

## Electronic Supporting Information

### Two synthetic routes generate two isopolyoxoniobates based on {Nb<sub>16</sub>} and {Nb<sub>20</sub>}

Zhijie Liang,<sup>a,b</sup> Yuanyuan Qiao,<sup>a</sup> Miaomiao Li,<sup>a</sup> Pengtao Ma,<sup>a</sup> Jingyang Niu,<sup>\*,a</sup> and  
Jingping Wang<sup>\*,a</sup>

<sup>a</sup>*Henan Key Laboratory of Polyoxometalate Chemistry, Institute of Molecular and Crystal Engineering, College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, Henan, People's Republic of China.*

<sup>b</sup>*College of Textile and Clothing, Nantong University, Nantong 226019, Jiangsu, People's Republic of China*

*E-mail: jyniu@henu.edu.cn, jpwang@henu.edu.cn, Fax: (+86)371-23886876*

## Synthesis

Synthesis of compound **1**: 0.137 g of  $\text{K}_7\text{HNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$  (0.1 mmol) (synthesized according to a literature method)<sup>S1</sup> and 0.022 g of  $\text{SeO}_2$  (0.2 mmol) were dissolved in 24 mL of water. Then, 0.0606 g of  $\text{Cu}(\text{CH}_3\text{COO})_2\cdot \text{H}_2\text{O}$  (0.304 mmol) and 0.028 g of 2,2'-bipy (0.179 mmol) dissolving in 1 mL of water were added with stirring to the previous solution. When the addition was completed, the solution was stirred during 20 min. The pH of the solution was adjusted to 10.8 using  $\text{KOH}_{\text{aq}}$ , heated to 90 °C for 3 hours, and then allowed to cool back to room temperature. After removing the precipitate from the solution, the filtrate was transferred to a tube and covered with alcohol/ $\text{H}_2\text{O}$  mixed solution and alcohol sequentially. After one month, blue, needle-like crystals were obtained. Yield: 6.32 mg (4 %, based on Nb). IR: 3318, 1602, 1568, 1496, 1473, 1448, 1313, 1252, 1159, 1106, 1062, 1035, 1021, 868, 827, 815, 772, 730, 712, 662, 651, 602, 537  $\text{cm}^{-1}$ . Elemental analysis, calcd for  $\text{C}_{60}\text{H}_{107}\text{N}_{12}\text{Cu}_6\text{Nb}_{16}\text{K}_3\text{O}_{77}$ : C, 17.10; H, 2.56; N, 3.99 %. Found: C, 17.14; H, 2.36; N, 3.60 %.

Synthesis of compound **2**: 0.274 g of  $\text{K}_7\text{HNb}_6\text{O}_{19}\cdot 13\text{H}_2\text{O}$  (0.2 mmol), 0.111 g of  $\text{SeO}_2$  (1.0 mmol) and additional 0.105 g NaCl were dissolved in 24 mL of water. Another aqueous solution containing 0.08 g of  $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$  (0.398 mmol) and 0.063 g 2,2'-bipy (0.403 mmol) in 1 mL of water was added dropwise to the first one, and the pH of the resultant solution was adjusted again to 10.8 using  $\text{KOH}_{\text{aq}}$ . Then, the solution was heated to 60 °C for 4 hours. The filtrate was kept in an open container at room temperature, and, after one month, blue-green, block-like crystals were obtained. Yield: 0.108 g (30 %, based on Nb). IR: 3390, 1642, 1601, 1568, 1495, 1475, 1448, 1385, 1313, 1253, 1175, 1158, 1106, 1059, 1033, 1019, 984, 889, 767, 736, 652, 597, 576  $\text{cm}^{-1}$ . Elemental analysis, calcd for  $\text{C}_{110}\text{H}_{176}\text{Cu}_{11}\text{N}_{22}\text{Nb}_{20}\text{O}_{105}$ : C, 21.86; H, 2.94; N, 5.10 %. Found: C, 21.51; H, 2.57; N, 5.45 %.

## Additional discussion

As far as we know, the synthesis of novel polyoxoniobates (PONb) remains a challenge up to now in polyoxometalate chemistry due to the lack of soluble niobate precursors, the low reactive activity and the narrow working pH region of niobate

species. In this work, the successful syntheses of two novel PONbs **1** and **2** are attributed to the following considerations and experiments: 1) according to literature, a kind of soluble niobate salt  $K_7HNb_6O_{19}\cdot 13H_2O$  was prepared as precursor, and the ion dominates the solution chemistry of Nb at pH higher than 9. 2) Considering the stable pH region of  $\{Nb_6O_{19}\}$  ion, the adduct  $SeO_2$  was employed, which makes the pH reducing to  $<7$  with the solution changing slight cloudy but becoming clear again once the pH was adjusted to higher. 3) The strategy for the crystallization is of great importance. In this work, the diffusion strategy was employed again indicating its feasibility and applicability. 4) As far as we know,  $Cu^{2+}$  ion could be seen as an excellent candidate for the isolation of inorganic-organic compounds because of the good coordination ability. Besides, we have tried to use other different 3d metals (e.g.,  $Mn^{2+}$ ,  $Fe^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ) reacting with  $K_7HNb_6O_{19}\cdot 13H_2O$  to synthesize analogues. However, we failed to obtain any other 3d-metal-containing inorganic-organic PONbs.

