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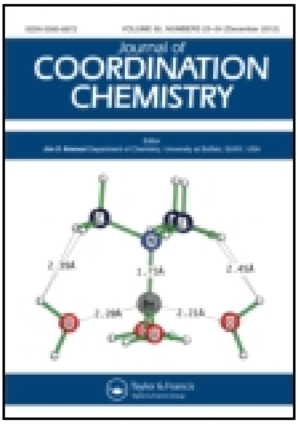

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Two supramolecular structures constructed from Keggin-type polyoxometalates and 4,4′-bipyridine

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Two supramolecular compounds based on Keggin-type polyoxometalates (POMs), (4,4′-H_2bpy)(4,4′-Hbpy)[$PMo_{12}O_{40}$] (**1**) and (4,4′-H_2bpy)(4,4′-Hbpy)$_2$[$SiW_{12}O_{40}$]·$4H_2O$ (**2**), have been synthesized hydrothermally and characterized by elemental analyses, IR, UV-Vis, XPS spectra, thermogravimetric analyses, and single-crystal X-ray diffraction analyses. The two compounds consist of 4,4′-bipyridine (4,4′-bpy) ligands and different Keggin-type POMs which are $[PMo_{12}O_{40}]^{3-}$ for **1** and $[SiW_{12}O_{40}]^{4-}$ for **2**. There are hydrogen-bonding interactions between the POMs, 4,4′-bipyridine, and/or water in **1** and **2**. In addition, **2** contains an uncommon $(H_2O)_2$ water cluster.

Keywords: Crystal structure; Hydrothermal synthesis; Keggin polyoxometalates; Hydrogen bonds

1. Introduction

Directed assembly of supramolecular arrays from discrete molecular building blocks has potential applications in molecular electronic, sensor design, catalysis, and optics [1–7]. In construction of supramolecular materials, an important strategy is that low-dimensional building blocks extend to high-dimensional networks through weak intermolecular interactions, including hydrogen-bonding, $\pi\cdots\pi$ stacking, and van der Waals interactions. Hydrogen-bonding interactions are the most familiar organizing force in supramolecular assemblies by virtue of its strength and directionality that may control short-range packing [8, 9].

Owing to its importance in non-linear optical materials, medicines, and catalysis [10–20], Keggin-type polyoxometalates (POMs) have been employed as discrete building blocks for constructing supramolecular arrays with various organic moieties as the spherical surface of POMs can give a better opportunity in forming different kinds of hydrogen bonds with organic moieties [21–28]. 4,4′-Bipyridine is a rod-like

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ligand employed as the rigid organic building block for the construction of coordination complexes based on POMs and transition metal coordination complexes [29, 30]. However, POMs directly combined with 4,4′-bpy for construction of supramolecular hybrids is less developed [31–33].

Our groups have reported supramolecular materials based on POMs and 4,4′-bpy [34, 35]. In this article, we report syntheses and characterizations of two new compounds constructed from 4,4′-bpy and Keggin POMs: (4,4′-H_2bpy)(4,4′-Hbpy)[$PMo_{12}O_{40}$] (**1**) and (4,4′-H_2bpy)(4,4′-Hbpy)$_2$[$SiW_{12}O_{40}$] $\cdot$ 4H_2O (**2**). Crystal structures reveal that Keggin POMs, 4,4′-bpy ligands, and/or water molecules form two different 3-D supramolecular networks through hydrogen-bonding interactions.

2. Experimental

2.1. *Materials and methods*

All chemicals were purchased and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer. P, Si, Mo, and W analyses were performed on a Perkin-Elmer Optima 3300DV spectrophotometer. IR spectra were obtained on a Perkin-Elmer spectrophotometer from 200 to 4000 cm^{-1} with pressed KBr pellets. UV-Vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer as saturated solution of *N*,*N*-dimethylformamide. The XPS measurements were performed on a Thermo ESCALAS 250 spectrometer with an Mg-Kα (1253.6 eV) achromatic X-ray source. Thermogravimetric (TG) curves were performed on a Perkin-Elmer TGA-7000 thermogravimetric analyzer in flowing air with a heating rate of 10°C$\cdot$min^{-1}.

