Journal of Alloys and Compounds 544 (2012) 37-41

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jalcom



Synthesis, crystal structure and conductive performance of tungstovanadophosphoric heteropoly acid $H_4PW_{11}VO_{40}\cdot 8H_2O$

Xia Tong^a, Naiqin Tian^a, Weiming Zhu^a, Qingyin Wu^{a,*}, Fahe Cao^a, Wenfu Yan^b

^a Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China ^b State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, PR China

ARTICLE INFO

Article history: Received 8 June 2012 Received in revised form 27 July 2012 Accepted 30 July 2012 Available online 7 August 2012

Keywords: Heteropoly acid Keggin structure Crystal structure Conductivity Conductive mechanism

1. Introduction

Heteropoly acids (HPAs) are formed by inorganic metal-oxygen cluster anions. They and their polyoxometalate salts currently receive considerable interest because of their significant applications in many fields such as catalysis, biomedicine and material science, especially for materials serving as solid electrolytes [1–8]. Many of the solution properties of HPAs are observed in the crystalline salts and free acids, since the large anion tend to have very weak atrractions for counteractions and solvate molecules. In particular, the electron- and proton-transfer characteristics are often retained in the solid-state. HPAs have received much attention attractive as conductive materials due to their high proton conductivity, fast charge transfer and good thermal stability [9–11]. There are many reports about syntheses and single-crystal structures of many monosubstituted HPAs and their salts [12-14]. However, few complete single crystal X-ray investigation about multisubstituted HPA seems to have been carried out. The aim of the present investigation was to perform a single crystal X-ray investigation of multisubstituted heteropoly acid in order to obtain the arrangements of heteroatoms within the acid. Moreover, recent studies have shown that as a kind of proton conductors, the conductivities of heteropoly acids are closely related to their component elements. There are many researches on tungstovanadophosphoric heteropoly acid H₄PW₁₁VO₄₀·8H₂O as a precursor to obtain the single crystals of all kinds of complexes, however its own single

ABSTRACT

Tungstovanadophosphoric heteropoly acid H₄PW₁₁VO₄₀·8H₂O with Keggin structure has been synthesized by the stepwise acidification and the stepwise addition of element solutions. The optimal proportion of component compounds and pH value in the synthesis reaction were given. The crystal structure was determined from single crystal X-ray diffraction. The complex crystallises in the space group I-4, with *a* = 18.7648(9) Å, *b* = 18.7648(9) Å, *c* = 14.5762(9) Å, α = 90°, β = 90°, γ = 90°, *V* = 5132.5(6) Å, *Z* = 2. The product possesses Keggin structure and its conductivity was 1.50×10^{-2} S cm⁻¹ at 26 °C and 75% relative humidity by electrochemical impedance spectroscopy (EIS) measurement, with an activation energy of 25.66 kJ mol⁻¹ for proton conduction. The mechanism of proton conduction for this compound is vehicle mechanism.

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crystals have still rarely reported. Herein, we report the synthesis, single-crystal structure and conductive performance of H_4PW_{11} VO₄₀, which not only exhibits high conductive property, but also has a small activation energy of proton conduction. The mechanism of proton conduction for this compound is also proposed.

2. Experimental

2.1. Instrument and reagent

Infrared (IR) spectrum was recorded on a NICOLET NEXUS 470 FT/IR spectrometer over the wave number range 600-4000 cm⁻¹ using KBr pellets. The UV spectrum was measured on a SHIMADZU U-2550 UV-vis spectrophotometer. X-ray powder diffraction analysis was obtained on a BRUKER D8 ADVANCE X-ray diffractometer using a Cu tube operated at 40 kV and 40 mA in the range of $2\theta = 4-40^{\circ}$ at a rate of 0.02° s⁻¹. The determinations of the unit cell and data collections for the crystal of this compound were performed on an Oxford Xcalibur Gemini Ultra diffractometer with an Atlas detector. The data were collected using graphitemonochromatic Mo-K radiation (= 0.71073 Å) at 293 K. The data sets were corrected by empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The thermogravimetry (TG) and differential thermal analysis (DTA) were performed using a SHIMADZU thermal analyzer from room temperature to 800 °C. Measurement was performed using a SHIMADZU thermal analyzer in a Nitrogen stream, with a scanning rate of 10 °C min⁻¹. Impedance measurements of these products were performed on a VMP2 Multichannel potentiostat electrochemical impedance analyzer.

All reagents were analysis grade.

2.2. Synthesis of H₄PW₁₁VO₄₀·8H₂O

 $H_4 PW_{11} VO_{40} \cdot 8H_2 O$ was synthesized by a modification of the method according to the literature available [15]. 20 mL aqueous solution of sodium phosphate (3.80 g, Na_3PO_4 \cdot 12H_2 O) was added dropwise to 80 mL aqueous solution of sodium



^{*} Corresponding author. Tel.: +86 571 88914042; fax: +86 571 87951895. *E-mail address:* qywu@zju.edu.cn (Q. Wu).

^{0925-8388/\$ -} see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jallcom.2012.07.145

tungstate (36.3 g, Na₂WO₄·2H₂O). Vanadium pentoxide (0.91 g, V₂O₅) was dissolved in 10 mL 1.0 mol L⁻¹ of sodium carbonate solution with stirring, then was added to the reaction solution. The mixture was adjusted to pH ~2.5 and continuously heated at 90 °C for 2 h under stirring. The cooled solution was extracted with ether (30 mL) in sulfuric acid medium. After the concentrated etherate solution was dried in vacuum, the orange power was obtained. Crystals suitable for single-crystal X-ray crystallography were grown for H₄PW₁₁VO₄₀ from dimethyl sulfoxide by slow evaporation at room temperature. Phosphorus, tungsten and vanadium were analysed by inductively coupled plasma mass spectrometry (ICP-MS), and the water content of the crystal was determined by thermogravimetric analysis. Found for the product: P = 1.10%, W = 68.75%, V = 1.73%, H₂O = 5.24%. Calculated for H₄PW₁₁ VO₄₀·8H₂O: P = 1.07%, W = 69.92%, V = 1.76%, H₂O = 4.98%.