### **Analytical details**

Elemental analyses (C, H and N) were performed by a PerkinElmer 2400-II CHNS/O elemental analyzer. IR spectra were collected on a Perkin-Elmer Spectrum Two spectrophotometer in the range  $4000\text{--}450\text{ cm}^{-1}$  with a KBr pellet dispersed with sample. Powder X-ray diffraction measurement was recorded ranging from  $4$  to  $45^\circ$  at room temperature on Bruker AXS D8 Advance diffractometer with  $Cu\text{-}K\alpha$  ( $\lambda = 1.5418\text{ \AA}$ ). Thermogravimetric analysis (TGA) of the samples was performed using a NETZSCH STA 449 F5 Jupiter thermal analyser heated from room temperature to  $1500\text{ }^\circ\text{C}$  under nitrogen. ESI-MS spectrometry was carried out using a Triple TOF 4600 mass spectrometer at an injection rate of  $5\text{ }\mu\text{L}\cdot\text{min}^{-1}$  with a syringe pump for direct source injection and the data were collected in negative-mode and analyzed using the Peak View software.

### **X-ray crystallography**

Suitable single crystals of **1** and **2** were sealed in a glass fiber and mounted on a goniometer. A Bruker APEX-II single crystal X-ray diffractometer and a Bruker D8 VENTURE PHOTON II equipped with monochromatized  $Mo\text{ }K\alpha$  radiation ( $\lambda = 0.71073$

Å) were used for data collection of compounds **1** and **2**, respectively (Table S1). After data collection, data reduction was performed by using *SAINTE* software.<sup>S2</sup> Multi-scan absorption correction was applied with *SADABS* program.<sup>S3</sup> The crystal structure was solved with *SHELXS* software by using direct method,<sup>S4,S5</sup> which found metal, oxygen, 2,2'-bipy and some H<sub>2</sub>O groups. Subsequent refinement cycles using *SHELXL* program found other atoms in the electron density map. Hydrogen atoms on the 2,2'-bipy groups were refined using the riding model. In addition, due to the existence of a large number of heavy atoms in this large structure **2**, it is very difficult to refine some light atoms such as C, N and O atoms, this can lead to the much ADP max/min ratio of many C, N and O atoms. Although, in the final refinement, almost all the heavy atoms were refined anisotropically, only the C atoms and lattice water O atoms were refined isotropically. The crystal data and structure refinement results revealed that the empirical formulas were K<sub>3</sub>[H{Cu(2,2'-bipy)}<sub>4</sub>{Cu(2,2'-bipy)(H<sub>2</sub>O)}<sub>2</sub>(Nb<sub>16</sub>O<sub>48</sub>)]□18H<sub>2</sub>O (**1**, C<sub>60</sub>H<sub>89</sub>N<sub>12</sub>Cu<sub>6</sub>Nb<sub>16</sub>K<sub>3</sub>O<sub>68</sub>) and [{Cu(2,2'-bipy)}<sub>2</sub>{Cu(2,2'-bipy)(H<sub>2</sub>O)}<sub>9</sub>(Nb<sub>20</sub>O<sub>61</sub>)]□9H<sub>2</sub>O (**2**, C<sub>110</sub>H<sub>124</sub>Cu<sub>11</sub>N<sub>22</sub>Nb<sub>20</sub>O<sub>79</sub>), respectively. The SQUEEZE program performed in PLATON was further used to calculate and evaluate the possible numbers of the solvent water molecules in the accessible voids of the crystal structures, respectively. A total of 27 (containing 26 solvent water molecules and one disordered bond to K<sup>+</sup>) and 52 extra solvent water molecules should be added to the chemical formulas K<sub>3</sub>[H{Cu(2,2'-bipy)}<sub>4</sub>{Cu(2,2'-bipy)(H<sub>2</sub>O)}<sub>2</sub>(Nb<sub>16</sub>O<sub>48</sub>)]□45H<sub>2</sub>O (**1**, C<sub>60</sub>H<sub>143</sub>N<sub>12</sub>Cu<sub>6</sub>Nb<sub>16</sub>K<sub>3</sub>O<sub>95</sub>) and [{Cu(2,2'-bipy)}<sub>2</sub>{Cu(2,2'-bipy)(H<sub>2</sub>O)}<sub>9</sub>(Nb<sub>20</sub>O<sub>61</sub>)]□61H<sub>2</sub>O (**2**, C<sub>110</sub>H<sub>228</sub>Cu<sub>11</sub>N<sub>22</sub>Nb<sub>20</sub>O<sub>131</sub>), respectively. However, the TGA and CHN elemental analysis results showed that the number of water molecules might be 27 and 35 for the empirical formulas K<sub>3</sub>[H{Cu(2,2'-bipy)}<sub>4</sub>{Cu(2,2'-bipy)(H<sub>2</sub>O)}<sub>2</sub>(Nb<sub>16</sub>O<sub>48</sub>)]□27H<sub>2</sub>O (**1**, C<sub>60</sub>H<sub>107</sub>N<sub>12</sub>Cu<sub>6</sub>Nb<sub>16</sub>K<sub>3</sub>O<sub>77</sub>) and [{Cu(2,2'-bipy)}<sub>2</sub>{Cu(2,2'-bipy)(H<sub>2</sub>O)}<sub>9</sub>(Nb<sub>20</sub>O<sub>61</sub>)]□35H<sub>2</sub>O (**2**, C<sub>110</sub>H<sub>176</sub>Cu<sub>11</sub>N<sub>22</sub>Nb<sub>20</sub>O<sub>105</sub>), respectively. This might be attributed to the weathering of crystals of them. CCDC numbers for compounds **1** and **2** are 1946988 and 1946990, respectively.