2.2. *Syntheses*

2.2.1. Synthesis of (4,4′-H_2bpy)(4,4′-Hbpy)[$PMo_{12}O_{40}$] (1). $(NH_4)_3[PMo_{12}O_{40}] \cdot xH_2O$ (0.563 g, 0.3 mmol), $AgNO_3$ (0.034 g, 0.2 mmol), 4,4′-bpy (0.079 g, 0.50 mmol), and distilled water (20 mL) were mixed, stirred for 60 min, and the pH of the mixture was adjusted to 5 with $NH_3 \cdot H_2O$. The mixture was transferred to a Teflon-lined autoclave (25 mL) and heated to 160°C in 90 min, maintained at that temperature for 3 days, and then gradually cooled to room temperature at 4°C$\cdot$h^{-1}. Orange block crystals of **1** suitable for X-ray diffraction were isolated in 68% yield (based on Mo). Anal. Calcd for $C_{20}H_{19}N_4Mo_{12}O_{40}P$ (%): C, 11.24; H, 0.90; N, 2.62; Mo, 53.86; P, 1.45. Found: C, 11.33; H, 0.99; N, 2.58; Mo, 53.76; P, 1.52.

2.2.2. Synthesis of (4,4′-H_2bpy)(4,4′-Hbpy)$_2$[$SiW_{12}O_{40}$] $\cdot$ 4H_2O (2). $H_4[SiO_4(W_3O_9)_4] \cdot xH_2O$ (0.863 g, 0.3 mmol), $AgNO_3$ (0.034 g, 0.2 mmol), 4,4′-bpy (0.079 g, 0.50 mmol), and distilled water (20 mL) were mixed, stirred for 60 min, and the pH was adjusted to 3 with $NH_3 \cdot H_2O$. The mixture was transferred to a Teflon-lined autoclave (25 mL) and heated to 160°C in 90 min, maintained at that temperature for 3 days, and then gradually cooled to room temperature at 4°C$\cdot$h^{-1}; purple block crystals of **2** suitable for X-ray diffraction were isolated in 72% yield (based on W). Anal. Calcd for

Table 1. Crystal data and structure refinement parameters for **1** and **2**.

	1	**2**
Empirical formula	$C_{20}H_{19}Mo_{12}N_4O_{40}P$	$C_{30}H_{36}W_{12}N_6O_{44}Si$
Formula weight	2137.64	3418.82
Crystal system	Monoclinic	Monoclinic
Space group	$C2/m$	$C2/c$
Unit cell dimensions (Å, °)		
a	16.2436(1)	15.133(3)
b	14.8184(1)	18.121(2)
c	11.6433(8)	21.369(4)
α	90	90
β	123.3100(1)	103.075(15)
γ	90	90
Volume ($Å^3$), Z	2342.2(3), 2	5708.0(18), 4
Calculated density, D_c ($mg\,m^{-3}$)	3.031	3.978
Absorption coefficient (mm^{-1})	3.247	24.206
θ range for data collection (°)	2.03–26.07	1.78–28.49
$F(000)$	2011	6045
Reflections collected	6559/2424	10,064/5335
Goodness-of-fit on F^2	1.094	1.042
Final R indices [$I > 2\theta(I)$]	$R_1{}^a = 0.0504$, $wR_2{}^b = 0.1593$	$R_1{}^a = 0.0399$, $wR_2{}^b = 0.1221$
Largest difference peak and hole ($e\,Å^{-3}$)	2.753 and −0.932	2.064 and −2.193

$^aR_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $^bwR_2 = \{[\sum w(F_o^2 - F_c^2)^2]/[\sum w(F_o^2)^2]\}^{1/2}$.

$C_{30}H_{36}N_6W_{12}O_{44}Si$ (%): C, 10.54; H, 1.06; N, 2.46; W, 64.53; Si, 0.82. Found: C, 10.63; H, 1.11; N, 2.38; W, 64.46; Si, 0.76.