2.3. Measurement of conductivity

The product was compressed to discs under a pressure of 20 MPa at room temperature (26 °C). The diameter was 10 mm and the thickness was 2.18 mm, respectively. Two copper sheets were attached to the faces of the disc. Copper slices and copper wires were used as electrodes and lines, respectively. The proton conductivity was measured using a cell: copper |sample| copper.

3. Results and discussion

3.1. Crystal structure

The crystal data and structure refinement detail for H_4PW_{11} - VO_{40} · $8H_2O$ are summarized in Table 1. Fig. 1 presents the crystal structure of $PW_{11}VO_{40}^{4-}$ anion. The marked M atom shows a statistically disordered state and each position was shared by W and V at the atomic stoichiometric ratio of n(W):n(V) = 11:1. This anion consists of a central PO_4^- tetrahedron surrounded by twelve MO_6 -octahedra. The twelve octahedra may be subdivided into four M_3O_{13} -groups. In these groups each MO_6 -octahedron is linked to its neighbour on either side by a shared edge making one corner common to the three octahedra. The four groups are then linked to each other by sharing corners and to the PO_4 -tetrahedron by the three-coordinated oxygen atoms. This structure which is a ball-like shape is often named the Keggin molecule. Some selected bond lengths (Å) and angles (°) for this compound were showd in Table 2.

Table 1

Summary of crystal structure determination for H₄PW₁₁VO₄₀·8H₂O.

Empirical formula	H ₄ PW ₁₁ VO ₄₀ (H ₂ O) ₈
Formula weight	2892.39
Crystal size	$0.38 \times 0.26 \times 0.20$
Volume	5132.5(6)
α (Å)	18.7648(9)
<i>b</i> (Å)	18.7648(9)
c(Å)	14.5762(9)
α°	90
β°	90
γ°	90
Crystal symmetry	Tetragonal
Space group	I-4
Hall group	I-4
F000	2344.0
$Dx,g cm^{-3}$	1.776
Ζ	2
h,k,l max	22,22,17
Nref	2462(4718)
T _{min} , T _{max}	0.029, 0.084
T _{min'}	0.006
$\mu(\text{mm}^{-1})$	13.510
$R_1(F_0)$	0.0703(3574)
$wR_2(F_0^2)$	0.2241(4667)

$${}^{\alpha}R = \sum ||F_0| - |F_c|| / \sum |F_0|; wR_2$$

= $\sum [w(F_0^2 - F_c^2)^2] / \sum [w(F_0^2)^2]^{1/2}]$



Fig. 1. The crystal structure of $PW_{11}VO_{40}^{4-}$ (M = 11/12 W + 1/12 V).

3.2. IR and UV spectra

The IR spectrum of HPA shows the jump between two vibration energy levels of electron basic state. The vibrations of the oxygen bond reflect the change of mechanical and electronic properties, each change has it own characteristic frequency. There are four kinds of oxygen atoms in $PW_{11}VO_{40}^{4-}$, four P-O_a in which oxygen atom connects with heteroatom, twelve M-O_b-M oxygen-bridges (corner-sharing oxygen-bridge between different M₃O₁₃ sets), twelve M-O_c-M oxygen-bridges (edge-sharing oxygen-bridge within M_3O_{13} sets) and twelve $M-O_d$ terminal oxygen atoms. The characteristic bands of heteropoly anion at 790–1080 cm⁻¹ are observed. The vibrational frequencies fall in the sequence of $\upsilon_{as}(P-O_a) > \upsilon_{as}(M-O_d) > \upsilon_{as}(M-O_b-M) > \upsilon_{as}(M-O_c-M) \quad (M = W, V).$ In the IR spectra (Fig. 2), there are four characteristic bands of H 4PW₁₁VO₄₀: 1078.4 cm⁻¹, $\upsilon_{as}(P-O_a)$; 984.0 cm⁻¹, $\upsilon_{as}(M-O_d)$; 889.6 cm⁻¹, $\upsilon_{as}(M-O_b-M)$; 795.2 cm⁻¹, $\upsilon_{as}(M-O_c-M)$. The corresponding characterisic bands of H₇P₂W₁₇VO₆₂ appear at 1087.5, 963.0, 919.6, and 793.1 cm⁻¹. The vibrational frequencies of P-O_a and M-O_b-M are red shifted, while that of M-O_d and M-O_c-M are blue shifted, compared with the corresponding vibration frequencies of heteropoly acid with Dawson structure. The similarity of IR spectrum of $H_4PW_{11}VO_{40}$ with that of $H_3PW_{12}O_{40}$ strongly indicates that it has the same structure as PW₁₂O₄₀³⁻, showing that they still maintain Keggin structure after introduction of vanadium atom [16]. The bands at about 3403.2 and 1609.6 cm^{-1} are assigned to the stretching vibration of O-H bonds and the bending vibration of H-O-H bonds, respectively.

The absorption band of the HPA UV spectrum shows the charge transfer between oxygen and a coordinate metal atom. In Fig. 3, the absorption peak of $H_4PW_{11}VO_{40}$ appear at 261.0 nm ($O_b/O_c \rightarrow W$).

3.3. X-ray powder diffraction

X-ray powder diffraction is widely used to study the structural feature of HPA and explain its property. Fig. 4 shows the XPRD patterns of $H_4PW_{11}VO_{40}$. The XRD pattern of the as-synthesized solid

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