Table S1 Crystal data for compounds **1** and **2**.

Compounds	<b>1</b>	<b>2</b>
-----------	----------	----------

Empirical formula	$C_{60}H_{143}Cu_6K_3N_{12}Nb_{16}O_{95}$	$C_{110}H_{228}Cu_{11}N_{22}Nb_{20}O_{131}$
Formula weight	4537.96	6512.27
Temperature/K	296.15	296.15
Crystal system	<i>Monoclinic</i>	<i>Triclinic</i>
Space group	<i>C2/c</i>	<i>P<math>\bar{1}</math></i>
<i>a</i> /Å	24.7006(16)	19.1459(7)
<i>b</i> /Å	24.1052(17)	19.6390(8)
<i>c</i> /Å	24.8467(16)	35.0769(15)
$\alpha$ /°	90	97.782(2)
$\beta$ /°	118.3019(11)	94.0890(10)
$\gamma$ /°	90	115.1800(10)
Volume/Å <sup>3</sup>	13025.6(15)	11703.0(8)
Z	4	2
$\rho_{calc}/cm^3$	2.314	1.848
$\mu/mm^{-1}$	2.518	2.011
<i>F</i> (000)	8936.0	6458.0
Crystal size/mm <sup>3</sup>	0.29 × 0.2 × 0.18	0.26 × 0.22 × 0.12
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\theta$ range for data collection/°	2.522 to 50.2	4.272 to 50.2
	-28 ≤ <i>h</i> ≤ 29	-22 ≤ <i>h</i> ≤ 22
Index ranges	-28 ≤ <i>k</i> ≤ 28	-23 ≤ <i>k</i> ≤ 23
	-29 ≤ <i>l</i> ≤ 15	-41 ≤ <i>l</i> ≤ 41
Reflections collected	33863	128012
Independent reflections	11621 [ <i>R</i> <sub>int</sub> = 0.0697, <i>R</i> <sub>sigma</sub> = 0.0834]	41481 [ <i>R</i> <sub>int</sub> = 0.0302, <i>R</i> <sub>sigma</sub> = 0.0357]
Data/restraints/parameters	11621/12/703	41481/35/1532
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.038	1.061
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0542 <i>wR</i> <sub>2</sub> = 0.1487	<i>R</i> <sub>1</sub> = 0.0573 <i>wR</i> <sub>2</sub> = 0.1551
Final <i>R</i> indexes [all data]	<i>R</i> <sub>1</sub> = 0.0900 <i>wR</i> <sub>2</sub> = 0.1755	<i>R</i> <sub>1</sub> = 0.0695 <i>wR</i> <sub>2</sub> = 0.1648
Largest diff. peak/hole / e Å <sup>-3</sup>	1.67/-0.78	2.89/-2.08

Table S2 The summary of reported organic-inorganic isopolyoxoniobates based on {Nb<sub>6</sub>O<sub>19</sub>}.

Formulas	References
Na <sub>5</sub> {M(en)Nb <sub>6</sub> O <sub>19</sub> (H <sub>2</sub> O)}·17H <sub>2</sub> O [M = Co, Cr]	S6
K <sub>7</sub> {M(CO) <sub>3</sub> Nb <sub>6</sub> O <sub>19</sub> } [M = Mn, Re]	S7
<i>trans/cis</i> -K <sub>6</sub> {[M(CO) <sub>3</sub> ] <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> } [M = Mn, Re]	S7
{ <i>trans</i> -[Nb <sub>6</sub> O <sub>19</sub> ][Ni(taci)] <sub>2</sub> }	S8
{ <i>cis</i> -[H <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> ][Ni(taci)] <sub>2</sub> }	S8

