.560	3.174	125.96
N(5)–H(5A)$\cdots$O(1)[a]	0.900	2.411	3.152	139.71
N(5)–H(5B)$\cdots$O(15W)[b]	0.900	2.015	2.909	171.93
N(6)–H(6A)$\cdots$O(5W)[c]	0.900	2.655	3.461	149.58
N(6)–H(6B)$\cdots$O(30)	0.900	2.640	3.169	118.41
N(7)–H(7A)$\cdots$O(6)[a]	0.900	2.187	3.085	176.30
N(7)–H(7B)$\cdots$O(30)	0.900	2.048	2.930	166.39
N(8)–H(8A)$\cdots$O(15W)[b]	0.900	2.499	3.366	161.87
N(8)–H(8B)$\cdots$O(18)[a]	0.900	2.288	3.118	153.22
N(8)–H(8B)$\cdots$O(8)[a]	0.900	2.495	3.198	135.30
N(9)–H(9A)$\cdots$O(2W)[d]	0.860	2.324	3.152	161.76
N(9)–H(9B)$\cdots$O(7)[e]	0.860	2.248	3.023	149.91
N(9)–H(9B)$\cdots$O(10)[e]	0.860	2.342	2.982	131.46
N(10)–H(10A)$\cdots$O(31)[d]	0.860	2.433	2.892	114.06
N(10)–H(10A)$\cdots$O(27)[d]	0.860	2.522	3.050	120.51
N(10)–H(10B)$\cdots$O(1)	0.860	1.988	2.803	157.60
N(11)–H(11A)$\cdots$O(4)[f]	0.860	2.479	2.977	117.61
N(11)–H(11A)$\cdots$O(4W)	0.860	2.487	3.314	161.53
N(11)–H(11B)$\cdots$O(26)[g]	0.860	2.210	2.929	141.03
N(11)–H(11B)$\cdots$O(35)[g]	0.860	2.609	3.360	146.48
N(12)–H(12A)$\cdots$O(12)	0.860	2.439	2.967	120.23
N(12)–H(12A)$\cdots$O(17)	0.860	2.492	2.916	111.22
N(12)–H(12A)$\cdots$O(15)	0.860	2.537	3.392	172.93
N(12)–H(12B)$\cdots$O(20)[d]	0.860	2.181	2.980	154.45
N(13)–H(13A)$\cdots$O(35)[h]	0.860	2.256	2.881	129.48
N(13)–H(13A)$\cdots$O(24)[h]	0.860	2.443	3.199	147.03
N(13)–H(13B)$\cdots$O(15)[i]	0.860	2.017	2.845	161.36
N(13)–H(13B)$\cdots$O(14)[i]	0.860	2.566	3.151	126.12
N(14)–H(14A)$\cdots$O(6)	0.860	2.255	2.714	113.47
N(14)–H(14A)$\cdots$O(23)[h]	0.860	2.615	3.177	124.06
N(14)–H(14B)$\cdots$O(12W)[h]	0.860	2.529	3.060	120.77
N(14)–H(14B)$\cdots$O(11W)	0.860	2.624	3.265	132.23
N(14)–H(14B)$\cdots$O(19W)	0.860	2.651	3.272	130.09
N(15)–H(15A)$\cdots$O(23)[h]	0.860	2.193	2.804	127.79
N(15)–H(15B)$\cdots$O(21W)[j]	0.860	2.253	2.904	132.47
N(15)–H(15B)$\cdots$O(12W)[h]	0.860	2.628	3.233	128.39
N(16)–H(16A)$\cdots$O(20W)	0.860	2.519	3.375	174.09
N(16)–H(16B)$\cdots$O(7)	0.860	2.042	2.784	143.92

Symmetry transformations used to generate the equivalent atoms: [a] x, $-y+1/2$, $z+1/2$; [b] x, $-y-1/2$, $z+1/2$; [c] x, $y-1$, z; [d] x, $y+1$, z; [e] $-x+1$, $y+1/2$, $-z+1/2$; [f] $-x$, $y-1/2$, $-z+1/2$; [g] $-x$, $y+1/2$, $-z+1/2$; [h] x, $-y+1/2$, $z-1/2$; [i] $-x$, $-y+1$, $-z$; [j] $-x+1$, $-y+1$, $-z$.

vibrations of –NH$_2$ and –CH$_2$ appear at 1620 cm^{-1} and 1520–1470 cm^{-1}, respectively. These characteristic vibrations confirm the presence of 1,3-dap [23].

