

A supramolecular complex based on poly-Keggin-anion chains: synthesis, structure characterization, and conductivity

Mei-Lin Wei · Hui-Hua Li · Xiao-Xiang Wang ·
Jun-Hua Wang

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Abstract A proton-conductive supramolecular complex, $\{[\text{Cu}(\text{H}_2\text{O})_8][\text{H}(\text{H}_2\text{O})_3](\text{HINO})_4(\text{PMo}_{12}\text{O}_{40})\}_n$, was constructed by a self-assembly of $\text{H}^+(\text{H}_2\text{O})_3$ clusters, $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ clusters, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions, and isonicotinic acid N-oxide (HINO). Single-crystal X-ray diffraction analysis at 293 K revealed that the complex presented the three-dimensional (3D) supramolecular framework built from non-covalent interactions. Interestingly, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions self-assembled into poly-Keggin-anion chains in the supramolecular framework. Thermogravimetric analysis shows no weight loss in the temperature range of 20–100 °C, indicating that all water molecules in the unit structure are not easily lost below 100 °C. Surprisingly, the proton conductivity of the complex in the temperature range of 85–100 °C under 98% RH condition reached good proton conductivity of $10^{-3} \text{ S cm}^{-1}$. A possible mechanism of the proton conduction was proposed according to the experimental results.

Keywords Polyoxometalates · Crystal structure · Supramolecular complex · Hydrogen bond · Conducting material

Introduction

Solid-state materials with proton conductivities have interested us from the point of view of transport dynamics and its applications in fuel cells [1–3]. Heteropolyacids and other inorganic or organic compounds [4, 5] have been studied and applied to electrochemical devices. Keggin-type heteropolyacids (HPAs), possessing a unique discrete ionic structure including heteropoly anions and counter-cations (H^+ , H_3O^+ , H_5O_2^+ , etc.), are widely known as proton-conducting electrolytes for low-temperature hydrogen–oxygen fuel cells [4–10]. However, the application of HPAs is limited by the extreme sensitivity of their conductivity to the relative humidity (RH) and the temperature of the surrounding atmosphere [11–15]. To overcome these problems, various attempts have been made to immobilize HPAs in silica gel and to disperse it in an organically modified electrolyte membrane and organic/inorganic hybrid membranes [9, 10, 16–21]. In addition, to enable fast ionic conduction in the hybrid materials, the molecular modification of organic ligands to inorganic structures of HPAs has been continuously investigated [15, 21, 22]. For a long time, we have focused on the proton conductivity of organic/inorganic complexes based on the transition metal salts of HPAs dispersing in self-ordered hydrogen-bonded networks. Salts crystallize with fewer water molecules than the acids, and are more stable. Incorporation of salts into the self-ordered hydrogen-bonded networks protects them from dehydration and enhances their thermal stability. Moreover, each transition metal ion could form an ionized water cluster with a special hydration number and a special structure. In this work, we have succeeded in constructing a proton-conductive organic/inorganic hybrid complex by a self-assembly of protonated water clusters, transition metal aqua ions, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions and isonicotinic acid

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M.-L. Wei (✉) · H.-H. Li · X.-X. Wang · J.-H. Wang
College of Chemistry and Environmental Science,
Henan Normal University, Xinxiang 453007, China
e-mail: weimeilinh@163.com

N-oxide (HINO). Here, we report its synthesis, crystal structure, and proton conductivity as a function of temperature.

Experiment

Materials and measurements

All organic solvents and materials used for synthesis were of reagent grade and used without further purification. $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ was prepared according to a literature method [23] and characterized by IR spectra and TG analyses. HINO was synthesized according to a literature method and characterized by IR spectra [24]. Elemental analyses were carried out on a Perkin-Elmer 240C analyzer for C, H, and N, as well as on a J-A1100 ICP analyzer for P, Mo, and Cu. IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 400–4000 cm^{-1} region at room temperature. Thermogravimetric analysis was performed on a Perkin-Elmer thermal analyzer under nitrogen at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. For an electrical conductivity study, the powdered crystalline sample was compressed to about 1.0 mm in thickness and 12.0 mm in diameter under a pressure of 12–14 MPa. Ac impedance spectroscopy measurement was performed on a chi660b (Shanghai chenhua) electrochemical impedance analyzer with copper electrodes [25] (the purity of Cu is more than 99.8%) over the frequency range from 10^5 to 10 Hz. Sample was placed in a temperature-humidity controlled chamber (GT-TH-64Z, Dongwan Gaotian Corp.). The conductivity was calculated as $\sigma = (1/R) \times (h/S)$, where R is the resistance, h is the thickness, and S is the area of the tablet. Powder X-ray diffraction pattern was recorded on a Bruker D8 Advanced diffractometer in Bragg–Brentano geometry with Ni-filtered $\text{Cu K}\alpha$ ($\lambda = 1.542 \text{ \AA}$) radiation at room temperature.

