第 28 卷第 11 期 无 机 化 学 学 报 Vol.28 No.11
2012 年 11 月 CHINESE JOURNAL OF INORGANIC CHEMISTRY 2485-2493

基于 Keggin 阴离子链镍化合物的结构和质子导电性

魏梅林* 王晓湘 李会华
(河南师范大学化学与环境科学学院,新乡 453007)

摘要:由 $H^+(H_2O)_{2.5}$ 阳离子,$[Ni(H_2O)_8]^{2+}$阳离子,$[PW_{12}O_{40}]^{3-}$阴离子和异烟酸氮氧化物(HINO)自组装成一个具有质子导电性的化合物$\{[Ni(H_2O)_8][H(H_2O)_{2.5}](HINO)_4(PW_{12}O_{40})\}_n$。293 K 的单晶 X-射线衍射分析表明标题化合物形成 1 个带有一维通道的三维氢键网络结构。$[PW_{12}O_{40}]^{3-}$阴离子填充在一维通道内并且自组装成多阴离子链。热重分析表明在 20~100 ℃范围内化合物没有失重,表明化合物结构单元内所有的水分子在 100 ℃以下不易失去。标题化合物在 85~100 ℃范围内表现出好的离子导电性(1×10^{-3}~2×10^{-3} $S\cdot cm^{-1}$)。

关键词:杂多酸;晶体结构;镍(Ⅱ)配合物;异烟酸氮氧化物
中图分类号:O614.81+3 **文献标识码**:A **文章编号**:1001-4861(2012)11-2485-09

Crystal Structure and Proton-Conductivity of a Nickel(Ⅱ) Complex Constructed by Poly-Keggin-anion Chains

WEI Mei-Lin* WANG Xiao-Xiang LI Hui-Hua
(*College of Chemistry and Environmental Science, Henan Normal University, Xinxiang, Henan* 453007, *China*)

Abstract: A proton-conductive complex $\{[Ni(H_2O)_8][H(H_2O)_{2.5}](HINO)_4(PW_{12}O_{40})\}_n$, was constructed by a self-assembly of cations, $[Ni(H_2O)_8]^{2+}$ cations, $[PW_{12}O_{40}]^{3-}$ anions and isonicotinic acid N-oxide (HINO). Single-crystal X-ray diffraction analysis at 293 K revealed that the title complex presented exactly a three-dimensional (3D) hydrogen-bonded network with large one-dimensional (1D) channels. Interestingly, $[PW_{12}O_{40}]^{3-}$ anions just filled in the 1D channels and self-assembled into poly-Keggin-anion chains. Thermogravimetric analysis shows no weight loss in the temperature range of 20~100 ℃, indicating that all water molecules in the unit structure are not easily lost below 100 ℃. The title complex was characterized by a satisfactory ionic conductivity (1×10^{-3}~2×10^{-3} $S\cdot cm^{-1}$) in the temperature range 85 to 100 ℃. CCDC: 825709.

Key words: polyoxometalates; crystal structure; nickel(Ⅱ) complex; isonicotinic acid N-oxide

Keggin-type heteropolyacids (HPAs), possessing a unique discrete ionic structure including heteropoly anions and countercations (H^+, H_3O^+, $H_5O_2^+$, etc.), are widely known as proton conducting electrolytes for low-temperature hydrogen-oxygen fuel cells[1]. 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[2]. 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[3-4]. 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[5]. For a long time,

收稿日期:2012-10-18。收修改稿日期:2012-08-03。
国家自然科学基金(No.20971038,21171050)资助项目。
*通讯联系人。E-mail:weimeilinhd@163.com

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 enhanced 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, $[PW_{12}O_{40}]^{3-}$ anions and isonicotinic acid N-oxide (HINO). Here, we report its synthesis, crystal structure, and proton conductivity as a function of temperature.

1 Experimental

1.1 Materials and instruments

All organic solvents and material used for synthesis were of reagent grade and used without further purification. α-$H_3PW_{12}O_{40}\cdot 6H_2O$ was prepared according to a literature method[6] and characterized by IR spectra and TG analyses. HINO was synthesized according to a literature method and characterized by IR spectra [7]. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analyzer. X-ray powder diffraction (XRD) was performed on a Bruker D8 Advanced Instrument using Cu $K\alpha$ radiation and a fixed power source (40 kV, 40 mA). IR spectra were recorded on a VECTOR 22 Bruker spectrophotometer with KBr pellets in the 400~4 000 cm^{-1} region at room temperature. Thermogravimetric analysis was performed on a Perkin-Elmer thermal analyzer under nitrogen at a heating rate of 10 ℃·min^{-1}. For an electrical conductivity study, the powdered crystalline samples were 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[8] (the purity of Cu is more than 99.8%) over the frequency range from 10^5 to 10 Hz. Samples were 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.

