Preparation, crystal structure, and characterization of an inorganic–organic hybrid polyoxoniobate [Cu(en)$_2$]$_3$[Cu(en)$_2$(H$_2$O)]$_{1.5}$[K$_{0.5}$Nb$_{24}$O$_{72}$H$_{14.5}$]2·25H$_2$O

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Abstract. An inorganic–organic hybrid polyoxoniobate compound [Cu(en)$_2$]$_3$[Cu(en)$_2$(H$_2$O)]$_{1.5}$ [K$_{0.5}$Nb$_{24}$O$_{72}$H$_{14.5}$]2·25H$_2$O (**1**) was synthesized by reaction of K$_7$HNb$_6$O$_{19}$·13H$_2$O, Cu(CH$_3$COOH)$_2$·H$_2$O and en (ethylenediamine) in aqueous solution and characterized by IR, ESR spectroscopy and single-crystal X-ray diffraction method. Structure analysis indicates that compound **1** consists of a new type polyoxoniobate anion [K$_{0.5}$Nb$_{24}$O$_{72}$H$_{14.5}$]$^{9-}$, three [Cu(en)$_2$]$^{2+}$, one point five [Cu(en)$_2$(H$_2$O)]$^{2+}$, and two point two five crystal water molecules. The structure contains N–H···O hydrogen bonds between the co-ordinated ethylenediamine and the polyniobate-anion. The whole molecule possesses the C_{3v} symmetry.

Keywords. Polyoxometalates; polyoxoniobate; crystal structure; characterization.

1. Introduction

Polyoxometalates (POMs) are a unique class of inorganic metal-oxygen clusters. They have found manifold potential applications in catalysis,[1–2] medicine,[3] material science,[4] nuclear waste processing.[5] Numerous new structural types with fascinating topological beauty and the associated multitude of properties are still being discovered.[6–9]

Polyoxoniobates have been less evolved in comparison with the structural diversities of polyoxotungstates, polyoxomolybdates and polyoxovandates because of the lack of soluble monomeirc precursors and only stable in alkaline media, whereas most other POMs can be easily formed over a wide pH range. The stability in highly alkaline solutions (polyoxoanions of niobium are stable only in pH > 10 basic media) and high surface ratio of polyoxoniobates render them appropriate for radionuclide separation from caustic nuclear wasters,[10–12] virology[13] and the base-catalysed de-composition of biocontaminants.[14] So, more researchers have taken their interest in the study of polyoxoniobate. Here, we have obtained a new inorganic–organic hybrid polyoxoniobate compound [Cu(en)$_2$]$_3$[Cu(en)$_2$(H$_2$O)]$_{1.5}$[K$_{0.5}$Nb$_{24}$O$_{72}$H$_{14.5}$]

2·25H$_2$O (**1**) and characterized by IR, ESR spectroscopy and single-crystal X-ray diffraction method.

2. Experimental

All chemicals were purchased from commercial sources and used without further purification. Potassium hexaniobate K$_7$HNb$_6$O$_{19}$·13H$_2$O were prepared by literature method.[15–16] IR spectra were recorded on a Nicolet 170SXFT-IR spectrometer with a KBr pellet, in the range of 4000 ~ 400 cm^{-1}. EPR spectra were recorded on a Bruker ER-200-DSRC 10 spectrometer at the X-band. Elemental analysis were performed on a Jarrel-Ash J-A1100 spectrometer.

2.1 *Preparation of compound* **1**

0·5 mL en (en = ethylenediamine) was added to an aqueous solution of Cu(CH$_3$COO)$_2$·H$_2$O (0·3 g, 1·5 mmol) while stirring at room temperature. The resulting purple solution was added drop-wise to a beaker containing an aqueous solution of K$_7$HNb$_6$O$_{19}$· 13H$_2$O (0·68 g, 0·5 mmol). This solution was stirred at 60°C for 4 h and then evaporated at room temperature. Deep purple single crystals were obtained after a week. Yield: 0·4 g (76% bases on Nb). IR:

Table 1. Crystallographic parameters of compound **1**.

