Organic functionalization of polyoxometalate in aqueous solution: Self-assembly of a new building block of {VM0₆O₂₅} with triethanolamine

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1. Materials and measurements

All chemicals were commercially purchased and used without further purification. For single crystal structure determination, Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer; metal elemental analyses were determined by a Leaman inductively coupled plasma (ICP) spectrometer. Infrared spectra of solid samples were obtained on a BRUKER Vertex 70 FTIR spectrometer in the 400–4000 cm-1 region with a KBr pellet. Powder X-ray diffraction measurement was recorded radiation ranging from 5 to 50° at room temperature on a Siemens D5005 diffractometer with Cu-K α ($\lambda = 1.5418$ Å). Thermogravimetric analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N₂ with a heating rate of 5°C min⁻¹.UV electronic spectra were obtained on a Varian Cary 50 Conc UV-vis spectrophotometer. Magnetic susceptibility data were recorded using a Quantum Design SQUID MPMS XL-5 magnetometer. Variable temperature susceptibility measurements were carried out in the temperature range of 2–300 K at a magnetic field of 1000 Oe on polycrystalline samples. The experimental susceptibilities were corrected for the Pascal's constants.

Synthesis. Compound 1 was synthesized by the mixture of NaVO₃·2H₂O (0.158 g, 1

mmol), Na₂MoO₄·2H₂O (0.968 g, 4 mmol), N(CH₂CH₂OH)₃ (1.283 g, 8.6 mmol) in H₂O (10 mL), and the pH was adjusted to 5.3 by addition of 1M hydrochloric acid. and then CuCl₂. 2H₂O (0.1364g, 0.8 mmol) was added, The pH was then adjusted back to 5.3 by the addition of 8 M ammonia solution. the mixture was refluxed at 45 °C for 2 h. The mixture was filtered and allowed to cool to ambient temperature. At this point, the pH was 5.0. After 2 days, the green crystals were isolated (yield: 100mg, 10.2% based on Mo).The crystals of 1 were characterized by elemental analysis§ and single-crystal X-ray diffraction. Elemental analysis (%): calcd (found) for 1: Cu 3.97 (4.03), V 3.36 (3.31), Mo 36.02(36.82), C 13.53 (13.48), N 3.50(3.42), H 3.72 (3.62).

IR spectroscopy: the bands at 1010.3, 886.10, 807.10 and 624.96 cm⁻¹ are due to the $v(V-O_a)$, $v(Mo-O_t)$, $v(Mo-O_b)$ and $v(Mo-O_c)$ of the $[VMo_6O_{26}]^{6-}$ fragment. The bands at 1626, 1428 and 1378 are attributed to characteristic vibrations of $[HN(CH_2CH_2OH)_3]^+$ groups.



Fig. S1 The IR spectrum of **1** in KBr pellets from 4000 cm^{-1} to 400 cm^{-1} .



Fig. S2 The PXRD pattern and simulated pattern of 1.



Fig. S3 The TGA curve of 1 measured under N_2 atmosphere from room temperature to 600 °C with a heating rate of 5°C min⁻¹.



Fig. S4 3D packing arrangement of compound 1. Color code: water molecules, red ball; C, grey; N, blue.