1.2 Synthesis of the title complex

The formation of heteropolyacid nickel salts was accomplished by neutralization of the acids. α-$H_3PW_{12}O_{40}\cdot 6H_2O$ (180 mg, 0.06 mmol) and adding $NiCl_2\cdot 6H_2O$ (15 mg, 0.06 mmol) dissolved in water (4 mL). The solution was heated at 80 ℃ in a water bath. Light 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 nickel salts (90 mg, 0.03 mmol) and HINO (17 mg, 0.12 mmol) was dissolved in enough acetonitrile/water (1∶1, V/V) to form a homogeneous solution. Finally, the solution was filtered and the solvent left to evaporate at room temperature. A week later, light blue crystals appeared and were collected and dried in air after quickly being washed with water. Yield: 76.4 mg, 85% based on α-$H_3PW_{12}O_{40}\cdot 6H_2O$. Molecular formula is $C_{24}H_{42}NiW_{12}N_4O_{62.5}P$. Elemental analysis calcd.(%): C, 7.83; H, 1.15; N, 1.52. Found (%): C, 7.92; H, 1.28; N, 1.61. Main IR bands (cm^{-1}): four characteristic vibrations resulting from heteropolyanions with the Keggin structure: 813 ν(W-Oc), 896 ν(W-Ob), 981 ν(W=Ot), 1 081 ν(P-Oa); and another vibrations resulting from the HINO molecules: 3 326 ν(O-H), 1 704 ν(C=O), 1 618 ν(C=C), 1 280 ν(N-O), 1 172 δ(C-H, in plane).

1.3 X-ray diffraction analysis

Intensity data of the title complex was collected on a Bruker SMART-CCD area detector with graphite-monochromatic Mo $K\alpha$ radiation λ=0.071 073 nm using SMART and SAINT programs[9]. The structure was solved by direct methods and refined on F^2 by using full-matrix least-squares methods with SHELXTL version 5.1[10]. All non-hydrogen atoms except solvent water molecules were refined anisotropically. Two O (3W) centers are crystallographically disordered into four symmetrical positions with each oxygen site half-

Table 1　Crystal and structure refinement data for 1

Empirical formula	$C_{24}H_{42}N_4NiO_{62.5}PW_{12}$	θ range / (°)	2.22~25.00
Formula weight	3682.5	F(000)	3 290
Temperature / K	293(2)	Reflns collected (R_{int})	27 185 (0.172 1)
Crystal system	Orthorhombic	Indep. reflns	2991
Space group	*Pnnm*	Refns obs. ($I>2\sigma(I)$)	2 742
a / nm	1.034 4(3)	Refinement method	Full-matrix least squares on F^2
b / nm	1.600 1(5)	GOF	1.038
c / nm	1.9859(6)	Data / restraints / parameters	2 991 / 6 / 270
V / nm^3	3.288 9(17)	Final weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.077\ 6P)^2+0.023\ 7P]$, $P=(F_o^2+2F_c^2)/3$
Z	2	R_1 / wR_2 ($I>2\sigma(I)$)	0.053 1 / 0.132 0
D_c / (g·cm^{-3})	3.718	R_1 / wR_2 (all data)	0.056 0 / 0.135 3
Absorp. coeff. / mm^{-1}	21.32	Larg. peak / hole / (e·nm^{-3})	4 032 / −3 235