2.3. *X-ray crystallography*

Reflection intensity data for **1** was collected on a Bruker Smart CCD diffractometer at room temperature with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation and **2** was measured on a Rigaku R-AXIS RAPID IP diffractometer with graphite monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. Neither crystal showed evidence of crystal decay during data collection. Both structures were solved by direct methods and refined using full-matrix least squares on F^2 with SHELXTL-97 crystallographic software. In final refinements, all atoms were refined anisotropically except water in **2**, hydrogen atoms were included in their ideal positions, while those of water were not added. Unfortunately, the completeness for **2** is low, perhaps due to poor crystal quality. A summary of the crystallographic data and structure refinements for **1** and **2** is given in table 1. Selected bond lengths of **1** and **2** are listed in table S1.

3. Results and discussion

3.1. *Syntheses*

Supramolecular **1** and **2** were prepared by hydrothermal methods from reactions of $(NH_4)_3[PMo_{12}O_{40}] \cdot xH_2O$ (or $H_4[SiO_4(W_3O_9)_4] \cdot xH_2O$) and $AgNO_3$ in the presence of 4,4′-bpy as a structure-directing agent. The pH is crucial for formation of **1** and **2**.

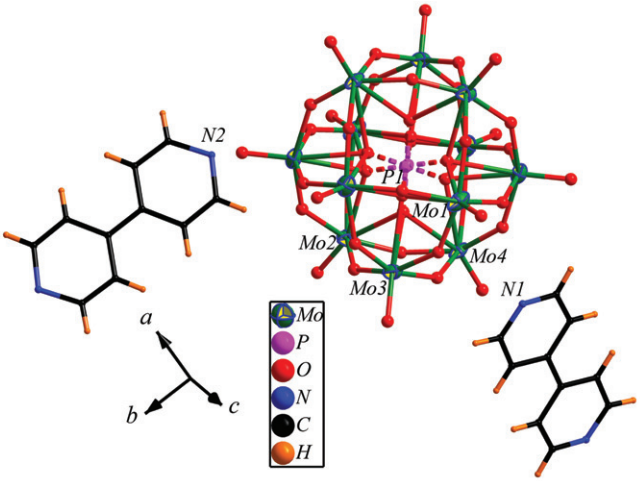


Figure 1. The building block of the Keggin-type polyoxomolybdate (4,4′-H_2bpy)(4,4′-Hbpy)[$PMo_{12}O_{40}$] (**1**).

When the pH value was 3–5, **1** can be formed, and only with pH 3, **2** was formed. This shows that preparations of **1** and **2** need strictly controlled pH of the reaction system. Although silver atoms were not introduced into the final products, $AgNO_3$ was important for formations of **1** and **2**; without $AgNO_3$, only undetermined powders were obtained. The role of the $AgNO_3$ is elusive.

3.2. *Crystal structure of 1*

Crystal structure analysis reveals that the asymmetric unit for **1** consists of a $[PMo_{12}O_{40}]^{3-}$, a di-protonated 4,4′-bpy, and a mono-protonated 4,4′-bpy. As shown in figure 1, the Keggin polyoxoanion $[PMo_{12}O_{40}]^{3-}$ exhibits a pseudo-Keggin core [36] with a central PO_4^{3-} which exhibits cubic geometry with all eight oxygen atoms half occupied surrounded by four internally edge-sharing tri-octahedra Mo_3O_{13}. The P–O distances vary from 1.518(11) to 1.562(11) Å. According to coordination mode, there are three kinds of oxygen atoms in $[PMo_{12}O_{40}]^{3-}$: terminal oxygen (O_t), bridging oxygen (O_b), and central oxygen (O_c). The Mo–O_t distances are 1.643(7)–1.660(7) Å, Mo–O_b distances are 1.813(8)–1.969(7) Å, and Mo–O_c distances are 2.435(11)–2.477(10) Å, respectively (table S1). These results show that bond lengths of **1** are comparable to phosphomolybdates reported previously [37, 38]. Bond valence sum (BVS) values [39] for the four crystallographically independent molybdenum atoms Mo1–Mo4 of **1** are 6.28, 6.13, 6.07, and 6.14, respectively, indicating molybdenum +6, consistent with $[X^{n+}Mo_{12}O_{40}]^{(8-n)}$ (X^{n+} represents a variety of heteroatoms with oxidation states +4 or +5, such as P, Si, V, As, and Ge) [40].