Formula	$C_{18}H_{94}Cu4 \cdot 5K_{0.5}N_{18}Nb_{24}O_{75.75}$
Formula weight	4310·27
Crystal system	Hexagonal
Space group	*R*-3
Unit cell dimensions	
a (Å)	24·506(5)
b (Å)	24·506(5)
c (Å)	48·175(7)
α (°)	90
β (°)	90
γ (°)	120
Volume (Å^3)	25055(8)
Z	6
D_{calc} (g cm^{-3})	1·707
Absorption coefficient (mm^{-1})	2·213
F(000)	12240
Θ range for data collection	2·09 to 25·00°
Limiting indices	$-28 \leq h \leq 21$
	$-29 \leq k \leq -29$
	$-57 \leq l \leq 55$
Reflections collected	37573
Independent reflections	9176
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9176/82/544
Goodness-of-fit on F^2	0·891
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0785$, $wR_2 = 0.2423$
Largest diffraction peak and hole	1·914 and −0·953 eÅ^{-3}

1173 (*m*), 1112 (*m*), 1045 (*s*), 864 (*m*), 728 (*s*), 647 (*s*), 524 (*m*) cm^{-1}. Elemental analysis calc. (%) for $C_{18}H_{94}Cu_{4.5}K_{0.5}N_{18}Nb_{24}O_{75.75}$: C, 5·02%; H, 2·20%; N, 5·85%. Found: C, 4·99%; H, 2·26%, N, 5·83%.

2.2 *Single crystal X-ray diffractometry*

Single crystal of compound **1** was mounted on a SMART Apex-II CCD detector using graphite monochromatized MoKα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 package.[17] Intensity data were corrected for Lorentz and polarization effects as well as for empirical absorption. All of the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the refinements. The organic hydrogen atoms were generated geometrically. Details for the structural determination of compound **1** are listed in table 1. Selected bond distances for compound **1** are represented in table 2.

3. Results and discussion

The X-ray diffraction analysis indicates that compound **1** contains a $[K_{0.5}Nb_{24}O_{72}]^{23.5-}$ polyoxoanion, three $[Cu(en)_2]^{2+}$, one point five $[Cu(en)_2(H_2O)]^{2+}$ cations and two point two five water molecules. The $[K_{0.5}Nb_{24}O_{72}]$ unit could be described as three $[Nb_7O_{22}]$ units linked alternately by three Nb(8)O$_6$ octahedra via corner-sharing (see figure 1). The fundamental building block $[Nb_7O_{22}]$ is derived from the Lindqvist $[Nb_6O_{19}]$ clusters (figure 2), three adjacent bridging oxygen atoms of which are combined with the seventh Nb atom, Nb7. Three $[Nb_7O_{22}]$ subunits are linked alternately by the Nb(8)O$_6$ octahedron via sharing two corners and formed a cavity in the center. And K$^+$, with the occupy ratio of 0.5, locates in the center of the cavity via combined with nine oxygen atoms from $[Nb_{24}O_{72}]$ unit. Thus, the $[K_{0.5}Nb_{24}O_{72}]^{23.5-}$ polyoxoanion constructs a discrete triangular 'bowl-shaped' cluster structure approaching the C$_{3v}$ point symmetry.

The fourteen point five protons that are added into per $[K_{0.5}Nb_{24}O_{72}]$ unit (i.e. $[K_{0.5}Nb_{24}O_{72}H_{14.5}]^{-9}$) are based on charge-balance considerations of compound **1**, because the high number of crystalographically independent atoms and variable parameters prevented direct location of the protons from the Fourier maps, as the description of Nyman.[18] The three long Nb-O$_t$ bonds of the NbO$_6$ octahedra, which linked alternately to three $[Nb_7O_{22}]^{9-}$ building

Table 2. Selected bond lengths [Å] for **1**.

