

Note

Hydrothermal synthesis and characterization of a novel 3D open framework structure of mixed valence ethylenediamine–vanadium phosphate: $[\text{C}_2\text{H}_{10}\text{N}_2]\text{[(HV}^{\text{IV}}\text{O}_3)(\text{HV}^{\text{V}}\text{O}_2)(\text{PO}_4)]$

Jian-Xin Chen^{*}, Chun-Xia Wei, Zhi-Chun Zhang, Yuan-Biao Huang, Ting-Yan Lan, Zhong-Shui Li, Wen-Jie Zhang

College of Chemistry and Materials Science, Fujian Normal University, Fuzhou, Fujian 350007, PR China

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Abstract

A new three-dimensional open framework structure of mixed valence ethylenediamine–vanadium phosphate $[\text{C}_2\text{H}_{10}\text{N}_2][(\text{HV}^{\text{IV}}\text{O}_3)(\text{HV}^{\text{V}}\text{O}_2)(\text{PO}_4)]$ (**1**), has been synthesized under mild hydrothermal conditions and characterized by elemental analyses, IR, fluorescent spectrum, TG-DTA and single crystal X-ray diffraction. Compound **1** exhibits a novel three-dimensional (3D) vanadium phosphate anion framework composed of vanadium, phosphate, and oxygen atoms through covalent bonds, with the diprotonated ethylenediamine $[\text{NH}_3\text{CH}_2\text{CH}_2\text{NH}_3]^{2+}$ cations residing in the channels along *c*-axis. The organic diprotonated ethylenediamine cations interact with the O atoms in the inorganic network through hydrogen bonds. The electrochemical behavior of **1** has also been studied in detail by cyclic voltammograms, which is very important for practical applications in electrode modification. Furthermore, the strong photoluminescence property of compound **1** is also measured at room temperature.

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1. Introduction

Vanadium phosphate phases have been intensively studied due to the wide diversity of their structural chemistry, a concomitant diversity of electronic and magnetic properties, and because of their potential applications in catalysis, adsorption, ion exchange [1–4], and their versatile intercalation properties [5–7]. An astonishing variety of novel phases arise from the combination of vanadium/phosphate progenitors and small organic molecules [8–15]. Such structural variety arises due to the versatility of vanadium in terms of its variable oxidation state (V^{III} , V^{IV} , V^{V}) and

coordination geometry (tetrahedral, square pyramidal, trigonal bipyramidal, and octahedral), combined with the structure-directing (Templating) effect of the organic moiety, although, as yet, we have little control over such synthesis processes. A large number of vanadium phosphates incorporating organic species such as monoammonium and diammonium cations are known. Depending on the charge, shape, and size of the organic cation, structures with rings/cages, cavities, or layers are formed [16]. Several vanadium phosphates containing diprotonated piperazine (pipz-VPOs) have been previously reported. Examples include layered structures closely related to the structure of $\alpha\text{-VOPO}_4 \cdot 2\text{H}_2\text{O}$ and framework structures with tunnels occupied by diprotonated piperazine cations [11,17–20].

In this paper, we report the synthesis, single-crystal structure, and characterization of the first example of

^{*} Corresponding author. Tel.: +86 591 83448669; fax: +86 591 83465376.

E-mail address: jxchen_1964@163.com (J.-X. Chen).

mixed-valence ethylenediamine–vanadium phosphate compound, $[\text{C}_2\text{H}_{10}\text{N}_2][(\text{HVO}_3)(\text{HVO}_2)(\text{PO}_4)]$. This phase has a crystal structure that is completely different from that of compounds [21–23] reported, and shows strong three-dimensional character and structural similarity to the 2D compound $[(\text{C}_6\text{H}_{16}\text{N}_2)_3(\text{VO})(\text{V}_2\text{O}_4)_2(\text{PO}_4)_4 \cdot 2\text{H}_2\text{O}]$ [24]. Both the title compound and the reported compound have an uniform V–O–V linkage in the structure. But the 2D compound has two kinds of V–O–V chains.

2. Experimental

2.1. Reagents

All analytical grade chemicals and solvents were purchased commercially and used without further purification.

2.2. Measurements

Infrared spectrum was measured on a Nicolet AVATAR 360 FT-IR spectrometer using KBr pellets in the 4000–400 cm^{-1} region. Emission/excitation spectra were recorded on a RF-540 fluorescence spectrophotometer. Elemental analyses were carried out on an EA1112 CHNS elemental analyzer. The thermal gravimetric analysis (TGA) and the differential analysis (DTA) were carried out under N_2 with a Switzerland METTLER TGA/SDTA 851 differential thermal analyzer at a rate of 10 $^\circ\text{C min}^{-1}$ in the range 50–800 $^\circ\text{C}$.