Table 2　Selected bond lengths (nm) and angles (°) for 1

W(2)-O(11)	0.166 9(8)	W(2)-O(1A)	0.247 2(13)	Ni(1)-O(1W)	0.205 2(15)
W(2)-O(5)	0.188 3(9)	W(2)-O(2B)	0.249 0(13)	Ni(1)-O(2W)	0.200 7(19)
W(2)-O(14A)	0.188 7(10)	P(1)-O(2)	0.152 4(19)	Ni(1)-O(3W)	0.205(2)
W(2)-O(4A)	0.188 8(10)	P(1)-O(3)	0.155(2)		
W(2)-O(10)	0.190 8(6)	P(1)-O(1)	0.156 1(13)		
O(5)-W(2)-O(4A)	86.4(5)	O(14A)-W(2)-O(1A)	61.8(5)	O(3WA)-Ni(1)-O(1W)	87.3(8)
O(14A)-W(2)-O(4A)	88.0(4)	O(4A)-W(2)-O(1A)	63.2(5)	O(2W)-Ni(1)-O(3WC)	89.8(10)
O(5)-W(2)-O(10)	88.5(5)	O(5)-W(2)-O(2B)	63.8(6)	O(2W)-Ni(1)-O(1W)	87.5(10)
O(14A)-W(2)-O(10)	87.1(6)	O(10)-W(2)-O(2B)	65.6(6)		

Symmetry code: A: $-x+4$, $-y$, z; B: $-x+4$, $-y$, $-z-2$; C: x, y, $-z-1$.

occupied, and two O(2W) centers are also crystallographically disordered into four symmetrical positions with each oxygen site half-occupied. The O(5W) with the occupancy of 50% is placed in a symmetry center and located in a tetragonal environment built from two water molecules(O(6W) and O(7W) centers), which are crystallographically disordered into two symmetrical positions with each oxygen site half-occupied, respectively. Hydrogen atoms of the organic molecules were localized in their calculated positions and refined using a riding model. Hydrogen atoms of water molecules (O(1W) and O(4W)) were localized by difference Fourier maps and refined by fixing the isotropic temperature factors 1.2 times that of mother atoms attached. Hydrogen atoms of coordination water molecules (O(2W) and O(3W)) and solvent water molecules were not treated because these oxygens are crystallographically disordered. The biggish absolute values of the final $(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$ might result from the many heavy metal atoms (W) in the title compound. The final $(\Delta\rho)_{max}$ and $(\Delta\rho)_{min}$ are located the W atoms. The crystal parameters, data collection and refinement results for the title 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.

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2　Results and discussion

2.1　IR spectra

Comparison of the IR spectra of heteropolyacid nickel salts, isonicotinic acid N-oxide and the studied crystal shows that the ν(C=O) band at 1 710 cm^{-1} and the ν (N-O) band around 1 280 cm^{-1} in spectrum of free HINO molecules[11] remains around the similar position in the complex, indicating that these groups are not involved in complex formation. The IR spectroscopic studies show that there are not strong interactions

Table 3 Selected hydrogen bond lengths and bond angles for 1

D–H···A(D···A)	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
O(1W)–H(1WA)···O(16A)	0.085	0.211	0.295(1)	169.47
O(17)–H(17A)···O(15A)	0.082	0.184	0.265(2)	169.8
O(4W)–H(4WB)···O(3W)	0.085	0.193	0.262(3)	137.9
O(2W)···O(9)			0.281(3)	
O(2W)···O(15B)			0.272(2)	
O(2W)···O(16D)			0.306(3)	
O(3W)···O(15B)			0.290(3)	
O(6W)···O(7W)			0.267(2)	
O(6W)···O(15C)			0.281(3)	
O(7W)···O(1WE)			0.299(2)	
O(4W)···O(10F)			0.306(2)	
O(4W)···O(12G)			0.285(2)	

Symmetry code: A: $-x+3/2$, $y+1/2$, $z-1/2$; B: $x+3/2$, $-y+1/2$, $-z$; C: $x+1$, y, z; D: $x+2$, $y+1$, $-z$; E: $x-1$, y, z; F: x, $y+1$, $-z+1$; G: $-x+4$, $-y$, $-z-2$.

between the metal ions and the organic groups in the solid state. The proton polarizabilities are particularly large in the case of hydrogen-bonded chains because in such chains a collective proton-tunnelling occurs. In the FT-IR spectra, these hydrogen bonds or hydrogen-bonded chains are manifested as continua because they interact very strongly with their environments because of large proton polarizabilities, and vice versa hydrogen bonds and hydrogen-bonded chains with large proton polarizabilities are indicated by these IR continua. Thus, such hydrogen-bonded chains are very effective proton pathways. They conduct protons within picoseconds. Water molecules are highly ordered for the entropic reasons if they are in a hydrophobic environment. Therefore, they build up a particularly stable pathway. An IR continuum indicates that this system shows proton polarizability due to collective proton motion.