Synthesis of $\{[\text{Cu}(\text{H}_2\text{O})_8][\text{H}(\text{H}_2\text{O})_3](\text{HINO})_4(\text{PMo}_{12}\text{O}_{40})\}_n$ (**1**)

The formation of heteropolyacid copper salt was accomplished by neutralization of the acid. $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ (120 mg, 0.06 mmol) and adding $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (11 mg, 0.06 mmol) dissolved in water (4 mL). The solution was heated at 80 $^{\circ}\text{C}$ in a water bath. Green crystals were formed by cooling the saturated solution and slow evaporation at room temperature, and characterized by IR spectrum. A mixture of result heteropolyacid copper salts (60 mg, 0.03 mmol) and HINO (17 mg, 0.12 mmol) dissolved in enough acetonitrile/water (1:1, v/v) to form a homogeneous solution. Finally, the solution was filtered and left to evaporate at room temperature. A week later,

yellow crystals appeared and were collected and dried in air after quickly being washed with water. Yield: 52.6 mg, 88% based on $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$. $\text{C}_{24}\text{H}_{43}\text{CuMo}_{12}\text{N}_4\text{O}_{63}\text{P}$ (2641.41): calcd. C 10.91, H 1.63, N 2.12, Cu 2.42, P 1.18, Mo 43.78; found C 10.85, H 1.66, N 2.16, Cu 2.29, P 1.02, Mo 43.59. IR (KBr disk): ν , cm^{-1} : four characteristic vibrations resulting from heteropolyanions with the Keggin structure: 803 $\nu(\text{Mo}-\text{Oc})$, 878 $\nu(\text{Mo}-\text{Ob})$, 961 $\nu(\text{Mo}=\text{Ot})$, 1065 $\nu(\text{P}-\text{Oa})$; and another vibrations resulting from the HINO molecules: 3326 $\nu(\text{O}-\text{H})$, 1697 $\nu(\text{C}=\text{O})$, 1618 $\nu(\text{C}=\text{C})$, 1204 $\nu(\text{N}-\text{O})$, 1168 $\delta(\text{C}-\text{H}, \text{in plane})$.

Crystal structure determination

Intensity data of the title complex was collected on a Siemens SMART-CCD diffractometer with graphite-monochromatic $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) using SMART and SAINT programs [26]. The structure was solved by direct methods and refined on F^2 by using full-matrix least-squares methods with SHELXTL version 5.1 [27]. All non-hydrogen atoms except solvent water molecules were refined anisotropically. Hydrogen atoms of the organic molecules were localized in their calculated positions and refined using a riding model. Hydrogen atoms of coordinated water molecules and solvent water molecules were not treated. The crystal parameters, data collection, and refinement results for the complex are summarized in Table 1, the selected bond lengths and bond angles are listed in Table 2, and the selected hydrogen bond parameters in Table 3.

Results and discussion

Structure description

The molecular structure of complex **1** was characterized by single-crystal X-ray diffraction, infrared spectroscopy, TG, and elemental analysis. X-ray diffraction analysis at 293 K revealed that the complex presented the 3D supramolecular framework built from non-covalent interactions among HINO molecules, $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ and $\text{H}^+(\text{H}_2\text{O})_3$ clusters, and $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions. Interestingly, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions self-assembled into poly-Keggin-anion chains in the supramolecular framework.

In $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ aqua complex (Fig. 1a), the Cu^{2+} ion is placed in a symmetry center and located in a coordination octahedral environment built from six water molecules (two O(1W) centers, two O(2W) centers, and two O(3W) centers), as well as two O(4W) centers are situated outside the coordination shell through short hydrogen-bonding interaction with the O(3W) centers. It should be noted that, two O(3W) centers are crystallographically disordered into

Table 1 Crystal data and structure refinement for complex **1**

Parameter	Value
Chemical formula	C ₂₄ H ₄₃ CuMo ₁₂ N ₄ O ₆₃ P
Formula weight	2641.41
Crystal system	Orthorhombic
Space group	<i>Pnnm</i>
<i>T</i> (K)	293(2)
<i>a</i> (Å)	10.364(4)
<i>b</i> (Å)	15.863(5)
<i>c</i> (Å)	19.749(6)
α (°)	90.00
<i>V</i> (Å ³)	3246.9(18)
<i>Z</i>	2
<i>D_c</i> (g cm ⁻³)	2.702
μ (mm ⁻¹)	2.711
<i>F</i> (000)	2534
<i>R_{int}</i>	0.0903
θ_{\min} , θ_{\max} (°)	3.13, 25.00
Measured reflections	26764
Independent reflections	2941
Parameters refined	270
<i>R</i> , <i>wR</i> (<i>I</i> > 2σ(<i>I</i>))	<i>R</i> ₁ = 0.0502, <i>wR</i> ₂ = 0.1144
<i>R</i> , <i>wR</i> (all data)	<i>R</i> ₁ = 0.0514, <i>wR</i> ₂ = 0.1149
Goodness-of-fit on <i>F</i>	0.993
Max, min Δρ (e Å ⁻³)	1.631, -1.109