---

Rb <sub>4</sub> [Cu(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>3</sub> [(Nb <sub>6</sub> O <sub>19</sub> H <sub>2</sub> ) <sub>2</sub> Cu(en) <sub>2</sub> ] <sub>2</sub> ·24H <sub>2</sub> O	S9
[Cu(en) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> [(Nb <sub>6</sub> O <sub>19</sub> H <sub>2</sub> )Cu(en) <sub>2</sub> ] <sub>2</sub> ·14H <sub>2</sub> O	S9
Rb <sub>2</sub> [Cu(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>4</sub> ][Cu(NH <sub>3</sub> ) <sub>4</sub> (H <sub>2</sub> O) <sub>2</sub> ] <sub>2</sub> {[Nb <sub>6</sub> O <sub>19</sub> ][Cu(NH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> ·6H <sub>2</sub> O	S9
{[Nb <sub>6</sub> O <sub>19</sub> ][Cu(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)] <sub>2</sub> [Cu(H <sub>2</sub> O) <sub>4</sub> ] <sub>2</sub> }□3H <sub>2</sub> O	S9
{[Nb <sub>6</sub> O <sub>19</sub> ][Cu(NH <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O)] <sub>2</sub> [Cu(H <sub>2</sub> O) <sub>4</sub> ] <sub>2</sub> }	S9
{Nb <sub>6</sub> O <sub>19</sub> [Cu(2,2'-bipy)] <sub>2</sub> [Cu(2,2'-bipy) <sub>2</sub> ] <sub>2</sub> }□19H <sub>2</sub> O	S10
K <sub>4</sub> - <i>trans</i> -{Nb <sub>6</sub> O <sub>19</sub> {Ru( <i>p</i> -cym)} <sub>2</sub> ·14H <sub>2</sub> O	S11
[Cu(dap) <sub>2</sub> ] <sub>3</sub> [H <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> ·6H <sub>2</sub> O	S12
Na[Cu(1,3-pda) <sub>2</sub> ] <sub>3</sub> [HNb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> ·3H <sub>2</sub> O	S13
{[Cu(1,3-pda) <sub>2</sub> ] <sub>3</sub> [HNb <sub>6</sub> O <sub>19</sub> ]}	S13
[Cu(en) <sub>2</sub> ] <sub>4</sub> {[Nb <sub>6</sub> O <sub>19</sub> H <sub>2</sub> ]K(H <sub>2</sub> O) <sub>5</sub> ] <sub>2</sub> ·(H <sub>2</sub> en)·17H <sub>2</sub> O	S14
[Cu(en) <sub>2</sub> ] <sub>2</sub> {[Cu(1,10-phen)][Cu(1,10-phen)(H <sub>2</sub> O)]Nb <sub>6</sub> O <sub>19</sub> }·10.5H <sub>2</sub> O	S15
[Cu(en) <sub>2</sub> ] <sub>2</sub> {[Cu(2,2'-bipy)][Cu(2,2'-bipy)(H <sub>2</sub> O)]Nb <sub>6</sub> O <sub>19</sub> }□9H <sub>2</sub> O	S15
[Cu(1,2-dap) <sub>2</sub> ] <sub>2</sub> {[Cu(2,2'-bipy)][Cu(2,2'-bipy)(H <sub>2</sub> O)]Nb <sub>6</sub> O <sub>19</sub> }·11H <sub>2</sub> O	S15
(H <sub>2</sub> en) <sub>2</sub> [Ni(en) <sub>3</sub> ][H <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> ·5.5H <sub>2</sub> O	S16
K <sub>8</sub> Na <sub>2</sub> {[Cu(en)(H <sub>2</sub> O)] <sub>2</sub> [HNb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> }·25H <sub>2</sub> O	S17
[Cu(1,3-dap) <sub>2</sub> (H <sub>2</sub> O)] <sub>2</sub> {[H <sub>6</sub> Nb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> Cu(1,3-dap) <sub>2</sub> }□4(1,3-dap)□20H <sub>2</sub> O	S18
[Cu(1,2-dap) <sub>2</sub> ]{[Cu(1,2-dap) <sub>2</sub> ][Nb <sub>6</sub> O <sub>19</sub> H <sub>2</sub> ]}□10H <sub>2</sub> O	S19
[Cu(1,3-dap) <sub>2</sub> ] <sub>2</sub> {[Cu(1,3-dap)] <sub>2</sub> [Nb <sub>6</sub> O <sub>19</sub> ]}□10H <sub>2</sub> O	S19
[Cu(en) <sub>2</sub> ] <sub>0.5</sub> {[Cu(en) <sub>2</sub> ][Nb <sub>6</sub> O <sub>19</sub> H <sub>3</sub> ]}·12H <sub>2</sub> O	S19
K <sub>6</sub> Na <sub>2</sub> [Co <sup>III</sup> H <sub>5</sub> (Nb <sub>6</sub> O <sub>19</sub> ) <sub>2</sub> ] <sub>2</sub> ·26.5H <sub>2</sub> O	S20
K <sub>4</sub> [(Cp*Rh) <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> ·20H <sub>2</sub> O	S21
Na <sub>8</sub> [H <sub>2</sub> {Cp*IrNb <sub>6</sub> O <sub>18</sub> }(O)] <sub>2</sub> ·47H <sub>2</sub> O	S22
Na <sub>4</sub> [ <i>trans</i> -{(C <sub>6</sub> H <sub>6</sub> )Ru} <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> ·14.125MeOH·2H <sub>2</sub> O	S23
K <sub>4</sub> [ <i>trans</i> -{Cp*Rh} <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> ·4MeOH·10H <sub>2</sub> O	S23
K <sub>4</sub> [ <i>trans</i> -{Cp*Ir} <sub>2</sub> Nb <sub>6</sub> O <sub>19</sub> ] <sub>2</sub> ·10MeOH·4H <sub>2</sub> O	S23
KNa[Co(en) <sub>3</sub> ] <sub>2</sub> [(HNb <sub>6</sub> O <sub>19</sub> )Co(en)] <sub>2</sub> ·30H <sub>2</sub> O	S24

