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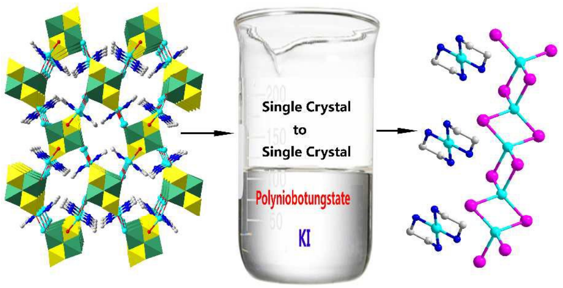
Lu Jin, Xin-Xiong Li, Dan Zhao, Hao-Hong Li and Shou-Tian Zheng*



The first transition-metal-bridged, polyniobotungstate-based three-dimensional framework constructed from lindqvist $[Nb_3W_3O_{19}]^{5-}$ polyoxoanions and mixed-valent copper ions has been made, which can undergo interesting solid-liquid reaction with KI solution to form a crystalline copper halide via a single-crystal-to-single-crystal process.

Journal Name

COMMUNICATION

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A Rare Three-Dimensional Polyniobotungstate-Based Framework and Its Structural Transformation in A Single-Crystal-to-Single-Crystal Process Induced by Iodide Ion

Lu Jin,[a] Xin-Xiong Li,[a] Dan Zhao,[b] Hao-Hong Li[a] and Shou-Tian Zheng*,[a]

The first transition-metal-bridged, polyniobotungstate-based 3D framework has been hydrothermally synthesized, which is constructed from bi-[Cu^{II}(en)$_2$(H$_2$O)]-decorating polyoxoanions [Nb$_3$W$_3$O$_{19}$]$^{5-}$ linked together by Cu^{I} ions. Interestingly, the 3D polyniobotungstate can undergo solid-liquid reaction with KI solution to generate a 1D copper halide of [Cu(en)$_2$][CuI$_2$]$_2$ in a single-crystal-to-single-crystal process.

Polyoxometalates (POMs) have received increasing interest due to their diverse structures and attractive applications in medicine, catalysis, and material science.[1] In the field of POMs, polyoxovanadates (POVs), polyoxomolybdates (POMos), and polyoxotungstates (POTs) have been studied extensively during the past two decades. In contrast, due to the lack of various soluble niobate salts, the design and synthesis of polyoxoniobates (PONs) and their derivatives are extremely challenging and thus remain largely undeveloped.[2] At present, the majority of reported PONs are the inorganic, discrete structures such as [Nb$_{10}$O$_{28}$]$^{6-}$, [Nb$_7$O$_{22}$]$^{9-}$, [Nb$_{20}$O$_{54}$]$^{8-}$, [H$_9$Nb$_{24}$O$_{72}$]$^{15-}$, [H$_{10}$Nb$_{31}$O$_{93}$(CO$_3$)]$^{23-}$, [HNb$_{27}$O$_{76}$]$^{16-}$, and {[Ti$_2$O$_2$][SiNb$_{12}$O$_{40}$]}$^{12-}$.[3-7] Because of the high charge/surface ratio of PONs and their potential applications in nuclear-waste treatment and virology,[8] striving to explore the synthetic methods for creating various PONs is of great interest.

