

# Synthesis and conductivity of substituted heteropoly acid with Dawson structure $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$

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A new solid high-proton conductor,  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ , a substituted heteropoly acid with Dawson structure, has been synthesized by the degradation/ion-exchange/freezing method. The product was characterized by potentiometric titration, chemical analysis, IR, UV, XRD and TG-DTA. Complex impedance measurements show a high conductivity ( $5.44 \times 10^{-3}$  S/cm at 50°C), with an activation energy for proton conduction of 36.04 kJ/mol. The mechanism of proton conduction is the Vehicle mechanism.

**heteropoly acid, Dawson structure, synthesis, conductivity, conductive mechanism**

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Heteropoly acids (HPAs) have attracted increasing interest because of their applications, as catalysts for organic reactions, corrosion resistant coatings, dopants in sol-gel matrixes, and as membranes in selective electrodes, in gas detection apparatus, in solid-state electrochromic devices, and in liquid and solid electrolytic cells [1,2]. There are two kinds of protons in the HPA crystals. One is the dissociated, hydrated proton that is combined with the HPA anion, the other is the unhydrated proton that is located on the bridging oxygen in the HPA anion. Because the dissociated protons have good mobility, the HPA crystals have some characteristics of a 'pseudo liquid phase'. They are, in effect, superionic protonic conductors, and are promising solid electrolytes [3,4]. In recent years, studies on the conductivity of heteropoly acids have progressed rapidly, and the research fields have also been expanded from the initial binary heteropoly acid to ternary or quaternary heteropoly acids. However, the structure is still limited to the Keggin Structure, and there are few reports of heteropoly acids with other structures (such as the Dawson

structure) [5–7]. This paper reports on the synthesis and characterization, as well as the proton conductivity, of a heteropoly acid with Dawson structure,  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ . A possible mechanism of proton conduction for this heteropoly acid is proposed.

## 1 Experimental

### 1.1 Instruments and reagents

Nicolet Nexus 470 FT/IR spectrometer; SHIMADZU U-2550 UV-Vis spectrophotometer; BRUKER D8 ADVANCE X-ray diffractometer; SHIMADZU thermal analyzer and VMP2 Multichannel potentiostat electrochemical impedance analyzer (Princeton Applied Research).

All reagents were analysis grade.

### 1.2 Preparation of HPA

(1) Preparation of  $[P_2W_{17}O_{61}]^{10-}$ .  $[P_2W_{18}O_{62}]^{6-}(P_2W_{18})$  was prepared according to the literature [8].  $[P_2W_{17}O_{61}]^{10-}$

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( $P_2W_{17}$ ) was prepared by a modification of this literature method.  $P_2W_{18}$  (20.0 g) was dissolved in 50 mL of water, and 5 g  $KHCO_3$  was dissolved in 50 mL of water. The latter solution was added dropwise to the former one with stirring. A white sediment appeared after stirring the mixed solution for an hour.  $P_2W_{17}$  was purified in 50 mL of water at  $70^\circ\text{C}$ . Although  $K_6P_2W_{18}O_{62}$  was more soluble than  $K_{10}P_2W_{17}O_{61}$ , it can still precipitate with  $K_{10}P_2W_{17}O_{61}$  when treated with potassium bicarbonate. In order to improve the purity of  $K_{10}P_2W_{17}O_{61}$ , we used sodium bicarbonate instead of potassium bicarbonate.

(2) Preparation of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$  ( $P_2W_{17}Ga$ ) can be prepared through initially degrading  $P_2W_{18}$  and then coordinating with Ga atoms using the vacancy formed in  $P_2W_{17}$  to form a  $GaO_6$  type octahedron.

$K_2CO_3$  (3 g) was dissolved in 30 mL of water and this solution was added dropwise to 8.7 mL 0.6031 mol/L  $Ga(NO_3)_3$  solution. The prepared  $P_2W_{17}$  was added to 80 mL water at  $70^\circ\text{C}$ , and the  $Ga(NO_3)_3$  solution was added dropwise to this  $P_2W_{17}$  solution. The solution was then stirred for 1 h at above  $95^\circ\text{C}$ , the pH was controlled at 5 with HAc during the reaction. Then the solution was filtered, cooled to room temperature, and the filtrate was put into an icebox. The crystals which separated from the solution were collected. The crystals were recrystallized three times from 30 mL boiling water to give the ion-exchanged material. The solution was filtered and the filtrate which contained  $P_2W_{17}Ga$  was concentrated. After drying the concentrated solution in the desiccator,  $H_7P_2W_{17}Ga$  was obtained.