As illustrated in figure 2, $[PMo_{12}O_{40}]^{3-}$ is linked to an adjacent one through O3 $(1-x,\ y,\ -z)\cdots$O3 $(1-x,\ -y,\ -z)$ interactions at 2.7629(2) Å to form a 1-D supramolecular "chain" structure along the *a*-axis. The di-protonated N1 4,4′-H_2bpy bridges two POMs from two different "chains" through complex hydrogen-bonding interactions of C2–H$\cdots$O9, C3–H$\cdots$O4(#1) with distances of 2.9344(2) Å and

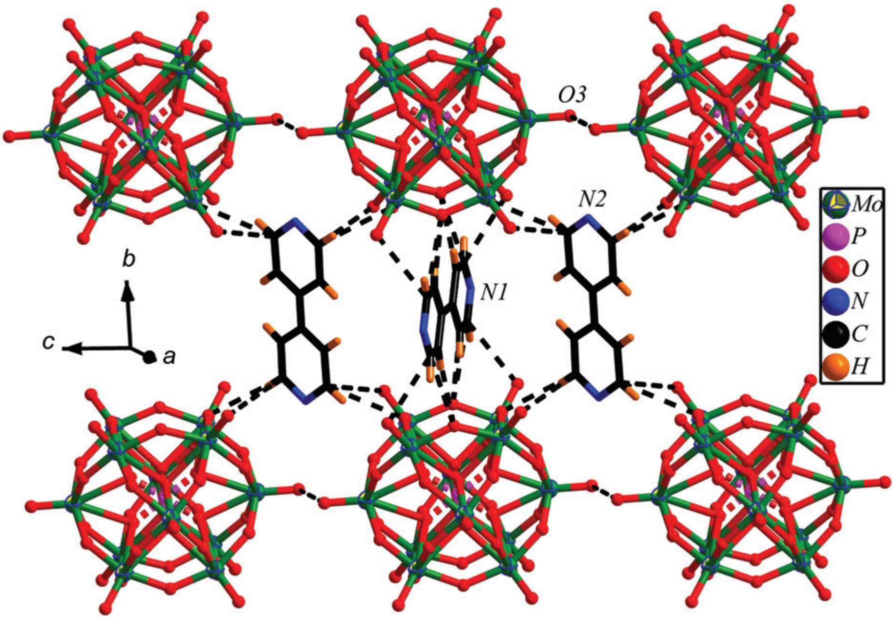
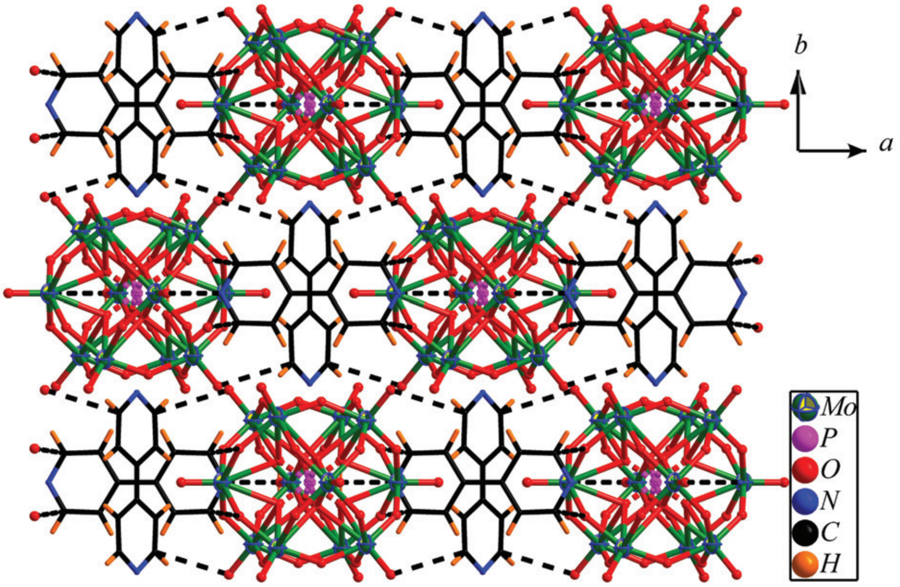


Figure 2. The 2-D supramolecular layer structure in **1**.