Cu(1)–N(1)	1·986(14)	Cu(1)–N(1)#1	1·986(14)
Cu(1)–N(2)	2·014(16)	Cu(1)–N(2)#1	2·014(16)
Cu(2)–N(3)	2·03(3)	Cu(2)–N(5)	2·04(2)
Cu(2)–N(4)	2·05(3)	Cu(2)–N(6)	2·07(3)
Cu(2)–O(1W)	2·37(2)	Cu(3)–N(9)	1·95(2)
Cu(3)–N(8)	1·99(3)	Cu(3)–N(10)	2·05(3)
Cu(3)–N(7)	2·29(3)	K(1)–O(7C)	2·789(11)
K(1)–O(7C)#2	2·789(11)	K(1)–O(7C)#3	2·789(11)
K(1)–O(7A)	3·015(10)	K(1)–O(7A)#2	3·015(10)
K(1)–O(7A)#3	3·015(10)	K(1)–O(8A)	3·365(17)
K(1)–O(8A)#2	3·365(17)	K(1)–O(8A)#3	3·365(17)
Nb(1)–O(1)	1·753(12)	Nb(1)–O(9)	1·962(11)
Nb(1)–O(10)	2·016(10)	Nb(1)–O(11)	2·038(10)
Nb(1)–O(12)	2·068(11)	Nb(1)–O(21)	2·406(9)
Nb(2)–O(2)	1·763(11)	Nb(2)–O(17)	1·999(10)
Nb(2)–O(13)	2·004(11)	Nb(2)–O(9)	2·019(11)
Nb(2)–O(16)	2·047(10)	Nb(2)–O(21)	2·450(10)
Nb(3)–O(3)	1·776(11)	Nb(3)–O(13)	1·952(12)
Nb(3)–O(10)	1·990(11)	Nb(3)–O(18)	2·035(10)
Nb(3)–O(14)	2·057(10)	Nb(3)–O(21)	2·444(9)
Nb(4)–O(4)	1·831(9)	Nb(4)–O(14)	1·915(9)
Nb(4)–O(11)	1·926(9)	Nb(4)–O(15)	2·111(10)
Nb(4)–O(19)	2·124(9)	Nb(4)–O(21)	2·284(10)
Nb(5)–O(5)	1·835(9)	Nb(5)–O(16)	1·871(10)
Nb(5)–O(12)	1·904(10)	Nb(5)–O(15)	2·033(9)
Nb(5)–O(20)	2·084(9)	Nb(5)–O(21)	2·299(9)
Nb(6)–O(6)	1·760(9)	Nb(6)–O(18)	1·929(9)
Nb(6)–O(17)	1·935(11)	Nb(6)–O(19)	2·094(8)
Nb(6)–O(20)	2·104(8)	Nb(6)–O(21)	2·398(9)
Nb(7)–O(7B)	1·805(10)	Nb(7)–O(7A)	1·910(9)
Nb(7)–O(7C)	1·951(10)	Nb(7)–O(20)	2·119(10)
Nb(7)–O(19)	2·143(8)	Nb(7)–O(15)	2·296(10)
Nb(8)–O(8B)	1·779(11)	Nb(8)–O(7C)	1·965(10)
Nb(8)–O(7A)#3	1·982(10)	Nb(8)–O(5)	2·073(10)
Nb(8)–O(4)#3	2·094(9)	Nb(8)–O(8A)	2·428(11)

Symmetry transformations used to generate the equivalent atoms #1 $-x + 1/3$, $-y–4/3, -z – 1/3$ #2 $-x + y + 1, -x – 1, z$ #3 $-y – 1, x – y – 2, z$

Table 3. Geometrical parameters of hydrogen bonds for compound **1** (Å, deg).

