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Synthesis, crystal structure and properties of a new bi-dentate decavanadate $[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]\cdot 12H_2O$

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ABSTRACT

A new bi-dentate decavanadate compound formulated $[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]\cdot 12H_2O$ (en = ethylenediamine) (**1**) has been hydrothermally synthesized and structurally characterized. And **1** crystallizes in the triclinic, space group *P*-1 with $a = 10.2606(5)$ Å, $b = 13.4690(6)$ Å, $c = 15.2084(7)$ Å, $\alpha = 102.8150(1)^\circ$, $\beta = 91.2380(1)^\circ$, $\gamma = 92.1010(1)^\circ$, $V = 2047.12(2)$ Å^3, $R_1(I > 2\sigma(I) = 0.0511)$, and $Z = 2$. X-ray diffraction analysis reveals that **1** is constructed from bi-dentate decavanadate formed by decavanadate clusters coordinated to $[Cu(en)_2H_2O]^{2+}$ complexes and free water molecules. Furthermore, a three-dimensional (3D) framework is achieved in **1** *via* hydrogen bonds between O/N atoms and H atoms of the neighboring $[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]$ subunits. The UV–vis spectrum, fluorescent and electrochemical properties of **1** in aqueous solution are also studied.

1. Introduction

Over the past decade, polyoxometalates (POMs) have been used as ideal inorganic building blocks for the construction of inorganic–organic hybrid materials, as they exhibit not only a wide variety of robust structural motifs of different sizes and topologies, ranging from closed cages and spherical shells to basket-, bowl-, barrel- and belt-shaped structures [1], but also their numerous practical applications and remarkable range of physical properties [2–7]. Among the various types of POMs, polyoxovanadates represent an important part of the group, and invariably contain highly symmetrical core assemblies of VO_n units, which assemble into either discrete molecular clusters or link together to form one-dimensional chains, two-dimensional layers or three-dimensional frameworks [8]. Up to now, most of the polyoxovanadates have already been applied to act as building blocks to be connected with transition-metal complexes (TMCs) into polyoxovanadate-functional organic–inorganic hybrid materials to conflate useful properties of POMs and TMCs components, providing access to a vast area of complex, multifunctional materials [9–14]. However, the compounds that consist of decavanadate anions linked to TMCs or organic cations have been rarely reported so far [15–25], and most of them are with discrete structures. Thus, the design and synthesis of such decavanadate compounds remain a challenge. We have recently been attempting to bind TMCs to the decavanadate anions. In this paper, we present the hydrothermal synthesis, crystal structure of a new compound $[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]\cdot 12H_2O$, in which the decavanadate anions acting as bi-dentate ligands are bonded to $[Cu(en)_2H_2O]^{2+}$ complexes *via* the bridging oxygen atoms to construct $[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]$ subunits. Furthermore, a 3D framework was formed *by* hydrogen bonds between O/N atoms and H atoms of the neighboring $[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]$ subunits in **1**.

2. Experimental

2.1. Materials and methods

All chemicals were of reagent grade and used without further purification. Elemental analyses (C, H and N) were recorded with a Perkin Elmer 2400 CHN Elemental Analyzer. V and Cu were determined by a Leaman inductively coupled plasma (ICP)

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spectrometer. The UV–vis spectra were recorded on a U-3010 UV–vis spectrophotometer made in Japan in the range 190–1100 cm^{-1}. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Nicolet AVATAR FT-IR360 spectrometer. TG analysis was performed on a Perkin Elmer Diamond TG-DTA 6300 thermal analyzer in nitrogen with a heating rate of 10 $°C\cdot min^{-1}$. Fluorescence spectra was performed with a Perkin Elmer LS55 luminescence spectrometer using a 150 W xenon lamp as excitation source. A CHI660 electrochemical workstation was used for control of the electrochemical measurements and data collection. A conventional three-electrode system was used, with a bare glassy carbon electrode (GCE) as a working electrode, a commercial Ag/AgCl as reference electrode and a twisted platinum wire as counter electrode. The GCE was polished with 1.0 and 0.3 μm α-Al_2O_3 powders, successively sonicated in water for about 5 min after each polishing step. Finally, the electrodes were sonicated in ethanol, washed with ethanol, and dried with high purity nitrogen stream immediately before use.

2.2. Synthesis of $[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]\cdot 12H_2O$, 1

Compound **1** was hydrothermally prepared in 53% yields (based on Cu). A mixture of 0.34 g $CuCl_2\cdot 2H_2O$, 0.95 g NH_4VO_3, 0.25 g $H_2C_2O_4\cdot 2H_2O$, 0.28 mL en and 18 mL water in a molar ratio of 1:4.1:1:2.1:500, was stirred for 2 h at 60 °C, then the solution was sealed in a 23 mL Teflon-lined autoclave and heated at 180 °C for 4 days with starting pH 6.47 adjusted by 6 M HCl. After cooling to room temperature slowly (20 h), dark-orange block crystals were isolated. The crystals were filtered and dried at room temperature. Anal. Calc. for **1** (%): C 6.1, H 3.9, O 42, N 7.1, V 32.3, Cu 8; Found (%): C 5.8, H 4.1, O 44, N 6.8, V 31.3, Cu 7.8.