3.1788(2) Å, respectively, while the mono-protonated N2 4,4′-Hbpy connects four neighboring POMs two of which from one "chain" and the other two from another "chain" *via* hydrogen-bonding interactions of C6–H···O4(#3) and C6–H···O5(#2) with distances of 3.0653(2) Å and 3.2795(2) Å, respectively. Thus, hydrogen-bonding interactions between oxygen atoms from POMs and carbon atoms from different 4,4′-bpy ligands connect the POM "chains" and the 4,4′-bpy cations into a 2-D supramolecular layer structure. Meanwhile, N1 of the N1 di-protonated 4,4′-H_2bpy interacts with O9, O3(#5) from one POM from adjacent layer through N–H···O interactions with N···O distances of 2.8215(2)–3.1038(2) Å, thus the hydrogen-bonding interactions between di-protonated N1 of 4,4′-H_2bpy and POMs connect the 2-D layers into a 3-D supramolecular network structure along the *c*-axis (figure 3).

From the topological perspective (figure 4), both N1 4,4′-H_2bpy and N2 4,4′-Hbpy linking six adjacent $[PMo_{12}O_{40}]^{3-}$ could be considered as 6-connected organic nodes. N1 4,4′-H_2bpy and N2 4,4′-Hbpy ligands which link $[PMo_{12}O_{40}]^{3-}$ anions, respectively, could be regarded as topological lines. From this aspect, one $[PMo_{12}O_{40}]^{3-}$ is surrounded by six N1 4,4′-H_2bpy and six N2 4,4′-H_2bpy. The $[PMo_{12}O_{40}]^{3-}$ unit could be regarded as 12-connected inorganic nodes, while 12-connected inorganic nodes and 6-connected organic nodes interlink into the inorganic–organic 3-D topology network through complex C–H···O and N–H···O hydrogen-bonding interactions with a Schläfli symbol $(4^{13}\cdot 6^{2})_2(4^{44}\cdot 6^{22})$ [41]. To the best of our knowledge, the 3-D supramolecular framework reported herein defines an unprecedented topology containing (6, 12)-connected nodes.

Analysis shows that there are three different interactions in **1** through O···O, the C–H···O, and N–H···O hydrogen bonds. These synergistic interactions increase the stability of **1**.



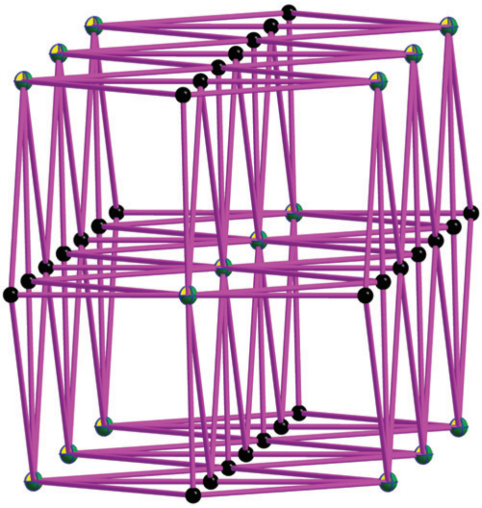


Figure 4. Topological representation of the 3-D supramolecular network structure of **1** formed through the C–H···O and N–H···O hydrogen bonds interactions between $[PMo_{12}O_{40}]^{3-}$ and 4,4′-bpy. The big circles represent $[PMo_{12}O_{40}]^{3-}$, the small circles represent 4,4′-bpy cation, and the lines represent hydrogen bonds.