### 1.3 Elemental analysis

Phosphorus, tungsten and gallium were analyzed by ICP, the amount of water was analyzed by thermogravimetry. Found: Ga, 1.49%; P, 1.31%; W, 67.84%;  $H_2O$ , 7.57%.

Calculated for  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ : Ga, 1.52%; P, 1.35%; W, 67.94%;  $H_2O$ , 7.43%.

### 1.4 Measurement of conductivity

$H_7P_2W_{17}Ga$  was compressed to a disc under a pressure of 15 MPa at room temperature ( $18^\circ\text{C}$ ). The diameter was 10 mm and the thickness was 3.50 mm. 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. The temperature was varied from 18 to  $50^\circ\text{C}$ . The cell was open to atmosphere during this measurement.

## 2 Results and discussion

### 2.1 Determination of basicity

The number of hydrogens and states of ionization in the

HPA can be determined by potentiometric titration [9]. The potentiometric titration (Figure 1) shows that the 7 protons of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$  are equivalent and are ionized in the same step.

### 2.2 IR spectra

The IR spectrum of HPA shows the jump between 2 vibrational energy levels of the electronic ground state. The vibrations of the oxygen bond reflect the change of mechanical and electronic properties of the bond, and every change has its own characteristic frequency. Vibrations corresponding to the Dawson-type heteropoly acid appear at  $700\text{--}1100\text{ cm}^{-1}$ . The vibration frequencies fall in the sequence of  $\nu_{as}(P-O_a) > \nu_{as}(M-O_d) > \nu_{as}(M-O_b-M) > \nu_{as}(M-O_c-M)$ , ( $M = W, Ga$ ). The vibration frequencies of  $M-O_c-M$  and  $M-O_d$  are red shifted, while that of  $M-O_b-M$  is blue shifted, compared with the corresponding vibration frequency of the Keggin-type heteropoly acid [10].

Figure 2 shows the IR spectra of  $P_2W_{18}$  and  $P_2W_{17}Ga$ . The characteristic bands of the heteropolyanion at  $700\text{--}1100\text{ cm}^{-1}$  were observed, which indicates that the Dawson structure of  $P_2W_{17}Ga$  was maintained. The characteristic bands of  $P_2W_{17}Ga$  appear at 1090, 964, 914 and  $796\text{ cm}^{-1}$ , which correspond to  $\nu_{as}(P-O_a)$ ,  $\nu_{as}(M-O_d)$ ,  $\nu_{as}(M-O_b-M)$  and  $\nu_{as}(M-O_c-M)$  vibrations, respectively, and the corre-

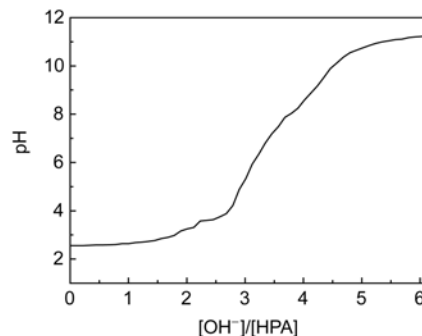


Figure 1 The potentiometric titration curve of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .

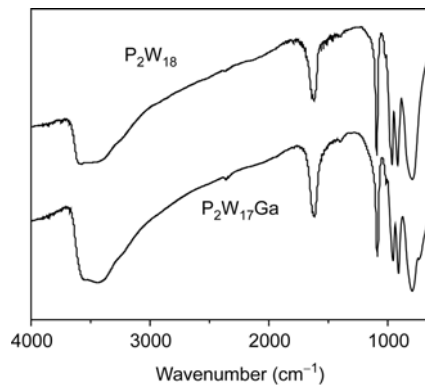


Figure 2 IR spectra of  $P_2W_{18}$  and  $P_2W_{17}Ga$ .

sponding characteristic bands of  $P_2W_{18}$  appear at 1091.4, 963.4, 916.0 and 792.9  $\text{cm}^{-1}$ . The difference between the bands of the two compounds probably arises from the substitution of Ga atom. The bands at about 3450 and 1640  $\text{cm}^{-1}$  were assigned to the stretching vibration of O–H bonds and the bending vibration of H–O–H bonds, respectively.