---

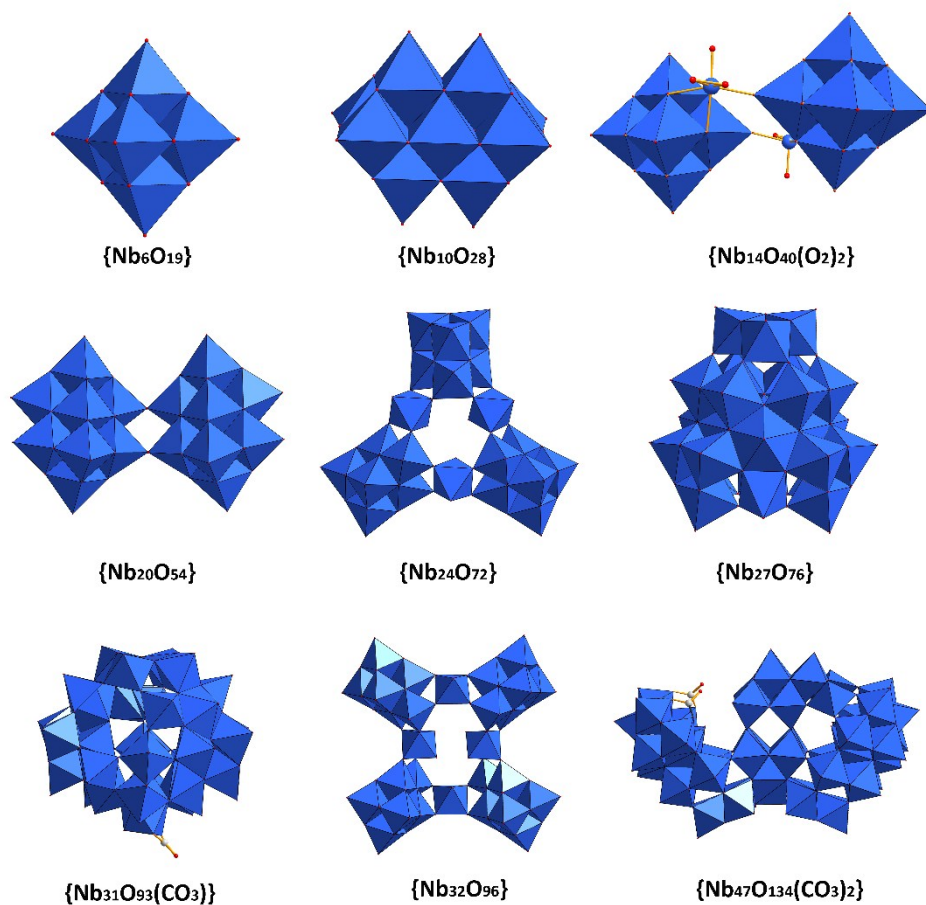


Fig. S1 Ball-and-stick/polyhedral representation of the reported building blocks.

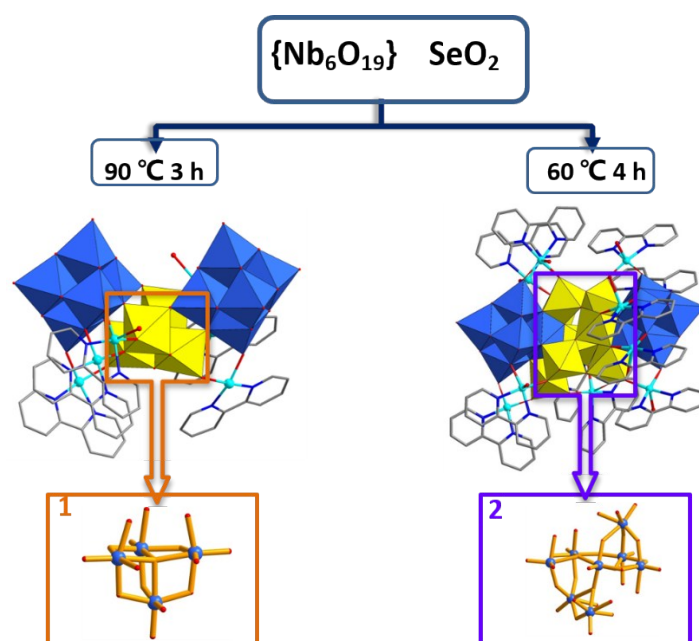


Fig. S2 Combined ball-and-stick/polyhedral representation of two compounds.

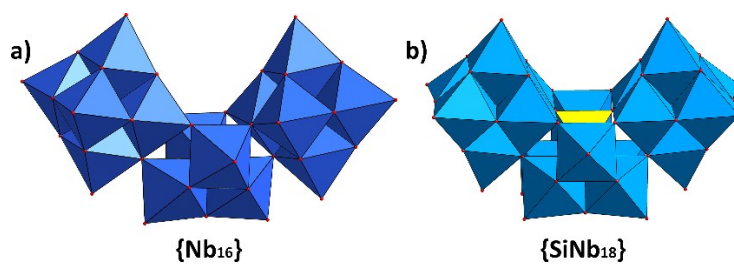


Fig. S3 View of the structures of a)  $\{Nb_{16}\}$  and b)  $\{SiNb_{18}\}$ .

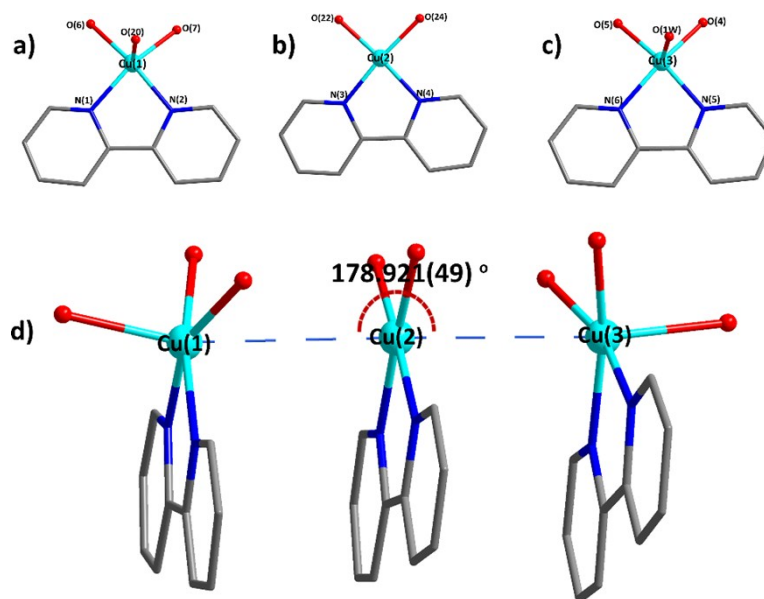


Fig. S4 a) The coordination geometric frameworks of the Cu(1) ion in compound **1**, b) Cu(2) ion and c) Cu(3) ion. d) Schematic of the line-type of three Cu ions.