four symmetrical positions with each oxygen site half-occupied, and two O(2W) centers are also crystallographically disordered into four symmetrical positions with each oxygen site half-occupied. In the H⁺(H₂O)₃ (the proton added to balance the charge) [28–33] (Fig. 1b), three water molecules, O(5W) and O(6W), formed an octahedral structure with each oxygen site crystallographically half-occupied. The existence of these half-occupied oxygen sites of water molecules in [Cu(H₂O)₈]²⁺ and H⁺(H₂O)₃ may be conducive to the forming of the H-bonding network and to the proton transport along the H-bonding network [34, 35]. It is far more difficult to experimentally establish the position of excess proton unambiguously for such a complex systems, since the presence of C–H vibrations of the ligand and solvent molecules, and the P–O, Mo–O vibrations of the anions all influence the observation of the IR signals of O–H vibrations related to the excess proton. X-ray diffraction analyses at 293 K revealed that the title complex crystallized in the orthorhombic space group *Pnnm*. Though the basic structure of the water cluster can be determined easily according to the result of the X-ray structure analysis, the X-ray structure is not refined at a level that can isolate the position of the hydrogens, and therefore cannot identify the position of the proton. The determination of the protonated water cluster is based on

Table 2 Selected bond lengths (Å) and angles (°) for complex **1**

Bonds	
Mo(1)–O(7)	1.657(5)
Mo(1)–O(5)	1.861(6)
Mo(1)–O(6)	1.885(7)
Mo(1)–O(4)	1.900(4)
Mo(1)–O(2)	2.467(9)
Mo(1)–O(3)	2.484(8)
Mo(1)–O(8)#1	1.914(6)
P(1)–O(3)	1.520(9)
P(1)–O(2)	1.533(12)
P(1)–O(1)	1.543(13)
Cu(1)–O(2W)	1.959(11)
Cu(1)–O(3W)	1.979(11)
Cu(1)–O(1W)	2.368(11)
Angles	
O(5)–Mo(1)–O(6)	88.6(3)
O(5)–Mo(1)–O(4)	88.8(4)
O(6)–Mo(1)–O(8)#1	85.4(3)
O(4)–Mo(1)–O(8)#1	87.2(3)
O(4)–Mo(1)–O(2)	64.0(4)
O(8)#1–Mo(1)–O(2)	64.4(4)
O(5)–Mo(1)–O(3)	63.9(3)
O(6)–Mo(1)–O(3)	63.2(3)
O(2W)–Cu(1)–O(1W)	86.9(4)
O(3W)–Cu(1)–O(1W)	96.5(4)
O(2W)#2–Cu(1)–O(3W)	89.2(5)

Symmetry transformations: #1 *x*, *y*, $-z$, #2 *x*, *y*, $-z + 1$

Table 3 Selected hydrogen bond lengths (Å) for complex **1**

D...A	<i>d</i> (D...A)	Symmetry
O(17)...O(15)	2.625(2)	$-x + 2, -y - 1, -z$
O(4W)...O(3W)	2.575(3)	
O(1W)...O(9)	2.936(3)	$-x + 1, -y, -z$
O(1W)...O(16)	2.900(3)	
O(1W)...O(5W)	3.062(3)	
O(2W)...O(12)	2.820(3)	$-x + 1, -y, z$
O(2W)...O(15)	2.613(2)	$x - 3/2, -y - 1/2, z - 1/2$
O(3W)...O(15)	2.866(2)	$x - 3/2, -y - 1/2, z - 1/2$
O(3W)...O(5W)	3.194(3)	$-x + 2, -y, z + 1$
O(4W)...O(9)	2.889(3)	$-x + 1, -y, -z$

the stoichiometry, the crystal data and relative references. It was reported that based on high-resolution solid-state ¹H and ³¹P NMR, there were at least three different states for protons of H₃PW₁₂O₄₀·*n*H₂O (i) protons present in highly hydrated samples, (ii) protonated water which is hydrogen-bonded to terminal oxygen, W = O...H⁺(H₂O)₂ (*n* = 6), and (iii) proton which is directly bonded to bridging oxygen, W–OH–W (*n* = 0) [36]. More recently, it was