It is expected that the introduction of organic species into PONs to make extended (1D, 2D, 3D) inorganic-organic hybrid PONs can significantly expand the study on the structural chemistry of PONs. During the past two decades, the construction of extended organic-inorganic POMs has been a research hotspot in the field of POMs owing to their fascinating structural features and widely potential applications.[9] Up to now, a large number of extended POMs based on POVs, POMos, and POTs as building blocks have been known, for instances, 1D chains [Co(en)$_3$][Co(en)$_2$As$_8$V$_{14}$O$_{42}$(H$_2$O)]·16H$_2$O, [GeMo$^{V}_8$Mo$^{VI}_4$O$_{36}$(μ$_2$-OH)$_4${Ni(pda)(H$_2$O)}$_2${Ni(pda)}{Ni(pda)(bpe)}(bpe)$_{0.5}$]$_n$, and (C$_2$H$_8$N)$_8$Na$_{10}$[{Sn(CH$_3$)$_2$}$_{10}${Sn(CH$_3$)$_2$(H$_2$O)}$_6$Se$_{11}$W$_{56}$O$_{211}$(OH)$_8$]·105H$_2$O,[10] 2D layers [Zn$_2$(en)$_5$]{[Zn(en)$_2$][(bpe)HZn$_2$As$_8$V$_{12}$O$_{40}$(H$_2$O)]$_2$}·7H$_2$O, [GeMo$_{12}$O$_{36}$(μ$_2$-OH)$_4${Ni(pda)}$_2${Ni(pda)(bpy)$_{0.5}$}{Ni(pda)(bpy)}]$_n$·nH$_2$O, and [P$_2$Mn$_4$W$_{18}$O$_{68}$]$^{10-}$,[11] 3D frameworks {[Cd$_3$(μdien)$_2$(Hdien)$_2$(H$_2$O)$_2$]Ge$_4$V$_{16}$O$_{42}$(OH)$_4$(H$_2$O)}·2H$_2$O, H$_4$[α-GeW$_{10}$Mo$^{V}_2$O$_{40}$]$_2$[CuK$_2$(DMF)$_6$][K$_4$(DMF)$_6$], and H$_2$K$_2$[(Hpic)(H$_2$O)$_5$Nd]$_2$[(H$_2$O)$_4$NdSiW$_{11}$O$_{39}$]$_2$·36H$_2$O,[12] and so on. While, the known extended organic-inorganic hybrid PONs, especially for these high-dimensional (3D) PONs, are very rare.

On the other hand, it is also expected that the introduction of Nb element into skeletons of the other POMs to create Nb-containing POMs can largely enrich the study on the structural chemistry of PONs. In recent years, Nb element has been successfully incorporated into the skeletons of POTs to form a lot of polyniobotungstates. Typical examples include [Si$_2$W$_{18}$Nb$_6$O$_{77}$]$^{8-}$,[13] [Nb$_4$O$_6$(*a*-Nb$_3$SiW$_9$O$_4$O)$_4$]$^{20-}$,[14] [P$_2$W$_{17}$(NbO$_2$)O$_{61}$]$^{7-}$,[15] [H$_{15}$Ge$_2$W$_{18}$Nb$_8$O$_{88}$]$^{5-}$,[16] [P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{9-}$,[17] [Nb$_4$O$_6$(SiW$_9$Nb$_3$O$_{40}$)$_4$]$^{22-}$,[18] [H$_{24}${Nb$_4$O$_6$(OH)$_4$}{Nb$_6$P$_2$W$_{12}$O$_{61}$}$_4$]$^{12-}$,[19] [H$_{13}${Nb$_6$(O$_2$)$_4$P$_2$W$_{12}$O$_{57}$}$_2$]$^{7-}$, [H$_{14}${P$_2$W$_{12}$Nb$_7$O$_{63}$(H$_2$O)$_2$}$_4${Nb$_4$O$_4$(OH)$_6$}]$^{16-}$,[20] {[Cu(en)$_2$(H$_2$O)]$_2$[Nb$_2$W$_4$O$_{19}$]·2H$_2$O}, {[Cu(NH$_3$)$_4$(H$_2$O)]$_2$[Nb$_2$W$_4$O$_{19}$]·8H$_2$O}.[21] Nevertheless, it can be found that most of these known polyniobotungstates are inorganic and low dimensional (0D or 1D) structures. To date, only some 2D inorganic-organic hybrid polyniobotungstate-based solids such as [Cu(dap)$_2$]$_3$[Nb$_4$W$_2$O$_{19}$]·7H$_2$O, [Cu(dap)$_2$]$_3$[H$_2$Nb$_6$O$_{19}$]·6H$_2$O, [Cu(dap)$_2$]$_3$[Nb$_3$W$_3$O$_{19}$]·Cl·6H$_2$O, and [Cu(en)$_2$]$_3$[Nb$_4$W$_2$O$_{19}$]·6H$_2$O have been known.[21]

Therefore, we would like to explore the assembly of Nb element with W element in the presence of organic species with the aim of obtaining novel inorganic-organic hybrid polyniobotungstate-based materials. Herein, we represent the first 3D inorganic-organic hybrid polyniobotungstate-based compound {[Cu(en)$_2$(H$_2$O)]$_2$[Nb$_3$W$_3$O$_{19}$][Cu]$_2$}·OH (**1**, en = ethylenediamine), which is built by Lindqvist-type [Nb$_3$W$_3$O$_{19}$]$^{5-}$ clusters decorated and bridged by bivalent copper complexes [Cu(en)$_2$(H$_2$O)]$^{2+}$ and monovalent Cu^{+} ions, respectively. Interestingly, upon crystal **1** is soaked in a solution of

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†Electronic Supplementary Information (ESI) available: Synthetic details, structural figures, and spectrum data. CCDC -1433428. See DOI: 10.1039/x0xx00000x

potassium iodide, it can interact with iodide ions via solid-liquid reaction and undergo structural transformation from a 3D PON framework to a 1D copper halide chain in a single-crystal-to-single-crystal (SCSC) process.