2.2 Structure description

The title complex, $\{[Ni(H_2O)_8][H(H_2O)_{2.5}](HINO)_4(PW_{12}O_{40})\}_n$, was synthesized by the reaction of $NiHPW_{12}O_{40}\cdot nH_2O$ and HINO at room temperature. It was characterized by single-crystal X-ray diffraction, infrared spectroscopy, TG and elemental analyses. X-ray diffraction analysis at 293 K revealed that the title complex presented a 3D supramolecular framework built from non-covalent interactions among HINO molecules, $[Ni(H_2O)_8]^{2+}$ and $H^+(H_2O)_{2.5}$ cations, and $[PW_{12}O_{40}]^{3-}$ anions. Interestingly, $[PW_{12}O_{40}]^{3-}$ anions self-assembled into poly-Keggin-anion chains in the supramolecular framework.

In $[Ni(H_2O)_8]^{2+}$ cations (Fig.1a), the Ni^{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 coordination water molecule. It should be noted that two O(3W) centers are crystallographically disordered into four symme-trical 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[12]. In the $H^+(H_2O)_{2.5}$ (the proton added to balance the charge)[11] (Fig.1b), 2.5 water molecules, O(5W), O(6W) and O(7W), formed an tetragon structure.

HINO is a good mono- or bidentate ligand for the construction of supramolecular complexes with versatile binding modes. Until now, a large number of metal-organic framework structures containing HINO ligands have been reported[11]. Interesting, in the title complex, HINO molecules are not bound to the Ni^{2+} ion, but remaining outside the coordination shell to form hydrogen-bonded chains along the b axis (Fig.2). Two oxygen atoms O(15)(N-O) and O(17)(O-H) of each