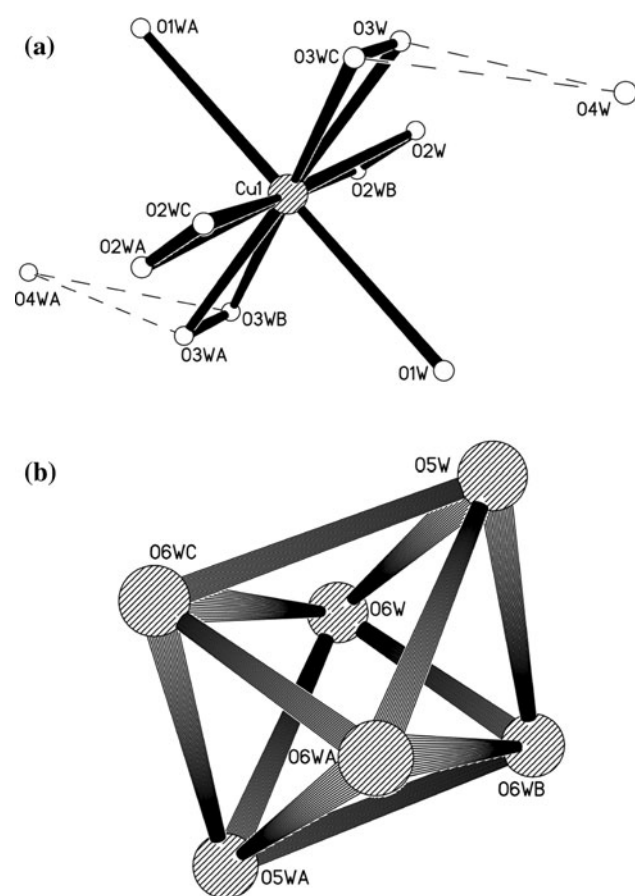


Fig. 1 Views of $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ (a) and $\text{H}^+(\text{H}_2\text{O})_3$ (b) clusters. Hydrogen atoms are omitted for clarity

reported that based on REDOR experiments acidic protons are localized on both bridging (O_c) and terminal (O_d) oxygen atoms of the Keggin unit in the anhydrous state of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ [37]. In title complex, there are three lattice water molecules and the separations between them are enough short to stabilize the excess proton to form such an oligomer as H_7O_3^+ , so, we think that the excess proton is not localized on the surface of the polyanion [28–33].

Interestingly, HINO molecules are not bound to the Cu^{2+} ion, but remaining outside the coordination shell to form hydrogen-bonded chains along the b axis (Fig. 2). Two oxygen atoms $\text{O}(15)(\text{N}-\text{O})$ and $\text{O}(17)(\text{O}-\text{H})$ of each HINO molecule are involved in the hydrogen-bonded chains. As shown in Fig. 3, these HINO hydrogen-bonded chains are linked together by $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ aqua complexes and small $\text{H}^+(\text{H}_2\text{O})_3$ clusters into a 3D cationic network with large 1D channels through hydrogen bonds between coordination water molecules $\text{O}(2\text{W})$ and oxygen atoms $\text{O}(15)$ of HINO molecules, as well as through weak hydrogen bonds between coordination water molecules and oxygen atoms of HINO molecules. Thus, all O atoms of each HINO molecule are involved in the hydrogen bonds, creating a 3D supramolecular assembly with 1D channels.

Moreover, there are hydrogen-bonding interaction between water molecules $\text{O}(5\text{W})$ in the $\text{H}^+(\text{H}_2\text{O})_3$ clusters and $\text{O}(1\text{W})$ and $\text{O}(3\text{W})$ centers of the $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ cluster. The section size of the channels based on the $\text{M}\cdots\text{M}$ separations is ca. $10.3 \times 16.0 \times 19.8 \text{ \AA}$, indicating that each pore could only accommodate a single Keggin anion. Interestingly, the $\text{M}\cdots\text{M}$ separation bridged by the $\text{H}^+(\text{H}_2\text{O})_3$ clusters along the a axis is much shorter than other two separations along the b and c axes, and even shorter than the diameter of the discrete $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anion (ca. 10.4 \AA), resulting in each cavity being heavily condensed along the a axis. In addition, the presence of positively charged species, $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ and $\text{H}^+(\text{H}_2\text{O})_3$ clusters, could attract the polyanions, as a result, the Keggin-type $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions for charge compensation are embedded in the voids of the 3D cationic framework and connect to one another leading to poly-Keggin-anion chains in the channel along the a axis (Fig. 4). In the polymeric polyanion, there are some short atom \cdots atom separations of $2.77(2) \text{ \AA}$, such as $\text{O}(7\text{A})\cdots\text{O}(8\text{BB})$, $\text{O}(8\text{A})\cdots\text{O}(7\text{BB})$, $\text{O}(7\text{AA})\cdots\text{O}(8\text{CB})$, $\text{O}(7\text{CB})\cdots\text{O}(8\text{AA})$.

