Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

An Unprecedented Organic-Inorganic Hybrid Based on the first $\{Nb_{10}V_4O_{40}(OH)_2\}^{12-}$ Clusters and Copper Cations†‡

Peng Huang, Chao Qin, Xin-Long Wang*, Chun-Yi Sun, Guang-Sheng Yang, Kui-Zhan Shao, Yan-Qing Jiao, Kun Zhou and Zhong-Min Su*

Institute of Functional Material Chemistry, Key Lab of Polyoxometalate, Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, 130024 Jilin, People's Republic of China. *Fax: +86-431-85684009; Tel: +86-431-85099108. E-mail: zmsu@nenu.edu.cn.*

1. Materials and Methods

All the chemicals were obtained from commercial sources, and were used without further purification. Elemental analyses (C, H and N) were measured on a Perkin-Elmer 2400 CHN elemental analyzer; Nb, V and Cu were determined with a Plasma-SPEC(I) ICP atomic emission spectrometer. IR spectrum was performed in the range 4000–400 cm^{-1} using KBr pellets on an Alpha Centaurt FT/IR spectrophotometer. Powder X-ray diffraction measurement was recorded radiation ranging from 5 to 50º at room temperature on a Siemens D5005 diffractometer with Cu–Kα (λ = 1.5418 Å). Thermogravimetric analysis (TGA) of the samples was performed using a Perkin-Elmer TG-7 analyzer heated from room temperature to 900 ºC under nitrogen at the heating rate of 5 °C·min^{-1}.

2. Synthesis

Syntheses of **1**: $K_7HNb_6O_{19}\cdot 13H_2O$ was prepared according to the literature method[1] and identified by IR spectra. 1,10–phenanthroline (0.099 g, 0.50 mmol) was added to the solution of $Cu(Ac)_2\cdot 3H_2O$ (0.242 g, 1.00 mmol) in water (10 mL) under stirring. Then the resulting blue solution was added dropwise to the solution of $K_7HNb_6O_{19}\cdot 13H_2O$ (1.370 g, 1.00 mmol) and $NaVO_3\cdot 2H_2O$ (0.3159 g, 2.00 mmol) in water (80 mL) under stirring. Subsequently, the mixture was adjusted to pH 11.2 using NaOH (1 $molL^{-1}$) solution, condensed to 50 mL at 58 □ for 8 h, filtered and then transferred to a straight glass tube. Over a period of 6 weeks, block-shaped Light-blue single crystals for X-ray crystallography were obtained, washed with distilled water and then air-dried to give **1** in 57% yield (based on $K_7HNb_6O_{19}\cdot 13H_2O$). Elemental analysis: Anal. Calc.: H 2.01; Nb 27.00; V 5.92; Cu 11.08; C 25.11; N 4.88. Found: H 1.92; Nb 27.53; V 5.88; Cu 11.76; C 25.04; N 5.21%.

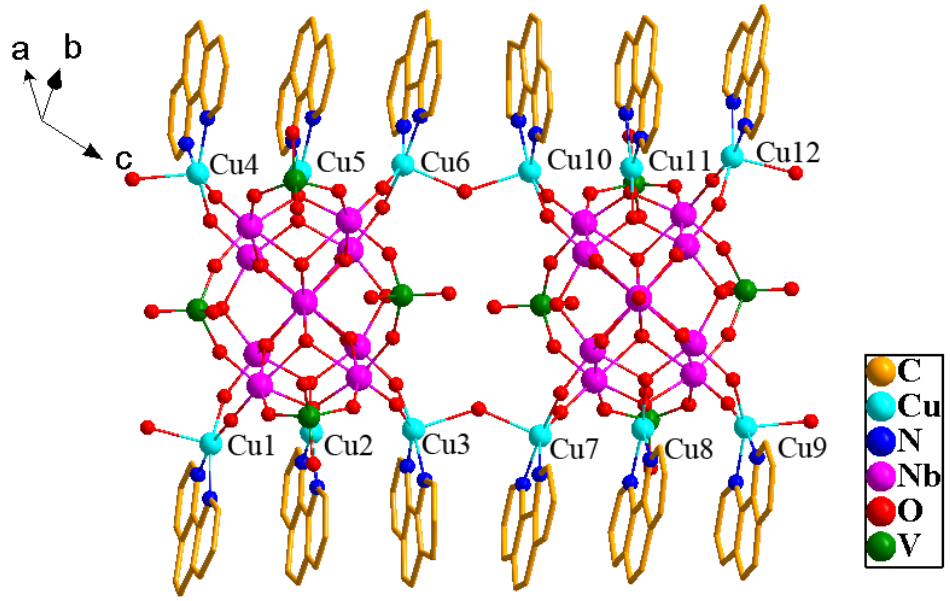

Fig. S1. Ball-and-stick representations of the **1**.