### 2.3 UV spectrum

The absorptive band of the HPA UV spectrum shows the charge transfer between oxygen and a coordinate metal atom.

Figure 3 shows the UV spectrum of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ , there is an intense absorption peak at 197.5 nm ( $O_d \rightarrow W$ ) and a relatively weak absorption peak at 255 nm ( $O_b/O_c \rightarrow W$ ).

### 2.4 X-ray powder diffraction

X-ray powder diffraction is widely used to study the structural features of HPA and explain their properties. Figure 4 shows the X-ray diffraction pattern of Dawson-type heteropoly acid  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ . The most intense peaks exist at about  $8.5^\circ$ . In 4 ranges of  $2\theta$  (i.e.  $7\text{--}10^\circ$ ,  $17\text{--}20^\circ$ ,  $23\text{--}28^\circ$  and  $28\text{--}30^\circ$ ), there are characteristic peaks of HPA anions with Dawson structure [11]. Combined with the IR and UV spectra, this confirms that  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot$

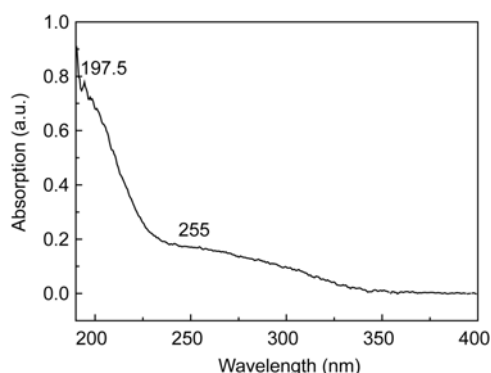


Figure 3 UV spectrum of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .

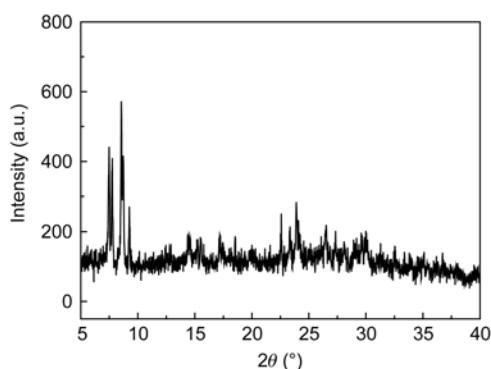


Figure 4 X-ray diffraction pattern of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .

$18H_2O$  has a Dawson structure.

Figure 5 shows a schematic diagram of the structure of the Dawson-type heteropoly acid  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .

### 2.5 TG-DTA analysis

HPA consists of protons, HPA anions and water. TG and DTA curves of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$  are shown in Figure 6. The TG curve shows that the total percent of weight loss is 7.57%, which indicates that each HPA molecule has 19.26 water molecules. The TG curve shows that there are 3 steps of mass loss. The first is the loss of hydration water, the second is the loss of protonized water and the third is the loss of structural water. There is an O atom of a water molecule which is coordinated with the Ga atom and hence is directly connected to that Ga atom. Thus, the accurate molecular formula of the product is  $(H_5O_2^+)_2H_5-[Ga(H_2O)P_2W_{17}O_{61}] \cdot 14H_2O$ .

In general, we take the temperature of the exothermic peak of DTA curves of compounds as a way of characterizing their thermostability [12]. Figure 6 is the thermogram of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ . In the DTA curve, there are both endothermic and exothermic peaks. The process of dehydration occurring at  $119.2^\circ\text{C}$  is an endothermic peak.

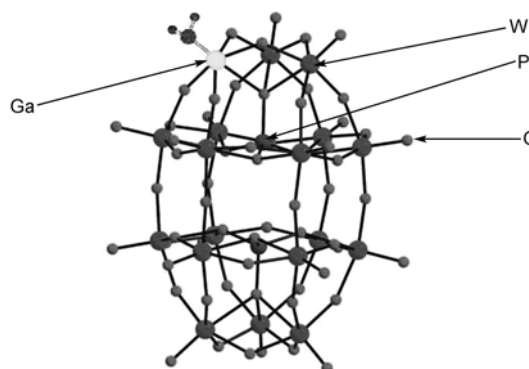


Figure 5 Schematic diagram of the structure of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .

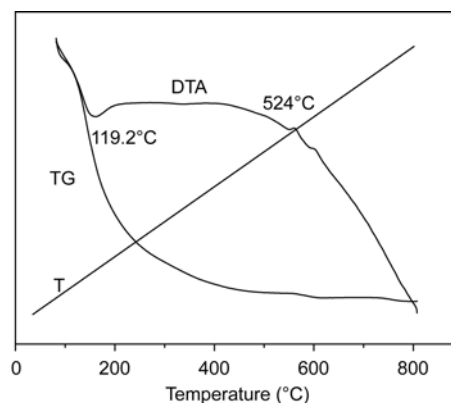


Figure 6 TG-DTA curve of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .

The exothermic peak at 524°C is due to the decomposition of Dawson-type heteropoly acid  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .

## 2.6 Conductivity

Conductivity is an important parameter. We have recorded the complex impedance spectra of the HPA (over a frequency range from  $0.01 \times 10^4$ – $9.99 \times 10^4$  Hz). We can calculate the conductivity from these results as  $\sigma = h/(SR)$ , where  $R$  is the resistance,  $h$  is the thickness, and  $S$  is the area of the tablet. The calculation shows that at 18, 30, 41 and 50°C, the conductivity values of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$  are  $1.25 \times 10^{-3}$ ,  $2.52 \times 10^{-3}$ ,  $4.56 \times 10^{-3}$  and  $5.44 \times 10^{-3}$  S/cm, respectively. This compound is a new solid high-proton conducting HPA.

The conductivity is a function of the movement of protons. There are two predominant mechanisms for proton conduction: the Vehicle mechanism and the Grotthuss mechanism [13]. In the Vehicle mechanism, water assists proton movement by facilitating transport as an  $H_3O^+$  species. This differs from the Grotthuss mechanism, in which a large amount of water can assist proton transport through a hydrogen-bonded network [14]. Kreuer [15] has suggested that the HPA acts as a Bronsted acid towards the hydration water, which is generally loosely bound in the structure, resulting in a high proton conductivity. Consequently, the conductivity of HPAs is strictly related to the numbers of water molecules coordinated to the Dawson unit. Generally, the activation energy of the Vehicle mechanism is higher (20 kJ/mol or more) than that of the Grotthuss mechanism (10 kJ/mol or less).

Figure 7 is an Arrhenius plot. From the slope we can calculate the activation energy of proton conduction is 36.04 kJ/mol, which indicates that its mechanism of proton conduction is the Vehicle mechanism. In the range of 18 to 50°C, the conductivity of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$  increases with increasing temperature.

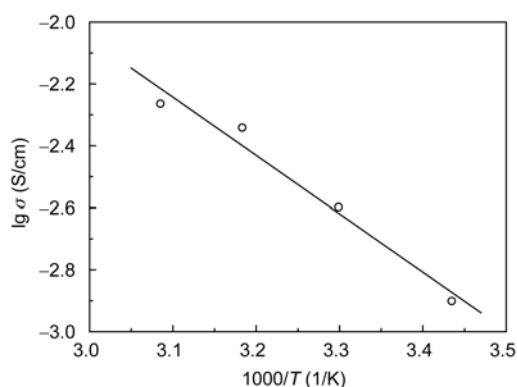


Figure 7 Arrhenius plot of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ .

## 3 Conclusion

$H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$ , a new solid high-proton conducting HPA, was prepared and characterized for the first time. We determined the conductivity values of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$  using complex impedance measurements. They are  $1.25 \times 10^{-3}$ ,  $2.52 \times 10^{-3}$ ,  $4.56 \times 10^{-3}$  and  $5.44 \times 10^{-3}$  S/cm at 18, 30, 41 and 50°C, respectively. The conductivity of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$  increases with temperature from 18 to 50°C. The activation energy of proton conduction of  $H_7[Ga(H_2O)P_2W_{17}O_{61}] \cdot 18H_2O$  is 36.04 kJ/mol, indicating that its mechanism of proton conduction is the Vehicle mechanism.

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