In the $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ unit, the central P atom is surrounded by a cube of eight oxygen atoms with each oxygen site half-occupied. These eight oxygen atoms are all crystallographically disordered, and this case can be found in many compounds [28–33]. In complex 1, the bond lengths of P–O and Mo–O are $1.520(9)$ – $1.543(13)$ and $1.644(8)$ – $2.487(9) \text{ \AA}$, respectively. In addition, the O–P–O angles are in the range of $108.5(7)$ – $110.3(4)^\circ$. All these results indicate that the $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ units have a normal Keggin structure in the polymeric-polyanion chains. The poly-Keggin-type anions play not only a charge-compensating role, but they can dramatically influence the overall solid-state architecture through their templating function, as well as the cationic framework with special channels also influences the polymerization of polyanions through its host function. In addition, several hydrogen bonds exist between the poly-Keggin-anion chain and the channel, such as between the $\text{O}(1\text{W})$, $\text{O}(3\text{W})$, and $\text{O}(4\text{W})$ centers belong to the $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ clusters and $\text{O}(9)$ and $\text{O}(12)$ centers of the polyanions. As a result, based on self-assembly of HINO molecules, $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ and $\text{H}^+(\text{H}_2\text{O})_3$ clusters, the complex forms 3D hydrogen-bonding network with 1D channels along the a axis, in which poly-Keggin anions chains were formed and stabilized based on electrostatic and H-bonding interactions, resulting in $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions being not easy dissociated from the hybrid networks. Moreover, the section size of the channels along the b and c axes is so larger than the diameter of the $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anion (ca. 10.4 \AA), that there is enough space outside the poly-Keggin-anion chains to admit some small species, such as water molecules or hydronium ions, to transport along the channels. All these

Fig. 2 View of the 1D HINOs chain along the *b* axis. Hydrogen atoms are omitted for clarity

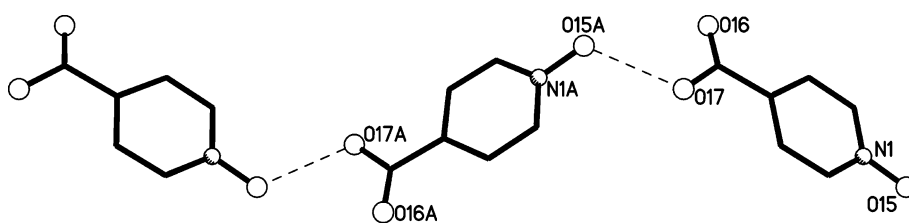
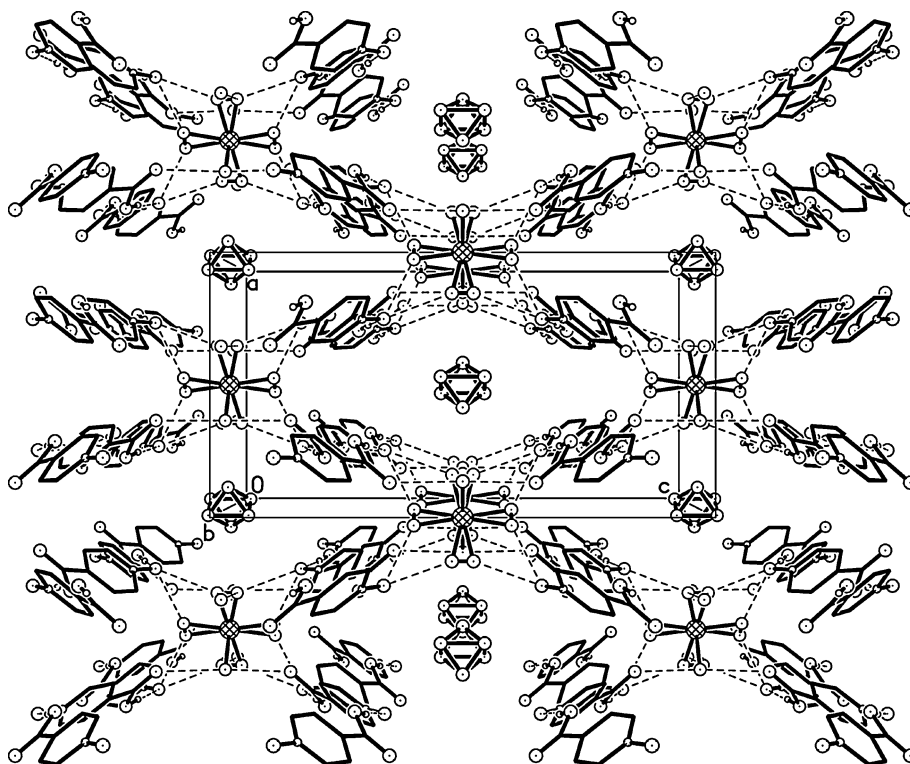


Fig. 3 The 3D hydrogen-bonded network constructed by HINO molecules, $[\text{Cu}(\text{H}_2\text{O})_8]^{2+}$ and $\text{H}^+(\text{H}_2\text{O})_3$ clusters. Hydrogen atoms are omitted for clarity



results indicate that **1** can potentially be a new good proton-conducting material.