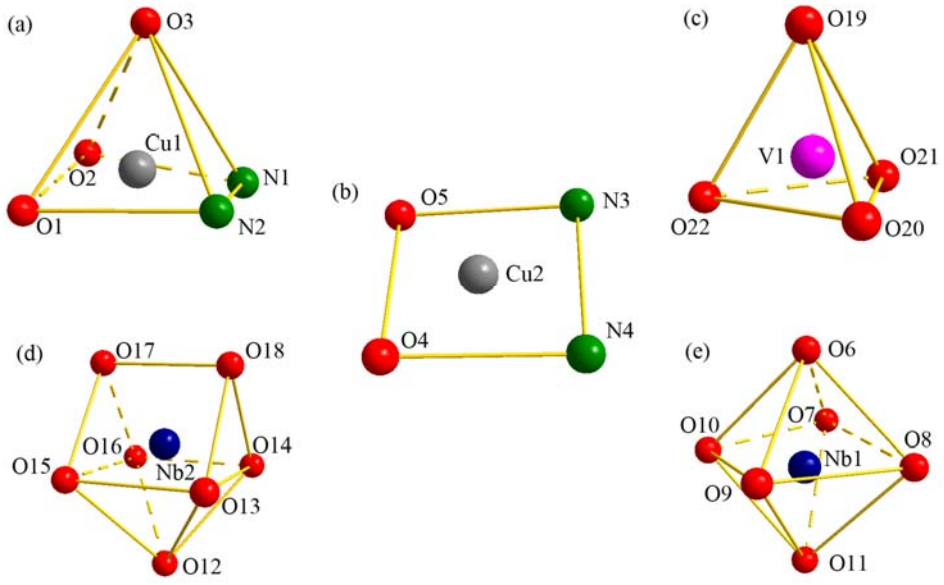

Fig. S2. The coordination geometric frameworks of the Cu^{2+}(1), Cu^{2+}(2), V^{5+}(1), Nb^{5+}(1) and Nb^{5+}(2).

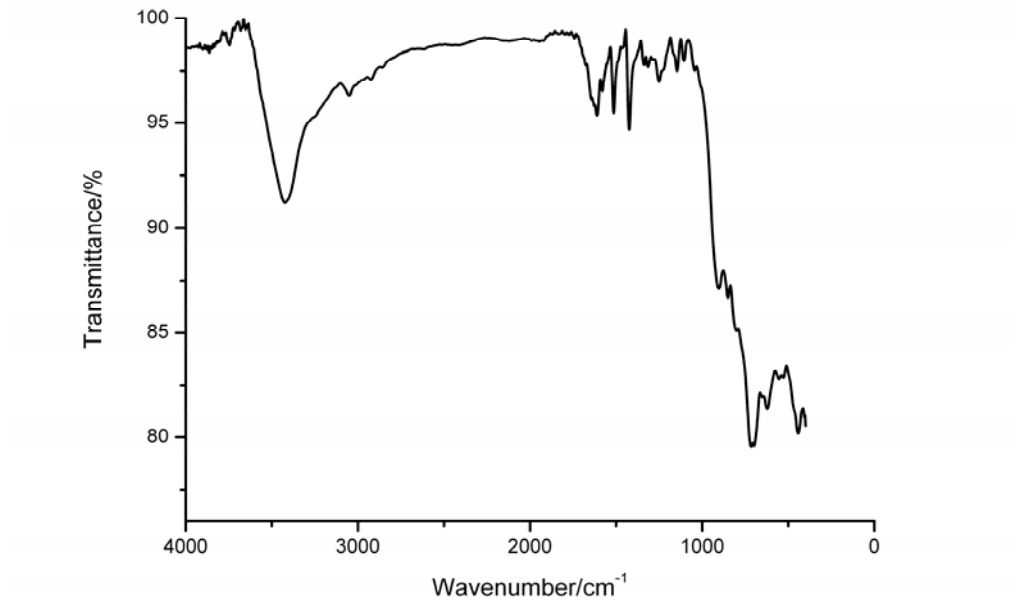

Fig. S3. The IR spectrum of **1**.