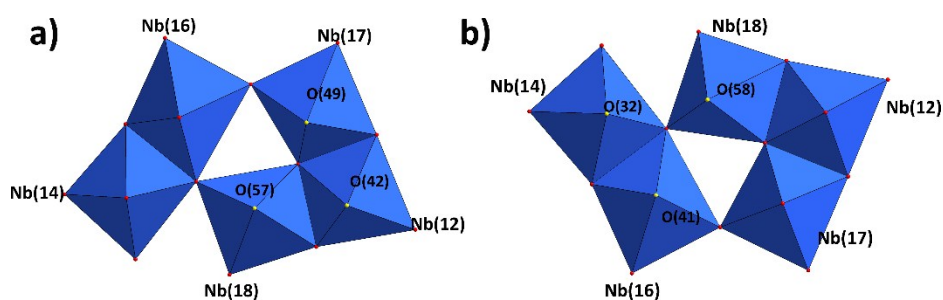


Fig. S5 The  $\{Nb_5O_{22}\}$  fragment in different sides. Nb(15) links to  $\{Nb_3\}$  fragment [Nb(17), Nb(18), Nb(12)] via O(49), O(57) and O(42), while Nb(10) links to  $\{Nb_3\}$  fragment [Nb(14), Nb(18), Nb(16)] via O(32), O(58) and O(41).



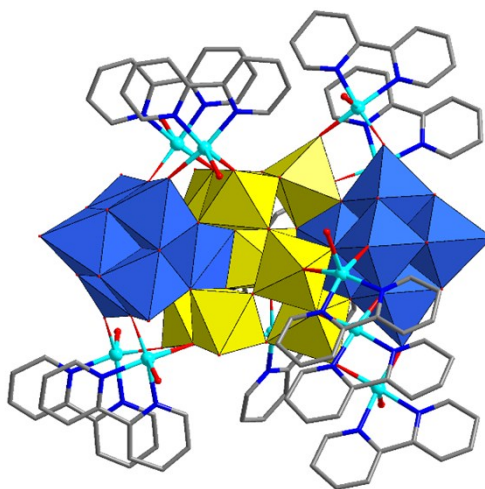


Fig. S6 Ball-and-stick/polyhedral representation of the polyoxoanion **2a**.

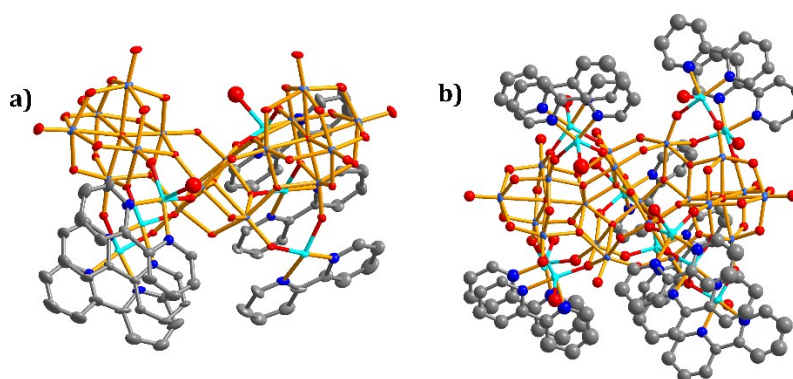


Fig. S7 Structural figures of polyoxoanions **1a** and **2a** with 30% probability ellipsoids.

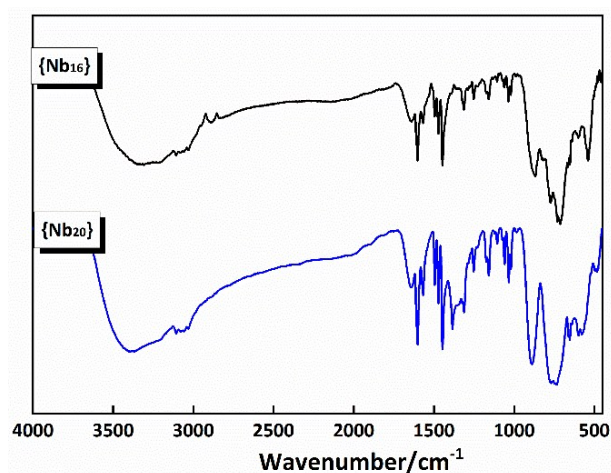


Fig. S8 The IR spectra of compounds **1** and **2** (abbreviate for {Nb<sub>16</sub>} and {Nb<sub>20</sub>}).

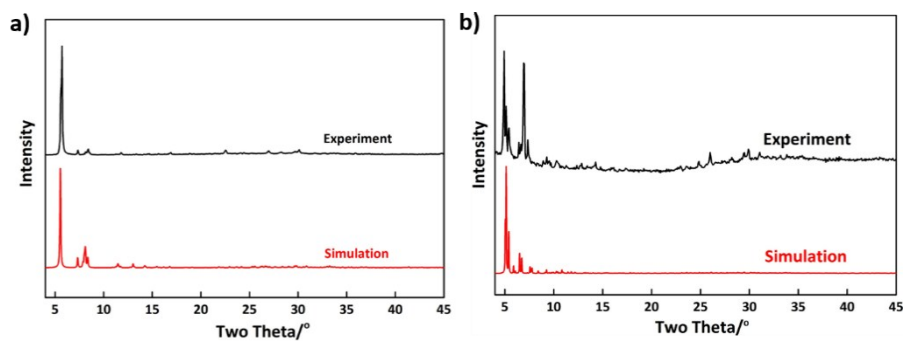


Fig. S9 The experiment and simulation of PXRD patterns of compounds **1** and **2**, respectively.