TG analysis

The title complex is insoluble in water (see the UV spectra analyses in Supplementary data). Water retention in the hybrid at high temperature is a key factor for having fast protonic conduction [9, 10, 16–21]. Thermogravimetric analysis of the powder of the crystalline sample of the complex in an atmosphere of N_2 (Fig. 5) shows no weight loss in the temperature range of 20–100 °C, indicating that all water molecules in the unit structure are involved in constructing the H-bonding network, which is consistent with the result of structural analysis, and are not easily lost below 100 °C. This is not like that observed in the proton conductors including the quasi-liquid water clusters (which are generally loosely bonded in the structure) like a Nafion membrane [3, 12, 38, 39], and pure tungstophosphoric acid (PWA-26) or molybdophosphoric acid (PMA-26), as well as many proton-conducting composite membranes doped

with HPAs [4, 6–15]. Interestingly, as shown in Fig. 6b, the powder X-ray diffraction analysis suggested that the global framework in the complex is retained when the water are lost at 200 °C. All these results also indicate that **1** can potentially be a good proton-conducting material.

Proton conductivity

The proton conductivity of **1** in the temperature range of 25–100 °C is therefore evaluated by the ac impedance method using a compacted pellet of the powdered crystalline sample. At 25 °C, the complex showed poor proton conductivity of $\sim 9.0 \times 10^{-9} \text{ S cm}^{-1}$ under 35% RH condition, estimated from the Nyquist plots shown in Supplementary data, but its proton conductivity reached $\sim 3.9 \times 10^{-6} \text{ S cm}^{-1}$ with RH up to 98%. Again, we measured its ionic conductivity up to 100 °C under 98% RH condition. Surprisingly, the complex reached good proton conductivity of $1.32\text{--}2.81 \times 10^{-3} \text{ S cm}^{-1}$ in the temperature range of 85–100 °C. These proton conductivities are about two orders of magnitude lower than that of a

Fig. 4 The 3D hydrogen-bonded network showing the 1D channels filled by polyanion chains down the *a* axis (*top*), and view of the polyanion chain along the *a* axis (*bottom*). Hydrogen atoms are omitted for clarity

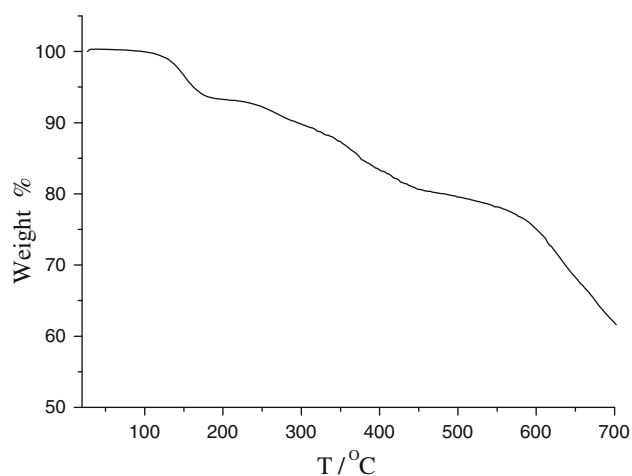
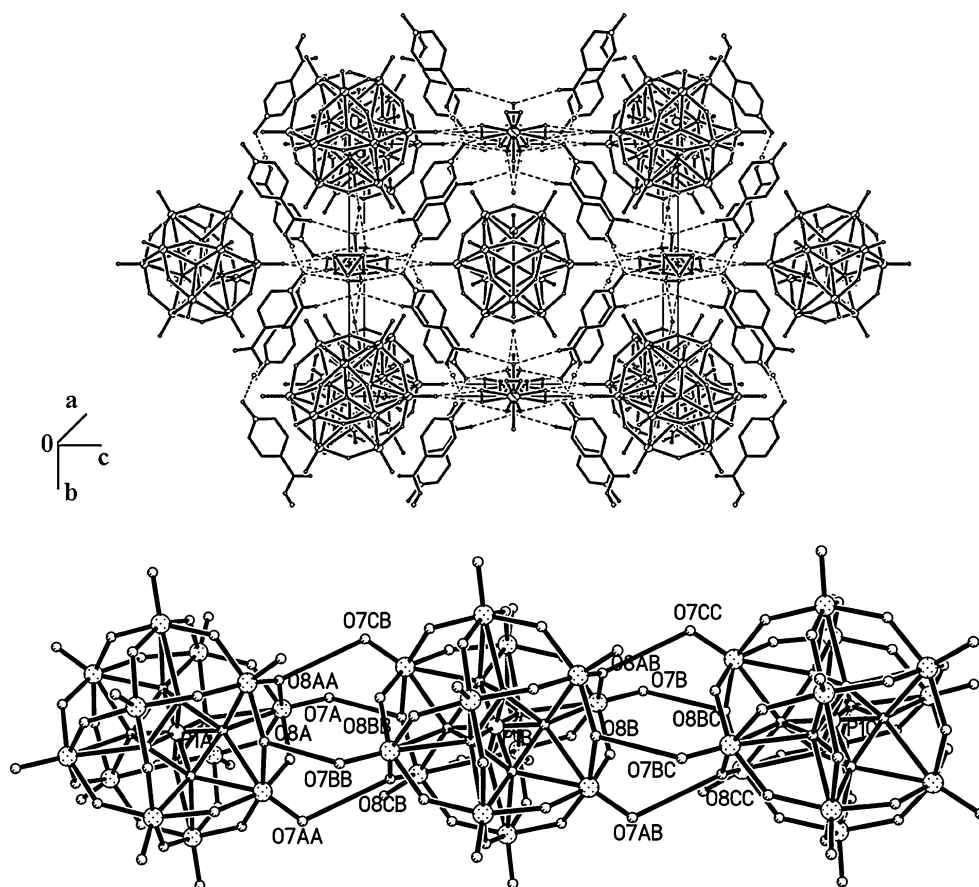