3.3. *Crystal structure of 2*

The asymmetric unit for **2** is composed of a Keggin-type polyanion $[SiW_{12}O_{40}]^{4-}$, a di-protonated 4,4′-bpy and two mono-protonated 4,4′-bpy ligands and four water molecules. The $[SiW_{12}O_{40}]^{4-}$ in **2** is similar to that of **1**; the differences are the metal

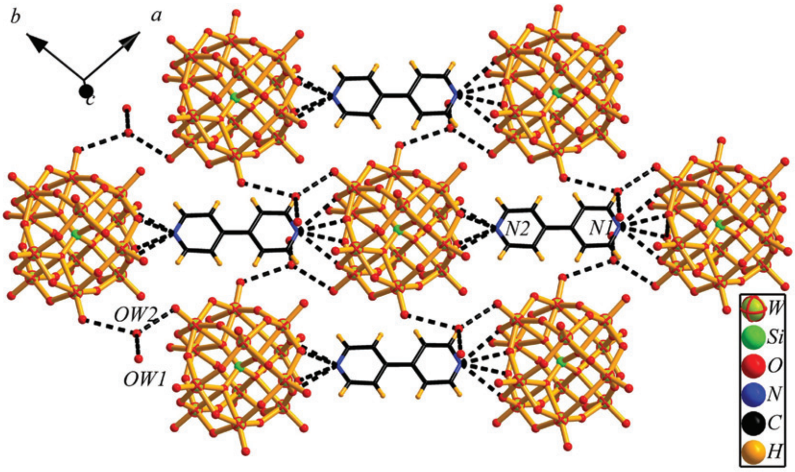


Figure 5. The 2-D supramolecular layer structure of **2** formed through the O–H···O and N–H···O hydrogen bonds in $(H_2O)_2$, $[PMo_{12}O_{40}]^{3-}$, and 4,4′-bipy.

with W replacing Mo and SiO_4^{4-} tetrahedra replacing the PO_4^{3-} cube. The Si–O distances are 1.618(8)–1.632(10) Å. According to the different coordination environments, oxygen atoms can be divided into three groups: terminal oxygen (O_t) with W–O_t distances of 1.665(11)–1.707(10) Å, bridging oxygen (O_b) with W–O_b distances of 1.888(9)–1.935(10) Å, and central oxygen (O_c) with W–O_c distances of 2.303(11)–2.372(8) Å (table S1). These results show that the bond lengths of **2** are comparable to the silicotungstate reported previously [42, 43]. The BVS values for the six crystallographically independent tungsten atoms W1–W6 of **2** are 6.07, 6.03, 6.12, 6.03, 5.96, and 6.18, respectively, indicating +6 tungsten. Therefore, the formula of $[SiW_{12}O_{40}]$ is $[SiW_{12}O_{40}]^{4-}$.

Analysis shows that there are five kinds of hydrogen bonds in **2**. As shown in figure 5, the 1-D chain $[(SiW_{12}O_{40})(4,4'\text{-}H_2bpy)]_\infty$ is made up of di-protonated N1 of 4,4′-bpy and $[SiW_{12}O_{40}]^{4-}$. N1 interacts with O7(#3), O7(#6), O9(#3), and O9(#6) from one POM through four N–H···O interactions with N···O distances of 3.1207(4) and 3.1461(4) Å, while N2 of 4,4′-H_2bpy interacts with O3(#2), O3(#5), O12(#2), and O12(#5) from another POM through four N–H···O interactions with N···O distances of 2.9989(4) and 3.0046(4) Å. Thus the di-protonated 4,4′-H_2bpy bridge the POMs into a 1-D chain structure $[(SiW_{12}O_{40})(4,4'\text{-}H_2bpy)]_\infty$.