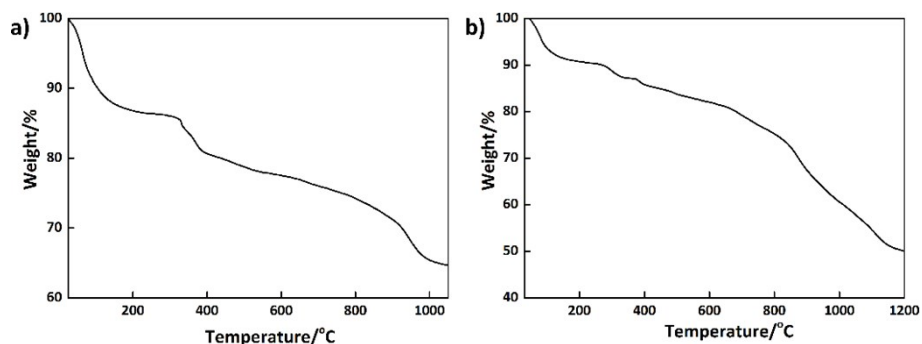


Fig. S10 TGA analyses for compounds **1** and **2**.

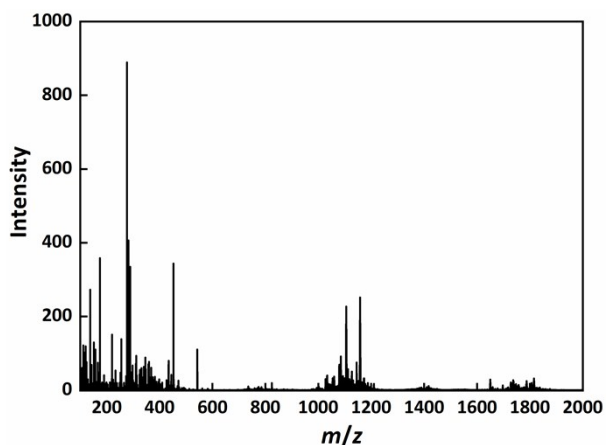


Fig. S11 Mass spectrometry peaks of compound **1** in water.

Table S3 Mass spectrometry peak assignments for compound **1**.

Entry	Identification	Charge	Cal. $m/z$	Exp. $m/z$
<b>1</b>	$\{K_3H_5Cu_3(C_{10}H_8N_2)_3(H_2O)_{33}(Nb_{16}O_{48})\}$	-2	1815.25	1815.33
<b>2</b>	$\{K_3H_5Cu_3(C_{10}H_8N_2)_3(H_2O)_{32}(Nb_{16}O_{48})\}$	-2	1806.24	1806.33
<b>3</b>	$\{K_2H_6Cu_3(C_{10}H_8N_2)_3(H_2O)_{32}(Nb_{16}O_{48})\}$	-2	1787.20	1787.35
<b>4</b>	$\{K_6H_2Cu_3(C_{10}H_8N_2)_3(H_2O)_{18}(Nb_{16}O_{48})\}$	-2	1737.27	1737.29
<b>5</b>	$\{K_6H_2Cu_3(C_{10}H_8N_2)_3(H_2O)_{17}(Nb_{16}O_{48})\}$	-2	1728.26	1728.29

6	$\{\text{KH}_9\text{Cu}_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_{31}(\text{Nb}_{16}\text{O}_{48})\}$	-2	1650.29	1650.23
7	$\{\text{K}_6\text{HCu}_{10}(\text{C}_{10}\text{H}_8\text{N}_2)_{10}(\text{H}_2\text{O})_8(\text{Nb}_{16}\text{O}_{48})_2\}$	-5	1417.17	1417.24
8	$\{\text{K}_5\text{H}_2\text{Cu}_{10}(\text{C}_{10}\text{H}_8\text{N}_2)_{10}(\text{H}_2\text{O})_8(\text{Nb}_{16}\text{O}_{48})_2\}$	-5	1409.58	1409.65
9	$\{\text{H}_7\text{Cu}_{10}(\text{C}_{10}\text{H}_8\text{N}_2)_{10}(\text{H}_2\text{O})_{13}(\text{Nb}_{16}\text{O}_{48})_2\}$	-5	1389.50	1389.63
10	$\{\text{K}_6\text{HCu}_3(\text{C}_{10}\text{H}_8\text{N}_2)_3(\text{H}_2\text{O})_{18}(\text{Nb}_{16}\text{O}_{48})\}$	-3	1157.85	1157.86
11	$\{\text{KH}_8\text{Cu}_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_{32}(\text{Nb}_{16}\text{O}_{48})\}$	-3	1105.86	1105.82
12	$\{\text{K}_7\text{H}_4\text{Cu}_1(\text{C}_{10}\text{H}_8\text{N}_2)_1(\text{H}_2\text{O})_{28}(\text{Nb}_{16}\text{O}_{48})\}$	-3	1085.45	1085.52
13	$\{\text{H}_4\text{Cu}_4(\text{C}_{10}\text{H}_8\text{N}_2)_4(\text{H}_2\text{O})_9(\text{Nb}_{16}\text{O}_{48})\}$	-4	824.89	824.88