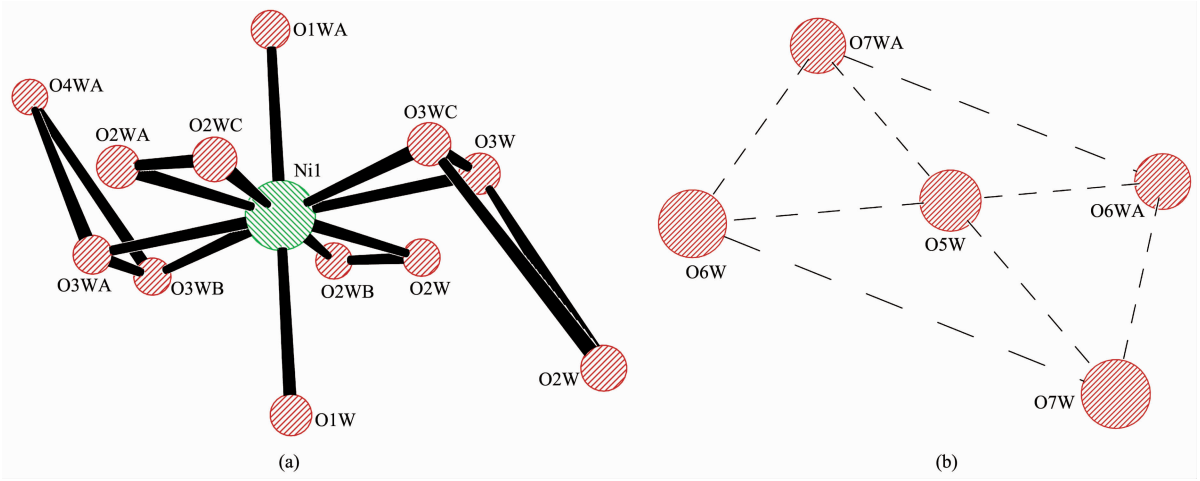

Fig.1　Views of $[Ni(H_2O)_8]^{2+}$ (a) and $H^+(H_2O)_{2.5}$ (b) cations

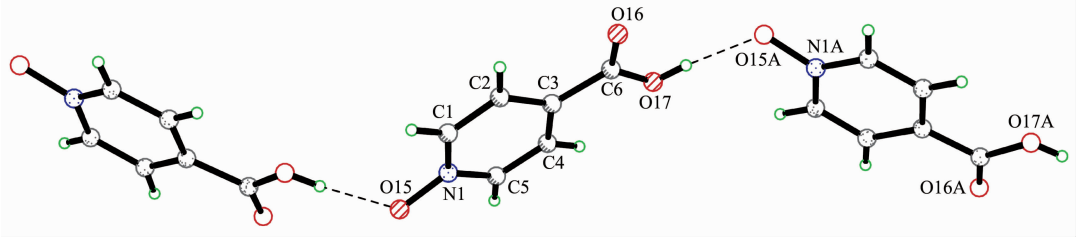

Fig.2　View of the 1D HINOs chain along the *b* axis

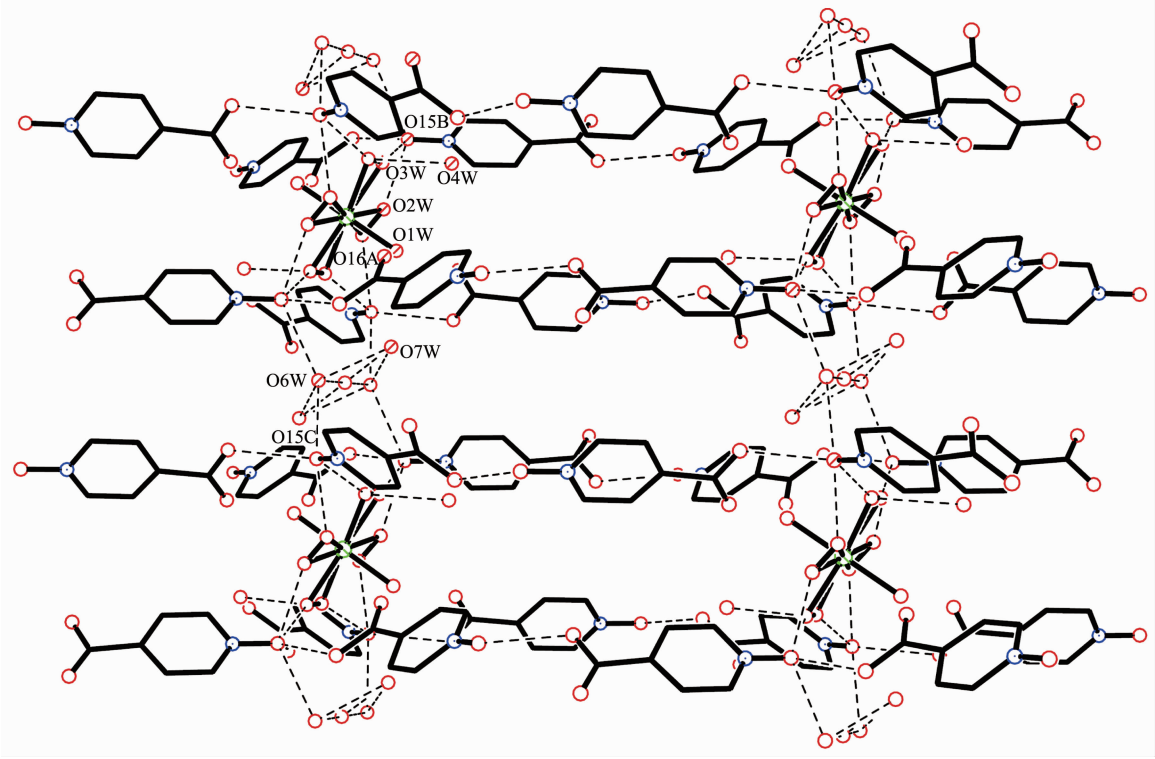

Fig.3　3D hydrogen-bonded network constructed by HINO molecules, $[Ni(H_2O)_8]^{2+}$ and $H^+(H_2O)_{2.5}$ cations

HINO molecule are involved in the hydrogen-bonded chains. As shown in Fig.3, these HINO hydrogen-bonded chains are linked together by $[Ni(H_2O)_8]^{2+}$ aqua-complexes and small $H^+(H_2O)_{2.5}$ cations into a 3D cationic network with large 1D channels through hydrogen bonds between coordination water molecules