D–H	A	d(D–H)	H···A	<D–H–A	D···A
N7–H7C	O11	0·859	1·994	141·78	2·721
N1–H1C	O18	0·860	2·249	144·54	2·991

block, are all 2·428 Å as a result of symmetry transformations. Bond valence sum[19] calculations provide value of 0·247 for these Nb–O_t terminal oxygen atoms and indicates the most obvious site for protonation. The BVS values of the remaining terminal oxygen atom in the range of 1·33–1·53, suggesting that some terminal oxygen atoms can be monoprotonated. However, bond-valence calculations did not provide an obvious solution as a result of a typical distor-

tions and the relatively wide variation of the Nb–O bond lengths[18–19] (table 2). Although they cannot be accurately located by X-ray and BVS calculations, these protons must be localized or delocalized in polyoxoniobate anion units.[18,20]

The $[Cu(en)_2]$ and $[Cu(en)_2(H_2O)]$ fragments are distributed symmetrically around the 'bowl'. And Cu(1) and Cu(3) atoms are coordinated separately by four nitrogen atoms from two en molecules displaying a CuN_4 square planar geometry. Cu(2) is linked to four nitrogen atoms from two en ligands and one oxygen atom from the water molecule exhibiting a CuN_4O square pyramid geometry. The $[Cu(en)(H_2O)]$ fragment combines with the polyoxoanion $[K_{0.5}Nb_{24}O_{72}H_{14.5}]^{-9}$ via N(7)–H(7C)···O(11) hydrogen bond. Neighbouring polyoxoanion $[K_{0.5}Nb_{24}$

$O_{72}H_{14\cdot5}]^{-9}$ are linked together by $[Cu(1)(en)_2]$ via weak $Cu-O_{19}$ $(3\cdot260\text{ Å})$ bond and $N(1)-H(1C)\cdots O(18)$ hydrogen bond, resulting in a 2D interlaced layer (figure 3). The disorder water molecules fill in the space of the layers. The hydrogen bonding parameters for compound **1** are presented in table 3.

The ESR spectra of compound **1** at room temperature and 110 K are shown in figure 4. The spectra at room temperature (figure 4a) exhibit the axial feature (as expected for a square pyramid and square

plane Cu^{2+} center) with $g = 2\cdot04$. At the lower 110 K the spectra (figure 4b) remain same ($g = 2\cdot10$). The ESR parameters are in good agreement with those of Cu^{2+} (d^9) systems in the literature.[21]