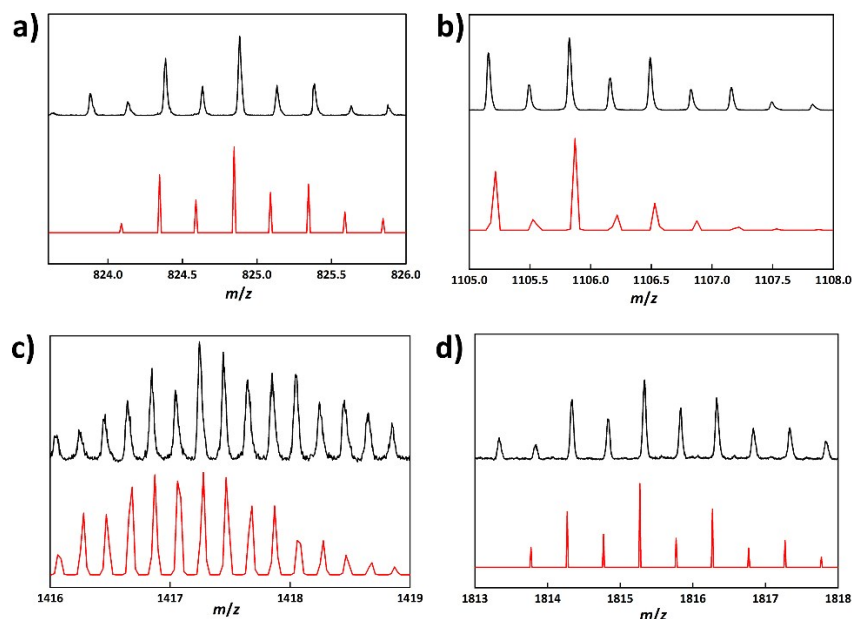


Fig. S12 The experimental and simulated peaks of selected mass spectrometry.

## References

- S1. M. Filowitz, R. K. C. Ho, W. G. Klemperer and W. Shum, *Inorg. Chem.*, 1979, **18**, 93.
- S2. Bruker, *SAINT.*, 2007, Bruker AXS Inc., Madison, Wisconsin, USA.
- S3. Bruker, *SADABS.*, 2001, Bruker AXS Inc., Madison, Wisconsin, USA.
- S4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.
- S5. G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3.
- S6. C. M. Flynn and G. D. Stucky, *Inorg. Chem.*, 1969, **8**, 178.
- S7. A. V. Besserguenev, M. H. Dickman and M. T. Pope, *Inorg. Chem.*, 2001, **40**, 2582.
- S8. K. Hegetschweiler, R. C. Finn, R. S. Rarig, J. Sander, S. Steinhauser, M. Wörle and J. Zubieta, *Inorg. Chim. Acta*, 2002, **337**, 39.
- S9. R. P. Bontchev, E. L. Venturini and M. Nyman, *Inorg. Chem.*, 2007, **46**, 4483.
- S10. J.-P. Wang, H.-Y. Niu and J.-Y. Niu, *Inorg. Chem. Commun.*, 2008, **11**, 63.

- S11. D. Laurencin, R. Thouvenot and K. Boubekeur, *Dalton Trans.*, 2007, **13**, 1334.
- S12. T. M. Anderson, M. A. Rodriguez, T. A. Stewart, J. N. Bixler, W. Xu, J. B. Parise and M. Nyman, *Eur. J. Inorg. Chem.*, 2008, 3286.
- S13. J. Wang, C. Yu, P. Ma and J. Niu, *J. Coord. Chem.*, 2009, **62**, 2299.
- S14. G. Guo, Y. Xu and C. Hu, *J. Coord. Chem.*, 2010, **63**, 3137.
- S15. J. Niu, X. Fu, J. Zhao, S. Li, P. Ma and J. Wang, *Cryst. Growth Des.*, 2010, **10**, 3110.
- S16. G. Chen, P. Ma, J. Wang and J. Niu, *J. Coord. Chem.*, 2010, **63**, 3753.
- S17. G. Chen, C. Wang, P. Ma, J. Wang and J. Niu, *J. Clust. Sci.*, 2010, **21**, 121.
- S18. G. Wang, P. Ma, F. Li and J. Wang, *J. Coord. Chem.*, 2011, **64**, 2718.
- S19. G. Guo, Y. Xu, B. Chen and C. Hu, *J. Coord. Chem.*, 2011, **64**, 1032.
- S20. P. T. Ma, G. Chen, G. Wang and J. P. Wang, *Russ. J. Coord. Chem.*, 2011, **37**, 772.
- S21. P. A. Abramov, M. N. Sokolov, A. V. Virovets, S. Floquet, M. Haouas, F. Taulelle, E. Cadot, C. Vicente and V. P. Fedin, *Dalton Trans.*, 2015, **44**, 2234.
- S22. P. A. Abramov, C. Vincent, N. B. Kompankov, A. L. Gushchin and M. N. Sokolov, *Eur. J. Inorg. Chem.*, 2016, 154.
- S23. P. A. Abramov, C. Vincent, N. B. Kompankov, J. A. Laricheva and M. N. Sokolov, *RSC Adv.*, 2016, **6**, 20240.
- S24. S. Zhao, Z. Liang, L. Song, P. Ma, D. Zhang and J. Wang, *Inorg. Chem. Commun.*, 2016, **73**, 187.