Another unusual feature of **2** is that OW1 and OW2 form a $(H_2O)_2$ water cluster with O···O distances of 2.8708(5) Å which links the 1-D chains into a 2-D layer structure. OW2 is connected to O8 and O16(#5) from two $[(SiW_{12}O_{40})(4,4'\text{-}H_2bpy)]_\infty$ chains through hydrogen bonds with distances of 2.9349(4) Å and 3.1881(5) Å. Thus a 2-D supramolecular layer structure was formed by the POMs, di-protonated 4,4′-H_2bpy, and one $(H_2O)_2$ cluster. To the best of our knowledge, $(H_2O)_2$ water clusters linking POMs and di-protonated N1 4,4′-H_2bpy to form 2-D $[(SiW_{12}O_{40})(4,4'\text{-}H_2bpy)(H_2O)_2]_\infty$ layer through hydrogen bonds is reported for the first time.

As shown in figure 6, N3 of 4,4′-Hbpy interacts with OW1(#2) through hydrogen-bonding with O···N distance of 2.6543(4) Å, while N4 of 4,4′-Hbpy interacts with OW1

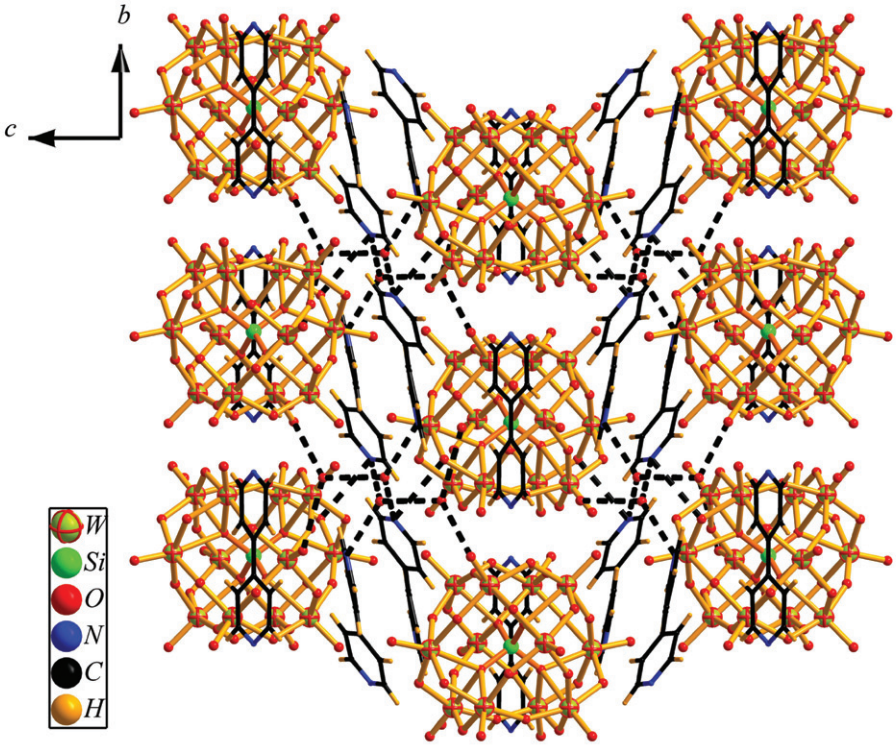


Figure 6. The 3-D supramolecular network in **2**.

through hydrogen bond with O···N distance of 2.7464(3) Å. Thus 4,4′-Hbpy and the $(H_2O)_2$ cluster are connected into a 1-D supramolecular "chain" along the *b*-axis. N3 of 4,4′-Hbpy is connected to oxygen atoms from the POMs of $[(SiW_{12}O_{40})(4,4'\text{-}H_2bpy)(H_2O)_2]_\infty$ layers through N–H···O hydrogen-bonding interactions of N3–H···O11(#2) with a distance 3.1730(4) Å, linking 2-D $[(SiW_{12}O_{40})(4,4'\text{-}H_2bpy)(H_2O)_2]_\infty$ layers into a 3-D supramolecular structure.

Further analysis of **2** reveals that spherical surface of the POMs gives a better opportunity in forming C–H···O hydrogen bonds with 4,4′-bpy. These hydrogen bonds also increase stability of the crystal of **2**; selected hydrogen bonds are listed in table 2.