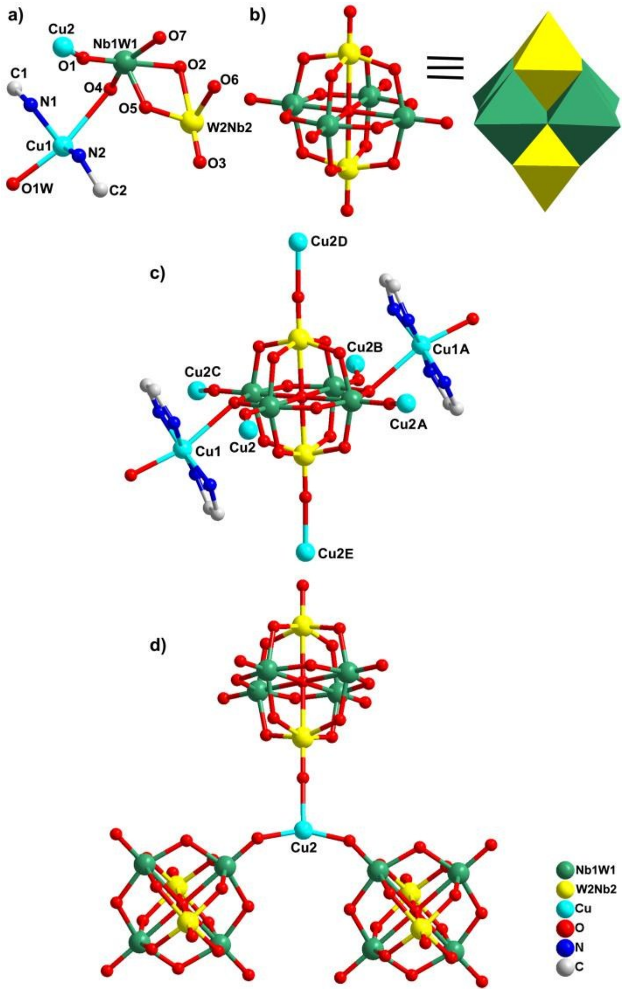

Figure 1. a) The asymmetric unit of **1**. b) Polyoxoanion $[Nb_3W_3O_{19}]^{5-}$ in **1**. c) Coordination mode of polyoxoanion $[Nb_3W_3O_{19}]^{5-}$ with copper ions. Symmetry codes: A: 1-x, -y, z; B: 1-x, -y, -1+z; C: x, y, -1+z; D: 1-x, -y, z; E: -0.5+x, 0.5-y, 0.5-z. d) Coordination mode of Cu^+ ion with adjacent polyoxoanions.