O(2W) and oxygen atoms 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 weakly hydrogen-bonding interaction between water molecules O(7W) in the $H^+(H_2O)_{2.5}$ cations and O(1W) center of the $[Ni(H_2O)_8]^{2+}$ cations. The section size of the channels based on the Ni⋯Ni separations is ca. 1.04 nm×1.60 nm×1.98 nm for the title complex (these separations are equal to three axial lengths respectively), indicating that each pore could only accommodate a single Keggin anion. Interestingly, the adjacent Ni ⋯ Ni separation 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 $[PW_{12}O_{40}]^{3-}$ anion (*ca.* 1.05 nm), resul-ting in each cavity being heavily condensed along the a axis. In addition, the presence of positively charged species, $[Ni(H_2O)_8]^{2+}$ and $H^+(H_2O)_{2.5}$ cations, could attract the polyanions, as a result, the Keggin-type $[PW_{12}O_{40}]^{3-}$ 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 atomatom separations of 0.279(2) nm, such as O(7A)⋯O(8BB), O(8A)⋯O(7BB), O(7AA)⋯O(8CB), O(7CB)⋯O(8AA).

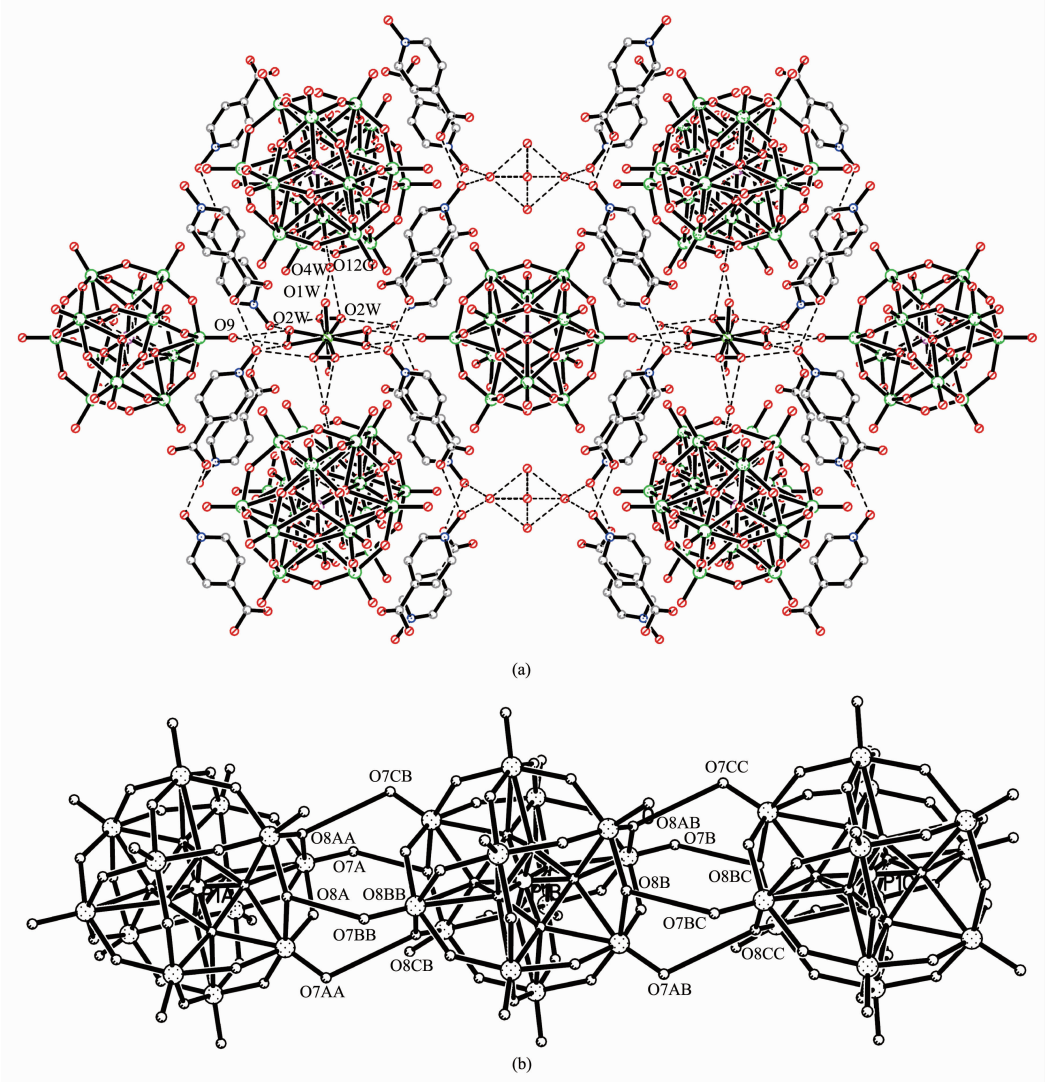

Fig.4 3D hydrogen-bonded network showing the 1D channels filled by poly-anion chains down the *a* axis (a), and view of the poly-anion chain along the *a* axis (b)