Fig. 5 The curve of the thermogravimetry analysis of complex **1** in the atmosphere of N₂

Nafion membrane, which shows conductivity of about 10^{-1} S cm⁻¹ in the conditions described [3, 12, 38, 39].

Figure 7 shows the Arrhenius plots of the proton conductivity of the complex in the temperature range of 25–100 °C under 98% RH condition. The $\ln \sigma T$ increases almost linearly with temperature range from 25 to 100 °C,

and the corresponding activation energy (E_a) of conductivity was estimated to be 0.73 eV from the equation below.

$$\sigma T = \sigma_0 \exp(-E_a/k_B T) \quad (1)$$

where σ is the ionic conductivity, σ_0 is the preexponential factor, k_B is the Boltzmann constant, and T is the temperature. The E_a value is very high. These results show that the general features of the changes in conductivities are different from that of protonic conducting polymer membrane such as Nafion, which has almost identical protonic conductivity over a wide temperature range from ambient to 100 °C with activation enthalpy of approximately 0.15 eV, when it is fully humidified [3, 12, 38, 39], and are different from that of PWA-26 or PMA-26, whose protonic conductivity decreased with the temperature from ambient to 60 °C [4, 6–15]. However, the title complex has thermally activated protonic conductivity [11, 14] from 25 to 100 °C; as the temperature increases, the proton conductivity increases on a logarithmic scale even with almost saturated humidities. This is probably due to the fact that protons belong to the protonated water clusters and those originating from water molecules need a thermally activated process for dissociation as hydrated forms such as H⁺,

Fig. 6 The powder X-ray diffraction data of the simulated powder pattern (a), the powder before the proton-conductive measurement (b), the powder after the proton-conductive measurement (c), and the powder of crystalline sample after heating polycrystals at 473 K for 20 min and subsequently cooling to 293 K (the whole process was performed in vacuum) (d)

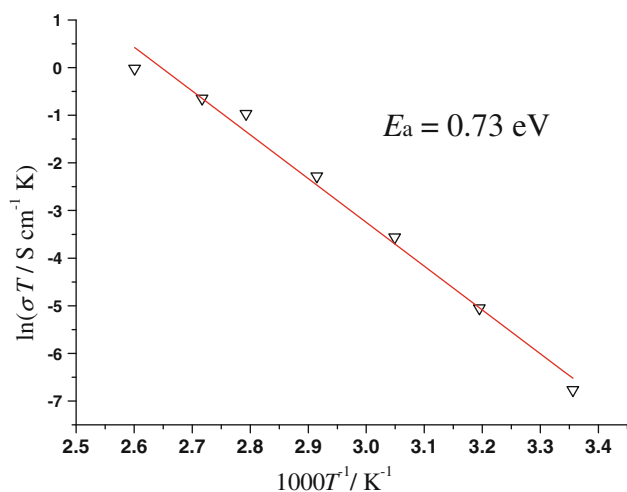
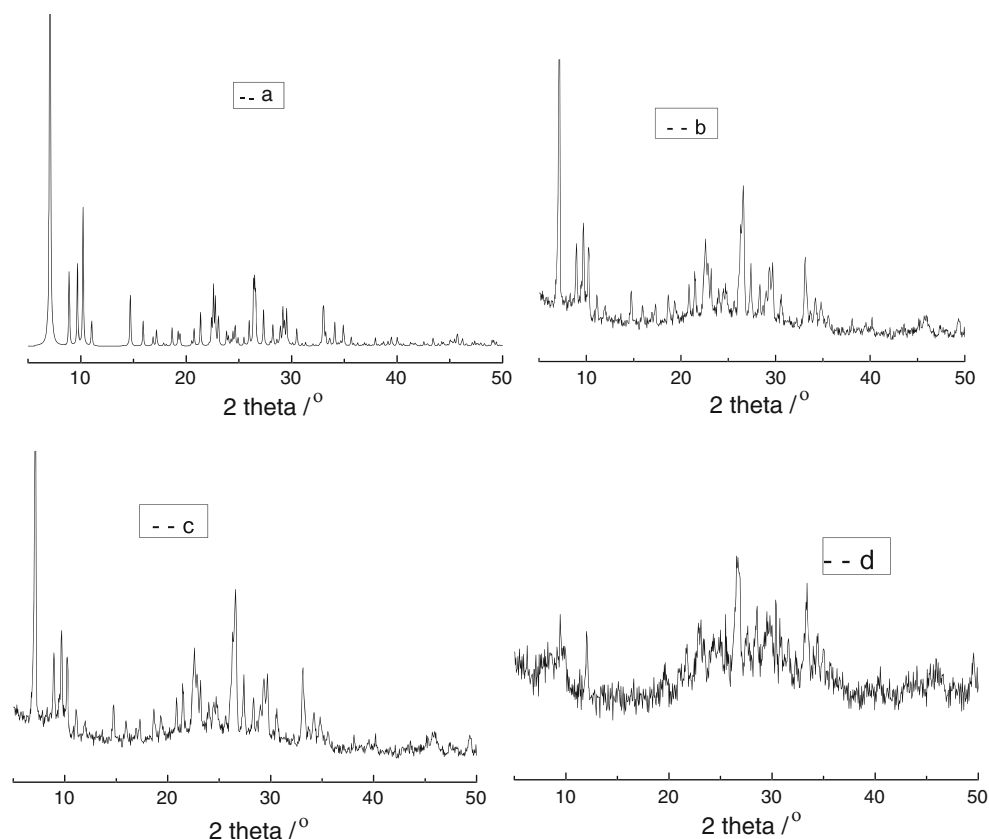