Cyclic voltammogram (CV) was recorded on a 384B polarographic analyzer. A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used. The working electrode was a modified carbon paste electrode (CPE). An Ag/AgCl (saturated KCl) electrode was used as a reference electrode and a Pt gauze as a counter electrode. All potentials were measured and reported versus the Ag/AgCl electrode.

Structural measurement for **1** was performed on Rigaku R-Axis RAPID Weissenberg IP diffractometer equipped with a graphite-monochromatized Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected at 293 K. Lorentz-polarization corrections and empirical absorption correction were applied to the data. The structure was solved by direct methods with SHELXS-97 [25a] and refined by full-matrix least-squares calculations with SHELXL-97 [25b]. All non-hydrogen atoms were refined with anisotropic thermal parameters, and most hydrogen atoms were located in the calculated positions. All calculations were performed on a Pentium IV computer. A summary of the crystallographic data and structural determination for compound **1** is listed in Table 1. Selected bond lengths are provided in Table 2. Atomic coordinates and equivalent isotropic displacement parameters are given in Table S1 (ESI) and Table S2 (ESI) for **1**, respectively.

Table 1
Crystallographic data for **1**

Compound	1
Formula	$\text{C}_2\text{H}_{12}\text{N}_2\text{O}_9\text{PV}_2$
Formula weight	340.99
Crystal system	orthorhombic
Space group	$P2(1)2(1)2(1)$
a (\AA)	8.3176(3)
b (\AA)	9.1539(3)
c (\AA)	12.6302(5)
α ($^\circ$)	90
β ($^\circ$)	90
γ ($^\circ$)	90
V (\AA^3)	961.64(6)
Z	4
D_{calc} (Mg m^{-3})	2.355
Crystal size (mm)	$0.51 \times 0.32 \times 0.31$
μ (mm^{-1})	2.151
$F(000)$	684
$\theta_{\text{max}}, \theta_{\text{min}}$ ($^\circ$)	27.50, 2.75
Index range	
h	$0 \rightarrow 10$
k	$0 \rightarrow 11$
l	$0 \rightarrow 16$
R_{int}	0.0270
No. of independent reflections	1285
No. of observed reflections	1270
No. of variables	152
R	0.0241
wR	0.0832
Goodness-of-fit	1.016
Largest difference in peak ^a (hole) (e \AA^{-3})	0.647 (–0.468)
Δ/σ	0.000, 0.000

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2} \right\}^{1/2}$$

^a Largest peak (hole) in difference Fourier map.

2.3. Preparation of the complex

A mixture of $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ($\text{C}_2\text{H}_8\text{N}_2$, ethylenediamine, 0.75 mmol), V_2O_5 (0.0455 g, 0.25 mmol), P_2O_5 (0.0355 g, 0.25 mmol), $\text{Cd}(\text{OAc})_2$ (0.0576 g, 0.25 mmol), HF (0.1 mL), and 12 mL H_2O was sealed in a 23 mL Teflon-lined stainless steel autoclave with about 60% filling. The pH value was up to about 3 through the addition of a 6 M HCl solution. The resulting mixture was heated at a rate of ca. 100 $^\circ\text{C h}^{-1}$ to 170 $^\circ\text{C}$ and held at this temperature for 2 days. Subsequently the autoclave was cooled at a rate of ca. 3 $^\circ\text{C h}^{-1}$ to 140 $^\circ\text{C}$ and held at this temperature for 3 days. Finally, it was cooled at a rate of ca. 4 $^\circ\text{C h}^{-1}$ to room temperature. The resulting prism black crystals were filtered off and washed with water, then dried at ambient temperature. Yield: 0.0341 g (20% based on V). Anal. Calc. for $\text{C}_2\text{H}_{12}\text{N}_2\text{O}_9\text{PV}_2$ (**1**): C, 7.04; H, 3.52; N, 8.21; P, 9.09; V, 29.90. Found: C, 7.06; H, 3.50; N, 8.26; P, 9.05; V, 29.92%. In this synthesis, without the incorporation of the metal cations Cd^{2+} , the role of this metallic cation is unknown but not unprecedented; for example, a barium vanadium(IV) phosphate hydrate, $\text{Ba}_2\text{VO}(\text{PO}_4) \cdot \text{H}_2\text{O}$ [26], required the presence of Zn^{2+} to form, although no zinc was incorporated in the majority product.

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