2.3. X-ray crystallography

The single crystal of **1** with dimensions 0.12 × 0.15 × 0.22 mm^3 was carefully selected for single-crystal X-ray diffraction analysis. Data collections were performed on a Rigaku RAXIS-RAPID equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated Mo Kα radiation, 0.71073 Å). The data were collected at a temperature of 20 ± 2 °C. The software SADABS was used for absorption correction [26]. The structure of **1** was solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL 97 crystallographic software package [27]. Anisotropic thermal parameters were used to refine all the non-hydrogen atoms. Positions of the hydrogen atoms attached to carbon and nitrogen atoms were fixed in ideal positions, and other hydrogen atoms were not located. Further details of the X-ray structural analysis for **1** are given in Table 1. The selected bond lengths are listed in Table S1.

The crystallographic data for **1** have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 729198. Copies of data can be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

3. Results and discussion

3.1. Structure description

The single-crystal X-ray diffraction analysis shows that **1** consists of $[H_2V_{10}O_{28}]^{4-}$ polyoxoanions, $[Cu(en)_2H_2O]^{2+}$ complexes and free water molecules (Fig. 1). The centrosymmetric $[H_2V_{10}O_{28}]^{4-}$ anions consists of five sharing edges $[VO_6]$, and has D_{2h} symmetry, which is similar to those reported in literatures [15–23]. Interestingly the decavanadate anions as a bi-dentate ligand, through the bridging oxygen atoms (O8, O8A) of two opposite $[VO_6]$ octahedral, coordinates to two $[Cu(en)_2H_2O]^{2+}$ complexes fragments to form a neutral molecular complex$[Cu(en)_2H_2O]_2[H_2V_{10}O_{28}]$, which is quite unusual among the decavanadates. There is only one symmetry independent Cu(II) ion in the structure of **1**, which is six coordinated by four nitrogen atoms from two en molecules (Cu1–N1 = 2.009(5) Å, Cu1–N2 = 2.012(5) Å, Cu1–N3 = 2.001(5) Å, Cu1–N4 = 2.004(5) Å) and two oxygen atoms from the decavanadate anions (Cu1–O8 = 2.530(5) Å) and one water molecules (Cu1–O15A = 2.668 (5) Å), forming a elongated octahedron geometry owing to Jahn–-Teller effect. In comparison with the compound $\{[Cu(H_2O)(C_5H_{14}N_2)_2]_2[V_{16}O_{38}(Cl)]\}\cdot 4(C_5H_{16}N_2)$ (**2**) [24], which also possesses a structure constructed by copper cations and polyoxovanadate anions, two main differences are described below. First, the POM

Table 1
Crystal data and structure refinements for compound **1**.

Empirical formula	$C_8H_{62}Cu_2V_{10}N_8O_{42}$
Formula weight	1578.92
T (K)	273(2) K
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	10.2606(5)
b (Å)	13.4690(6)
c (Å)	15.2084(7)
α (deg)	102.8150(1)
β (deg)	91.2380(1)
γ (deg)	92.1010(1)
V (Å^3)	2047.12(2)
Z	2
D_{calcd} ($g\ cm^{-3}$)	2.331
Absorption coefficient (mm^{-1})	6.909
F(000)	1406
θ range (deg)	1.37–28.27
Reflections collected	12974
Unique reflections/(R_{int})	9414/0.0293
μ (mm^{-1})	3.299
GOF on F^2	1.028
Final R_1, wR_2 ($I > 2\sigma(I)$)	0.0511, 0.1119
Final R_1, wR_2 (all data)	0.0853, 0.1359
Largest diff. peak/hole (e·Å^{-3})	0.848/−0.657

$R_1 = \sum||F_o| - |F_C||/\sum|F_o|$; $wR_2 = \sum[w(F_0{}^2 - F_C{}^2)^2]/\sum[w(F_0{}^2)^2]^{1/2}$.

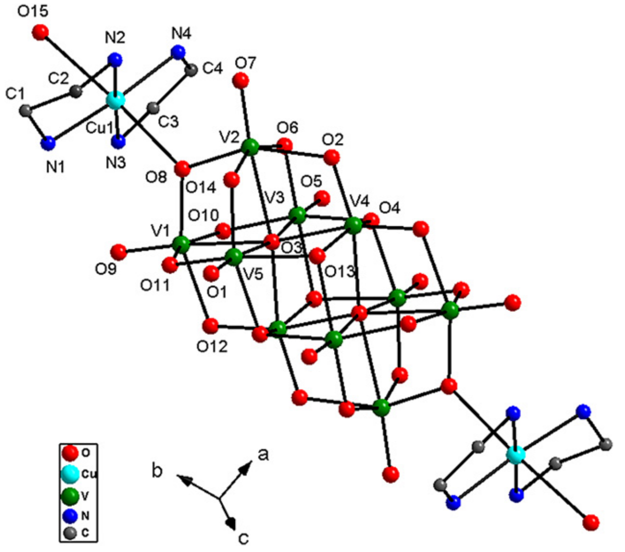

Fig. 1. View of the fundamental unit of **1**. All the hydrogen atoms and water molecules are omitted for clarity.