Fig. 7 The Arrhenius plot of the proton conductivity of complex **1**

H_3O^+ or other proton species at a distance from $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ clusters [14, 40, 41]. The mechanism of proton conduction of **1** is, therefore, expected to be similar to that of the vehicle mechanism [42], that is, the direct diffusion of additional protons with water molecules. In addition, the existence of H-bonding networks suggests that proton conduction in the complex includes some other process such as proton transport of additional protons along H-bonding networks (Grotthus mechanism) [43]. The fact

that the complex exhibits good proton conductivity in the temperature range of 85–100 °C is indicative of a high carrier concentration based on a thermally activated process, as well as the existence of H-bonding networks. Moreover, there is the possibility of hydrolysis of the complex when it is held at 100 °C with a RH higher than 98% (100%, or condensed water that attack the metal centers). The powder X-ray diffraction data in Fig. 6c suggested that the powder sample after the proton-conductive measurement have the same supramolecular framework as that of complex **1**. The proton conductivities of the title complex were also measured at 100 °C in the RH range 35–98% by a complex-plane impedance method. Figure 8 shows the $\log \sigma$ (S cm^{-1}) versus RH plots of complex **1** at 100 °C under 35–98% RH. The conductivity under 35% RH is $\sim 3.95 \times 10^{-5} \text{ S cm}^{-1}$, and the conductivity increases with RH to reach a high conductivity of $1.70\text{--}2.81 \times 10^{-3} \text{ S cm}^{-1}$ in the range 60–98% RH.

Conclusions

A good proton-conductive organic–inorganic complex has been constructed by introducing Keggin-type $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ anions as counteranions and templates into the 3D cationic hydrogen-bonded networks formed by mixed ionized water

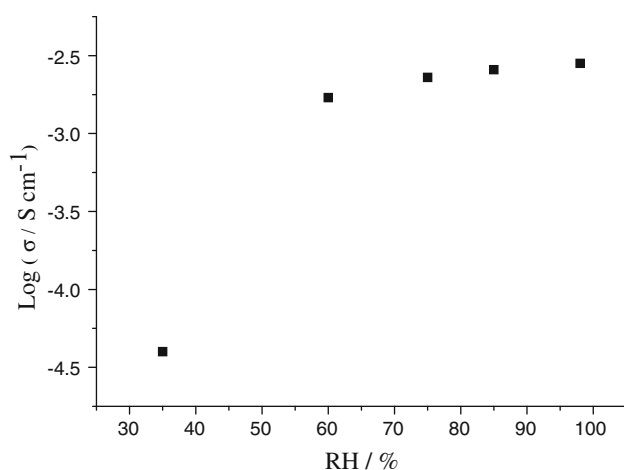


Fig. 8 Log σ (S cm⁻¹) versus RH plots of complex **1** at 100 °C

clusters and HINO molecules. The complex provides a new route in increasing the stability and proton conductivity of organic–inorganic hybrid materials based on salts of HPAs at high temperature, as well as may become a new type of proton-conducting additives in proton exchange composite membranes for use under dry and/or elevated temperature conditions of fuel cell.

Supplementary data

Crystallographic data for the complex in this article have been deposited at the Cambridge Crystallographic Data Center (CCDC) as supplementary publication, CCDC 807158. Copies of the data can be obtained free of charge from the CCDC, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; Email: deposit@ccdc.ac.uk; url: www.ccdc.cam.ac.uk. The Nyquist plots for the complex at 25–100 °C under 98% relative humidity and the UV spectra.

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