Single crystal structural analysis reveals that compound **1** crystallizes in the orthorhombic space group *Pnnm* and its structure represents some interesting characteristics.[22] Firstly, compound **1** consists of relatively rare lindqvist-type polyniobotungstate clusters $[Nb_3W_3O_{19}]^{5-}$ with unique Nb/W disordered distribution. As shown in Figures 1a and S1, the asymmetric unit of **1** contains two crystallographically independent metal sites simultaneously occupied by both Nb and W, which are initially refined freely to give W/Nb ratios of 0.405:0.595 and 0.699:0.301, followed by fixing them to 0.40/0.60 (marked as Nb1W1 in Fig 1a) and 0.70/0.30 (marked as W2Nb2), respectively. Since each lindqvist-type polyniobo-tungstate polyoxoanion in **1** has four Nb1W1 sites and two W2Nb2 sites (Fig 1b), the whole ratio of W/Nb in each polyoxoanion is exactly 1:1 and thus the formula of the anion is written as $[Nb_3W_3O_{19}]^{5-}$. The whole W/Nb ratio in **1** is further confirmed by EDS analyses (Table S1). To our knowledge, before our work, compound $[Cu(dap)_2]_3[Nb_3W_3O_{19}]\cdot Cl\cdot 6H_2O$ is the only known $\{Nb_3W_3O_{19}\}$-based inorganic-organic hybrid compound which has been structurally characterized by single-crystal X-ray diffractions. The disordered Nb/W sites in **1** are different from these in $[Cu(dap)_2]_3[Nb_3W_3O_{19}]\cdot Cl\cdot 6H_2O$ where all mixed W/Nb sites have identical W/Nb ratio of 0.5:0.5.[21] In $[Nb_3W_3O_{19}]^{5-}$ of **1**, all Nb1W1 centers have an octahedral environment with Nb1W1-O bond distances of 1.780(12) Å for the terminal oxygen atoms, 1.960(9) – 1.976(8) Å for μ_2-O atoms, and 2.349(1) Å for μ_4-O atom. Compared with the Nb1W1 centers, all W2Nb2 centers have the same octahedral environment but with shorter W2Nb2-O bond distances of 1.706(19) Å for the terminal oxygen atoms, 1.952(10) – 1.958(10) Å for μ_2-O atoms, and 2.341(1) Å for μ_4-O atom. The Nb-O bonds are longer than the W-O bonds, and thus the higher Nb/W ratio will lead to longer bond length for the mixed Nb/W metal sites. So, the bond length differences between Nb1W1-O and W2Nb2-O bonds are consistent with their W/Nb ratios determined by X-ray diffractions.

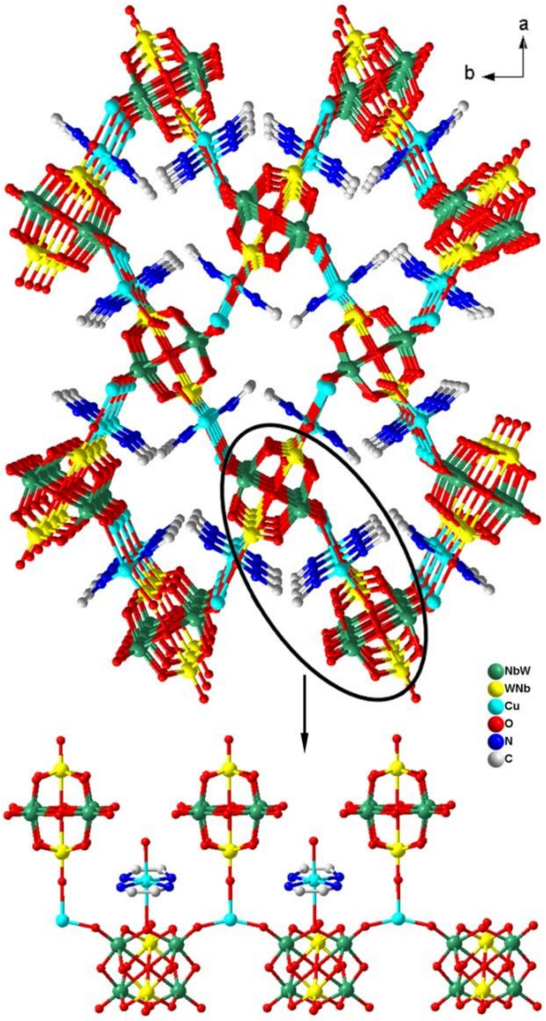

Figure 2. View of 3D structure of **1**.

The second interesting structural feature of **1** is that each polyoxoanion $[Nb_3W_3O_{19}]^{5-}$ acts as an octadentate ligand bonding to eight copper ions with two kinds of valences. As shown in Figure 1b, the eight copper ions can be divided into two groups according to their different valences, coordination configurations, and roles they play. One group includes the bivalent Cu1 ion and its symmetry equivalent ion Cu1A, and another group includes the monovalent Cu2 ion and its symmetry equivalent ions Cu2A, Cu2B, Cu2C, Cu2D, and Cu2E. Each bivalent Cu^{2+} ion (Cu1), acting as a decorating role, is octahedrally coordinated by four equatorial N donors from two chelating en ligands, one axial oxygen atom from polyoxoanion $[Nb_3W_3O_{19}]^{5-}$, and one axial H_2O molecule. The axial Cu-O bonds (Cu-O: 2.787(20) Å, Cu-H_2O: 2.318(18) Å) are considerably longer than the equatorial Cu-N bonds (Cu-N: 2.004(14) – 2.022(14) Å) owing to Jahn-Teller distortion. While, each monovalent Cu^+ ion (Cu2) plays as bridging ion bonding to three terminal oxo atoms from three polyoxoanions $[Nb_3W_3O_{19}]^{5-}$ to give rise to a trigonal planar configuration with Cu-O distances in the range of 1.929(12) – 2.220(20) Å. Bond valence sum (Σ_s) calculations show the oxidation states of Cu1 and Cu2 ions are +2 (Σ_s = 1.69) and +1 (Σ_s = 0.99), respectively,[23] which match with their coordination geometries.