4. Conclusions

In this paper we have prepared a new inorganic–organic hybrid polyoxoniobate compound and enriched polyoxoniobates chemsitry. We compared compound **1** with the previously reported polyoxoniobate anion $[Nb_{24}O_{72}H_9]^{15-}$ **(2)**,[18] $[Nb_{24}O_{72}H_{21\cdot5}]^{2\cdot5-}$ **(3)**,[20] and dimeric fragment $[(\{KNb_{24}O_{72}H_{10\cdot25}\}\{Cu(en)_2\})_2 \{Cu_3(en)_3(H_2O)_3\}\{Na_{1\cdot5}Cu_{1\cdot5}(H_2O)_8\}]^{11-}$ **(4)**.[20] Both **1** and **4** use the potassium salts of hexaniobate as pre-
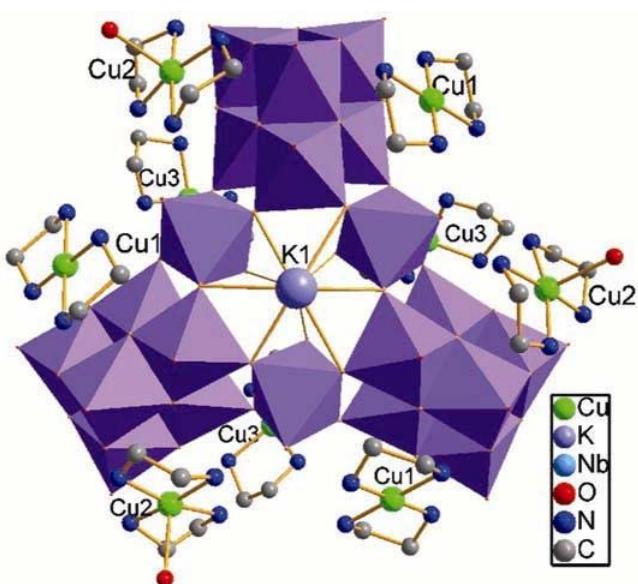
**Figure 1.** View of the molecule structure of compound **1** (H atom and water molecules are omitted for clarity).
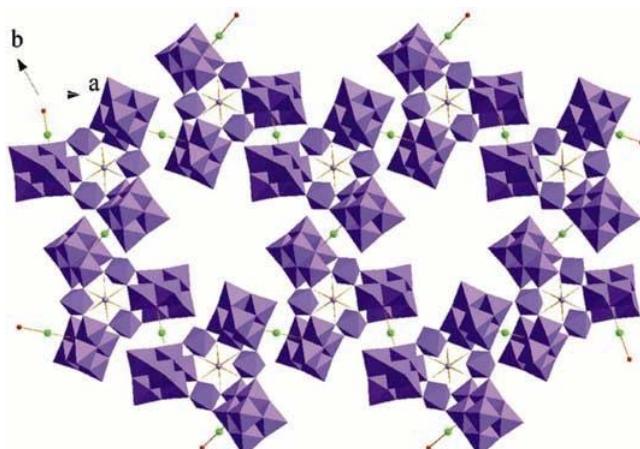
Figure 3. The 2D interlaced layer of compound **1** (C, H, N atoms and hydrogen bond are omitted for clarity).
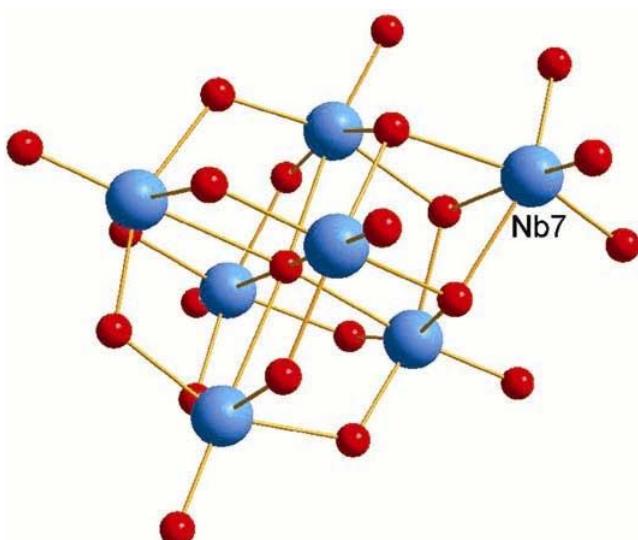
**Figure 2.** Structure unit of the Nb_7O_{22}.
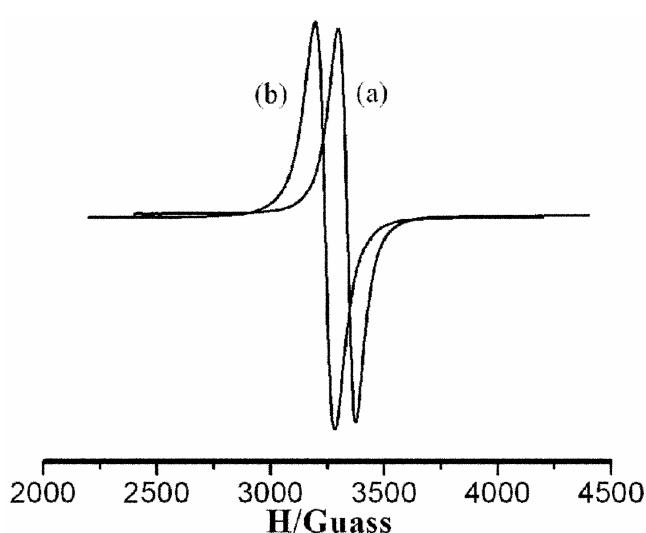
Figure 4. ESR spectra of compound **1**.

cursors and have the K^+ cation located at the center of the aperture of the $\{Nb_{24}O_{72}\}$ unit. However, **2** and **3** adopt the sodium or rubidium salts and there is no cation located at the aperture center. These indicate the aperture that possesses selectivity for K^+ cation and could deduce the potential application of the polyoxoniobate in the transport of (biologically relevant) cations.

Acknowledgements

Supplementary material

CCDC-664094 contains the supplementary crystallographic data for the structure reported in this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retriving.html (or from the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk).

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