As depicted in figure 5, the UV spectrum shows one strong absorption band at 193 nm and two wide shoulder absorptions at *ca* 235 and *ca* 300 nm. The higher energy absorptions (193 and 235 nm) originate from O $\rightarrow$ Nb charge transfer transitions, whereas the lower energy band (300 nm) is assigned to ligand-to-metal (Cu^{II}) charge
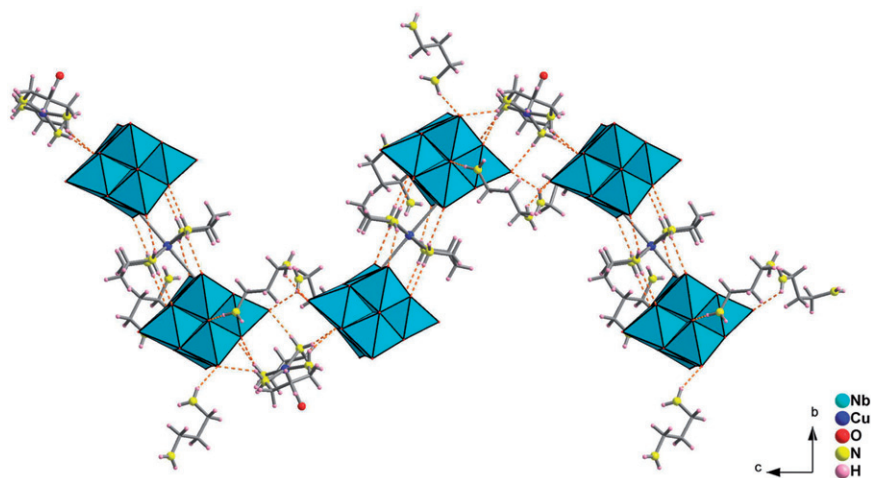
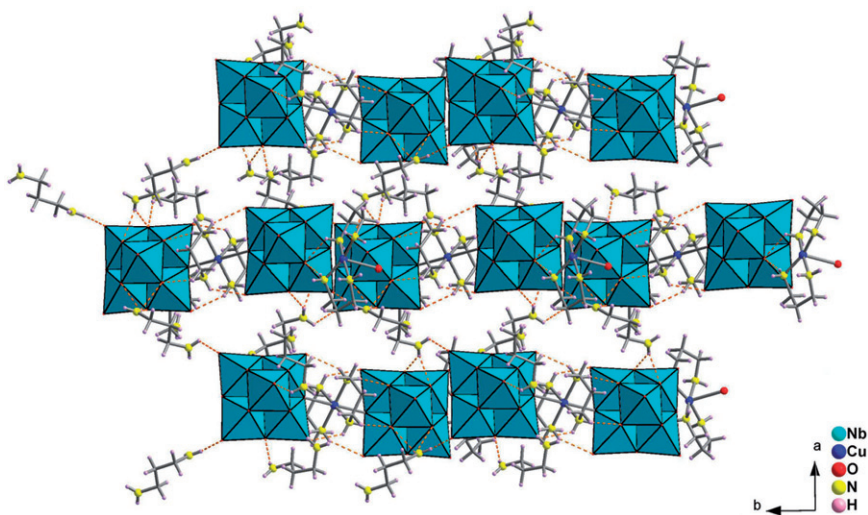Figure 2. 1-D hydrogen-bonded 1-D zigzag chain of **1** along the *c*-axis.

Figure 3. Polyhedral representation of the 3-D supramolecular framework of **1** in the *ab*-plane.

transfer (LMCT) transitions [15, 16]. Compared with the UV spectrum of $K_7HNb_6O_{19} \cdot 13H_2O$ (*ca* 192 and 233 nm) [15], the absorption bands are slightly shifted, also related to the coordination interactions between the hexaniobate anions and copper coordinated cations.

4. Conclusion

A new PON based on Lindqvist-type anions and copper complex has been synthesized by the diffusion strategy. The synthesis of **1** enriches the structural diversity of PONs
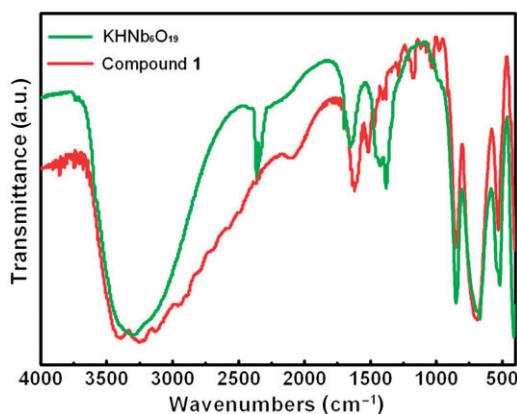
Figure 4.   Comparison of IR spectra of **1** and $K_7HNb_6O_{19} \cdot 13H_2O$.
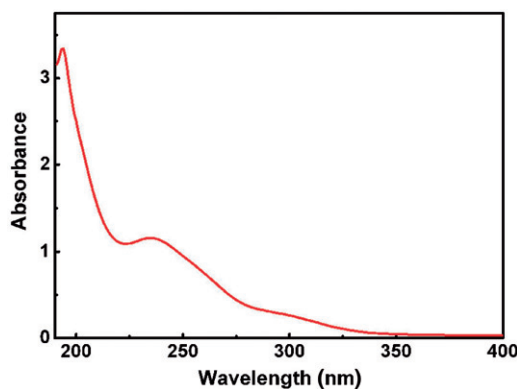

Figure 5.   UV spectrum of **1** in aqueous solution $(1 \times 10^{-5} \, \text{mol L}^{-1})$.

and further provides a synthetic strategy that other transition-metal cations and organic ligands can be introduced to this system to construct new PONs.

Supplementary material

CCDC 804812 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

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