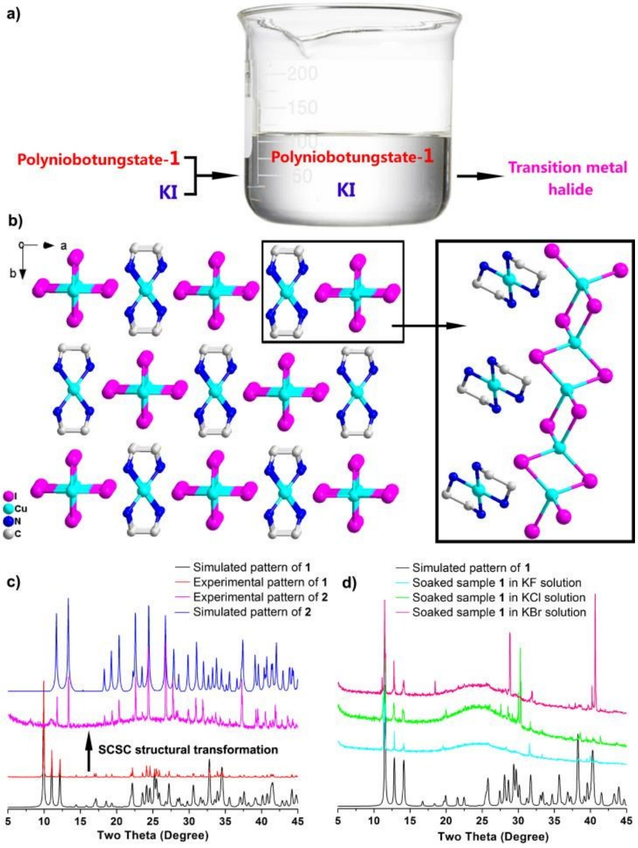

Figure 3. a) A illustration of solid-liquid reaction between **1** and KI solution. b) View of structure of **2**. c) PXRD patterns of **1** and **2**. d) PXRD patterns of samples of **1** soaked in KF, KCl, and KBr solutions for 45 days.

The third structural feature is that the structure **1** represents the first transition-metal-bridged, polyniobotungstate-based 3D inorganic-organic hybrid framework, which can be described as follows: each polyoxoanion $[Nb_3W_3O_{19}]^{5-}$ is decorated by two $[Cu(en)_2(H_2O)]^{2+}$ complexes (Cu1) to form an inorganic-organic hybrid bi-copper supported polyoxoanion as secondary building unit (SBU). Further, every SBU is linked to six Cu^+ ions (Cu2) and each Cu^+ ion bridges three SBUs, giving rise to a 3,6-connected rtl-type 3D structure (Fig 2, S2).

Finally, an interesting phenomenon is that the polyniobotungstate-based structure **1** can undergo a unique SCSC structural transformation via solid-liquid reaction with I^- ions to yield a copper halide chain (Fig 3). To begin with, the phase purity of **1** was confirmed by PXRD measurement (Fig 3c). When a sample of 33 mg (ca. 0.02 mmol) compound **1** was soaked in a 4ml of 0.4 mM KI solution, the solution color slowly changed from original colorless to final violet after six days. Meanwhile, the purple blue crystals **1** were turned into new claybank crystals. Single crystal X-ray diffractions showed this new crystal has the same unit cell as the reported copper halide $[Cu^{II}(en)_2][Cu^{I}I_2]_2$ (denoted here as **2**) made up of 1D copper-iodine chains $[CuI_2]^-$ with copper complexes $[Cu(en)_2]^{2+}$ as charge compensation (Fig 3b).[24] Obviously, the structural feature of the coexistence of both Cu^{2+} and Cu^+ ions in **1** provides the possibility to undergo the structural transformation. The phase purity of the obtained claybank crystals of **2** was confirmed by the PXRD pattern in comparison with the simulated single-crystal data of **2** (Fig 3c), revealing that **1** can completely change to **2** after 6 days. While, differing from its sensibility to I^- ion, compound **1** is insensitive to the other halide ions. As shown in Figure 3d, even as-synthesized samples of **1** were soaked in 0.4 mM KF, KCl, and KBr solutions for 45 days, the sharp PXRD peaks in the low-angle region of **1** still can be clearly observed in the PXRD patterns of soaked samples. These results indicate compound **1** has capability of sensitive response to I^- ion.