In the $[PW_{12}O_{40}]^{3-}$ 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[13]. In the title complex, the bond lengths of P-O and W-O are 0.151(2)~0.156 4 (19) and 0.166 6 (8)~0.249 6 (18) nm respectively. The bond lengths of P-O and W-O in the title complex are respectively comparable to those in the 3D porous polyoxometalates-based organic-inorganic hybrid materials with Keggin anions as guests[13]. In addition, the O-P-O angles are in the range of 108.3(6)° ~111.4 (6)° for the title complex. All these results indicate that the $[PW_{12}O_{40}]^{3-}$ 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 water molecules (O(1W), O(2W) and O(4W)) belong to the $[Ni(H_2O)_8]^{2+}$ cations and oxygen atoms of the polyanions (O(9), O(10) and O(12) centers). As a result, based on the self-assembly of HINO molecules, $[Ni(H_2O)_8]^{2+}$ and $H^+(H_2O)_{2.5}$ cations, the title complex form 3D hydrogen-bonding networks 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 $[PW_{12}O_{40}]^{3-}$ anions being not easy dissociated from the hybrid network. Moreover, the section size of the channels along the *b* and *c* axes is so larger than the diameter of the $[PW_{12}O_{40}]^{3-}$ anion (*ca.* 1.05 nm) 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 results indicate that the title complex can potentially be a new good proton-conducting material.

2.3 TG Analysis

The complex is insoluble in water. Water retention in the hybrid at high temperature is a key factor for having fast protonic conduction[8-9]. 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 ℃, 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 ℃. 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 pure tungstophosphoric acid with 26 water molecules (PWA-26) or molybdophosphoric acid with 26 water molecules (PMA-26), as well as many proton-conducting composite membranes doped with HPAs[1-2].

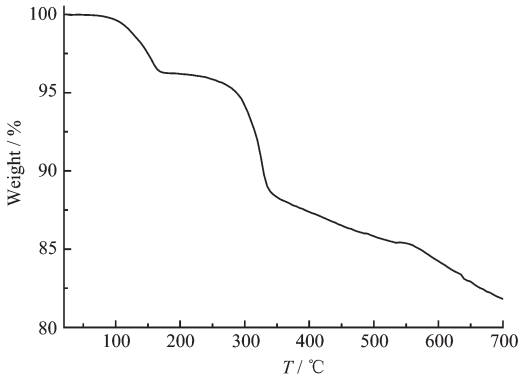

Fig.5　Curve of the thermogravimetric analysis of **1** in the atmosphere of N_2

2.4 Proton conductivity

The proton conductivities of the title complex in the temperature range of 25~100 ℃ under 98% RH conditions were evaluated by the ac impedance method using a compacted pellet of the powdered crystalline sample, which has the same structure as the single-crystal (Fig.6). Surprisingly, the title complex reached good proton conductivities of 1×10^{-3} ~2.1×10^{-3} $S\cdot cm^{-1}$ in the temperature range of 85~100 ℃, estimated from the Nyquist plots.

Fig.7 shows the Arrhenius plots of the proton conductivities of the title complex in the temperature range of 25~100 ℃ under 98% RH conditions. The $\ln(\sigma T)$ increases almost linearly with temperature range from 25 to 100 ℃, and the corresponding

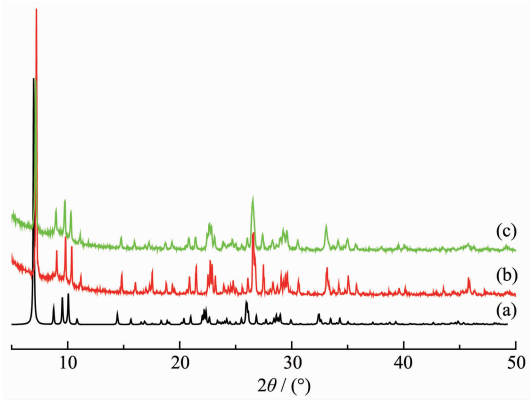

Fig.6 Powder X-ray diffraction data of the simulated powder pattern (a), the powder before the protonconductive measurement (b), and the powder after the proton-conductive measurement (c)