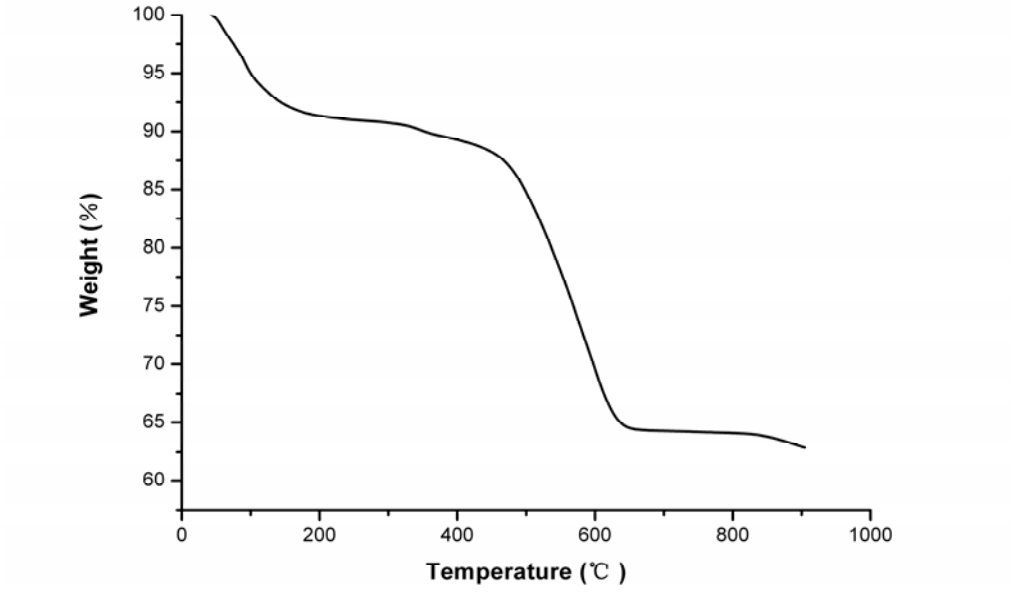

Fig. S4. The TGA curve of **1**.

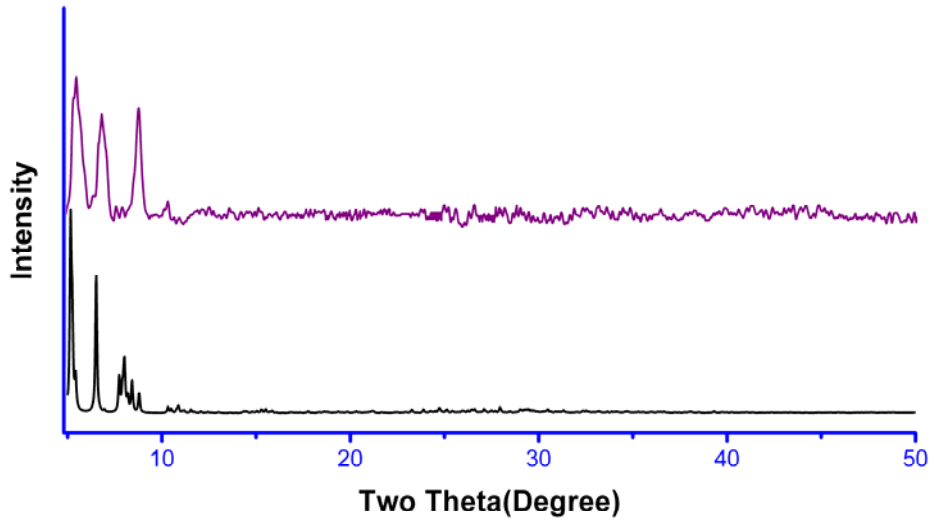

Fig. S5. The XRPD pattern (top) and simulated pattern (bottom) of **1**.

References

1 M. Filowitz, R. K. C. Ho, W. G. Klemperer, W. Shum, *Inorg. Chem.,* 1979, **18**, 93.