In summary, a rare 3D transition-metal-bridged, polyniobotungstate-based organic-inorganic hybrid framework **1** has been hydrothermally created by the assembly of niobate salt with tungstate salt in the presences of copper cations and organoamines. In **1**, the SBU $[Nb_3W_3O_{19}]^{5-}$ is found to have a unique Nb/W disordered distribution, which is decorated by bivalent copper complexes $[Cu(en)_2]^{2+}$ and further connected to adjacent ones by monovalent Cu^+ ions to generate a rtl-type 3D framework. The incorporation of both Cu^{2+} and Cu^+ ions endows **1** with an interesting property to react with I^- solution to form a new phase in a SCSC process accompanying with color changes of both crystals and I^- solutions before and after reaction, which indicates that compound **1** has a potential capability of sensitive response to I^- ions.

Acknowledgements

The work was funded by the National Natural Science Foundation of China (No. 21371033 and 21303018).

Notes and references

1 (a) H. N. Miras, J. Yan, D. L. Long, L. Cronin, *Chem. Soc. Rev,* 2012, **41**, 7403; (b) M. Nyman, P. C. Burns, *Chem. Soc. Rev*, 2012, **41**, 7354; (c) S. T. Zheng, G. Y. Yang, *Chem. Soc. Rev*, 2012, **41**, 7623; (d) D. Y. Du, J. S. Qin, S. L. Li, Z. M. Su, Y. Q. Lan, *Chem. Soc. Rev,* 2014, **43**, 4615.

2 (a) M. Nyman, *Dalton Trans*, 2011, **40**, 8049, (b) P. Huang, C. Qin, Z. M. Su, Y. Xing, X. L. Wang, K. Z. Shao, Y. Q. Lan, E. B. Wang, *J. Am. Chem. Soc*, 2012, **134**, 14004; (c) J. H. Son, J. Wang, F. E. Osterloh, P. Yub, W. H. Casey, *Chem. Commun,* 2014, **50**, 836.

3 E. J. Graeber, B. Morosin, *Acta Crystallogr*, 1977, **B33**, 2137.

4 M. Nyman, F. Bonhomme, T. M. Alam, M. A. Rodriguez, B. R. Cherry, J. L. Krumhansl, T. M. Nenoff, A. M. Sattler, *Science*, 2002, **297**, 996.

5 M. Maekawa, Y. Ozawa, A. Yagasaki, *Inorg. Chem*, 2006, **45**, 9608.

6 R. P. Bontchev, M. Nyman, *Angew. Chem. Int. Ed*, 2006, **118**, 6822.

7 J. Niu, P. Ma, H. Niu, J. Li, J. Zhao, Y. Song, J. Wang, *Chem. Eur. J*, 2007, **13**, 8739

8 (a) F. Bonhomme, J. P. Larentzos, T. M. Alam, E. J. Maginn, M. Nyman, *Inorg. Chem*, 2005, **44**, 1774; (b) C. A. Ohlin, E. M. Villa, J. C. Fettinger, W. H. Casey, *Angew. Chem. Int. Ed*, 2008, **47**, 5634.

9 (a) F. Li, L. Xu, *Dalton.Trans*, 2011, **40**, 4024; (b) B. Nohra, H. E. Moll, L. M. R. Albelo, P. Mialane, J. Marrot, C. Mellot-Draznieks, M. O'Keeffe, R. N. Biboum, J. Lemaire, B. Keita, L. Nadjo, A. Dolbecq, *J. Am. Chem. Soc*, 2011, **133**, 13363; (c) J. Zhou, J. W. Zhao, Q. Wei, J. Zhang, G. Y. Yang, *J. Am. Chem. Soc*, 2014, **136**, 5065; (d) H. Chen, Z. B. Yu, Z. Bacsik, H. Zhao, Q. Yao, J. Sun, *Angew. Chem. Int. Ed*, 2014, **53**, 3608.