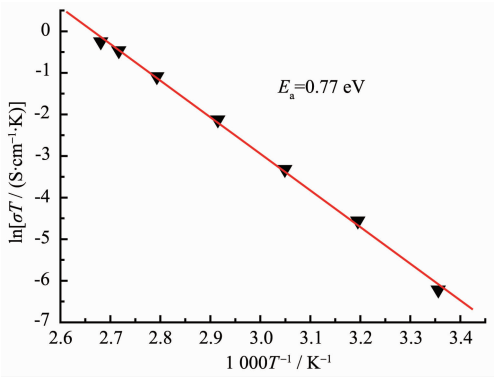

Fig.7 Arrhenius plot of the proton conductivity of **1**

activation energy (E_a) of conductivity was estimated to be 0.77 eV for the title complex from the equation below[12-13e].

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

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 high in the temperature range of 25~100 ℃. The results show that the general features of the changes in conductivities are different from that of PWA-26 or PMA-26, whose protonic conductivity decreased with the temperature from ambient to 60 ℃[1-2]. However, the title complex has thermally activated protonic conductivities[11] from 25 to 100 ℃; as the temperature increases, the proton conductivities increase 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^+, H_3O^+ or other proton species at a distance from $[PW_{12}O_{40}]^{3-}$ clusters[14]. The mechanism of proton conduction of the title complex is, therefore, expected to be similar to that of the vehicle mechanism[15], that is, the direct diffusion of additional protons with water molecules. The existence of these half-occupied oxygen sites of water molecules in $[Ni(H_2O)_8]^{2+}$ and $H^+(H_2O)_{2.5}$ cations may be derived from direct-jump diffusion and be conducive to formation of the H-bonding network. In addition, the existence of H-bonding network suggests that proton conduction in the title complex includes some other process such as proton transport of additional protons along H-bonding network (Grotthus mechanism)[16]. It is possible that in higher temperature and humidity some of isonicotinic acid N-oxide molecules can be deprotonated and the protons can be incorporated by the water molecules and therefore conductivity can be a result of dissociation of organic acid. The results of measurement of the proton conductivity of HINO molecules in the temperature range of 85~100 ℃ at 98% RH showed the free HINO molecules reached proton conductivities of 10^{-5}~10^{-4} S·cm^{-1} in the temperature range of 85~100 ℃, these proton conductivities are about 1~2 orders of magnitude lower than that of the title complex, which shows conductivity of about 10^{-3} S·cm^{-1} in the conditions described. Therefore, the fact that the title complex exhibits good proton conductivities in the temperature range of 85~100 ℃ is indicative of a high carrier concentration based on a thermally activated process, as well as the existence of the whole H-bonding networks. Moreover, there is the possibility of hydrolysis of the complex when it is held at 100 ℃ with a RH higher than 98% (100%, or condensed water that attack the metal centres). The powder X-ray diffraction data in Fig.6 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 ℃ in the RH range 35% ~98% by a complex-plane impedance method. Fig.8 shows the lgσ versus RH plots of complex **1** at 100 ℃ under 35% ~98% RH. The

conductivity under 35% RH is ~3.95×10^{-5} S·cm^{-1}, and the conductivity increases with RH to reach a high conductivity of 1.70×10^{-3}~2.05×10^{-3} S·cm^{-1} in the range 60%~98% RH.

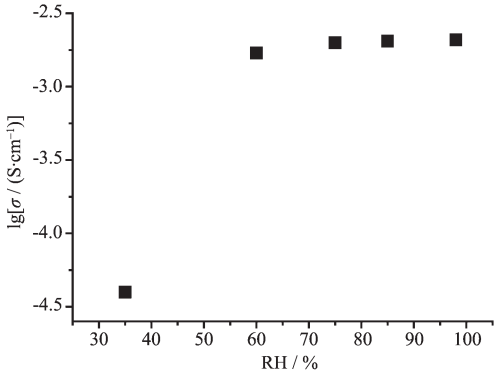

Fig.8　lgσ versus RH plots of **1** at 100 ℃

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