10 (a) Y. F. Qi, Y. G. Li, E. B. Wang, Z. M. Zhang, S. Chang, *Dalton Trans*, **2008**, 2335; (b) W. J. Wang, L. Xu, G. G. Gao, L. Liu, X. Z. Liu, *CrystEngComm*, 2009, **11**, 2488; (c) W. C. Chen, C. Qin, Y. G. Li, H. Y. Zang, K. Z. Shao, Z. M. Su, E. B. Wang, H. S. Liu, *Chem. Commun*, 2015, **51**, 2433.

11 (a) Y. F. Qi, Y. G. Li, C. Qin, E. B. Wang, H. Jin, D. R. Xiao, X. L. Wang, S. Chang, *Inorg. Chem*, 2007, **46**, 3217; (b) C. Ritchie, E. M. Burkholder, D. L. Long, D. Adam, P. Kögerlerb, L. Cronin, *Chem. Commun*.,**2007**,468.

12 (a) J. Zhou, J. Zhang, W. H. Fang, G. Y. Yang, *Chem. Eur. J,* 2010, **16**, 13253; (b) Y. C. Wang, L. Xu, N. Jiang, L. L. Zhao, F. Y. Li, X. Z. Liu, *CrystEngComm*, 2011, **13**, 410; (c) H. Y. An, H. Zhang, Z. F. Chen, Y. G. Li, X. Liu, H. Chen, *Dalton Trans*, 2012, **41**, 8390.

13 R. G. Finke, M. W. Droege, *J. Am. Chem. Soc*, 1984, **106**, 1211.

14 G. S. Kim, H. d. Zeng, D. V. Derveer, C. L. Hill, *Angew. Chem., Int. Ed*, 1999, **38**, 3205.

15 D. A. Judd, J. H. Nettles, N. Nevins, J. P. Snyder, D. C. Liotta, J. Tang, J. Ermolieff, R. F. Schinazi, and C. L. Hill, *J. Am. Chem. Soc*, 2001, **123**, 886.

16 J. Li, S. X. Liu, C. C. Li, F. J. Ma, D. D. Liang, W. Zhang, R. K. Tan, Y. Y. Zhang, and L. Xu, *Chem. Eur. J*, 2010, **16**, 13435.

17 C. C. Li, S. X. Liu, S. J. Li, Y. Yang, H. Y. Jin, F. J. Ma, *Eur. J. Inorg. Chem*, **2012**, 3229.

18 Z. X. Yang, P. Huang, L. Zhao, M. Zhang, Y. T. Zhang, Z. M. Su, *Inorg. Chem. Comm*, 2014, **44**, 195.

19 D. D. Zhang, Z. J. Liang, S. Q. Xie, P. T. Ma, C. Zhang, J. P. Wang, J. Y. Niu, *Inorg. Chem*, 2014, **53**, 9917.

20 D. Zhang, C. Zhang, P. T. Ma, B. S. Bassil, R. Al-Oweini, U. Kortz, J. P. Wang, and J. Y.Niu, *Inorg. Chem. Front*, 2015, **2**, 254.

21 T. M. Anderson, M. A. Rodriguez, T. A. Stewart, J. N. Bixler, W. Q. Xu, J. B. Parise, M. Nyman, *Eur. J. Inorg. Chem*, **2008**, 3286.

22 Crystal data of **1**: $C_8H_{37}Cu_4N_8Nb_3O_{22}W_3$, M_r = 1681.90, Orthorhombic, *Pnnm*, a = 11.2042(13) Å, b = 14.7102(17) Å, c = 9.5638(11) Å, $\alpha = \beta = \gamma = 90$ °, V = 1576.3(3) Å^3, Z = 2, ρ_{calcd} = 3.554 g cm^{-3}, μ = 14.680 mm^{-1}, *F(000)* = 1556. A tatol of 5807 reflections were collected, 1477 of which were unique (R_{int} = 0.0149). $R_1(wR_2)$ = 0.0506 (0.1317) for 118 parameters and 1470 reflections ($I > 2\sigma(I)$). CCDC-1433428 contains the supplementary crystallographic data for this paper.

23 N. E. BRESE, M. O'KEEFFE， *Acta Cryst,* 1991, **B47**, 192.

24 L. Fotouhi, S. Dehghanpour, M. M. Heravi, M. D. Ardakani, *Molecules,* 2007, **12**, 1410.