3.4. *Characterizations of the compounds*

3.4.1. IR spectra. The IR spectrum of **1** exhibits characteristic Keggin anion peaks at 975.1 cm^{-1} associated with the $\nu(Mo–O_t)$, 921.5 cm^{-1} to $\nu(Mo–O_b–Mo)$, and 780.4 cm^{-1} to $\nu(Mo–O_c–Mo)$ [44]. Bands at 1018.8 cm^{-1} can be ascribed to ν(P–O) in **1**. Bands at 1204.5–1594.6 cm^{-1} are due to vibrations of the 4,4′-bpy (figure S1(a)). In the IR spectrum of **2**, bands at 1023.6 cm^{-1} are ascribed to ν(Si–O). Strong bands at 981.2, 928.2, and 788.5 cm^{-1} are attributed to $\nu(W–O_t)$, $\nu(W–O_b–W)$ and $\nu(W–O_c–W)$. A series of bands from 1208.9 to 1600.9 cm^{-1} are characteristic of 4,4′-bpy (figure S1(b)).

Table 2. Hydrogen-bond parameters for **1** and **2**.

	D–H···A (Å)		D–H···A (Å)
Compound **1**			
C2–H···O8(#1)	3.1188(2)	C3–H···O9	2.9344(1)
C3–H···O4(#1)	3.1788(2)	C5–H···O10(#3)	3.1934(2)
C6–H···O4(#3)	3.0650(2)	C6–H···O5(#2)	3.2795(2)
N1–H···O9	3.1038(2)	N1–H···O9(#4)	3.1038(2)
N1–H···O3(#5)	2.8215(2)		
Compound **2**			
C1–H···O4(#1)	3. 2338 (6)	C12–H···O20(#2)	3.2879(5)
C1–H···O9(#3)	3.0536(5)	C13–H···O16	3.2205(5)
C4–H···O10	2.9370(6)	N1–H···O7(#6)	3.1461(4)
OW1···OW2(#4)	2.8708(5)	N2–H···O3(#2)	3.0046(4)
OW2···O8	2.9349(4)	N3···OW1(#2)	2.6543(4)
OW2···O16(#5)	3.1881 (5)	N4···OW1	2.7464(3)

Symmetric components for **1** #1: $1/2-x, 1/2-y, 1-z$; #2: $1-x, y, 1-z$; #3: $1/2-x, 1/2-y, -z$; #4: $x, -y, z$; #5: $x, y, 1+z$; for **2** #1: $-x, y, 1/2-z$; #2: $1/2+x, 1/2+y, z$; #3: $1/2-x, -1/2+y, 1/2-z$; #4: $-1/2+x, 1/2-y, 1/2+z$; #5: $1/2-x, 1/2+y, 1/2-z$; #6: $1/2+x, -1/2+y, z$.

3.4.2. UV-Vis spectroscopy. The UV-Vis spectra for **1** and **2** from 250 to 800 nm are presented in figure S2. The UV-Vis spectrum for **1** consists of a band at 255.9 nm assigned to O → Mo charge transfer in the polyanion of **1**. The UV-Vis spectrum for **2** exhibits an absorption at 256.3 nm attributed to charge transfer of O → W in the polyanion of **2** [45]. UV-Vis spectra for **1** and **2** are very similar, indicating that **1** and **2** contain similar Keggin-type POMs.

3.4.3. XPS spectra. Figure S3 shows the XPS spectrum of **1** with two peaks at 236.5 and 233.2 eV attributed to Mo^{6+} $3d_{3/2}$ and $3d_{5/2}$, respectively. The XPS spectrum of **2** gives two peaks at 37.9 and 35.9 eV attributed to W^{6+} $4f_{5/2}$ and W^{6+} $4f_{7/2}$ (figure S4), respectively. The XPS estimation of valence is in reasonable agreement with those calculated from BVS calculations.

3.4.4. TG analysis. The TG analysis curves for **1** and **2** are shown in figure S5. Complex **1** exhibits two steps of weight loss, the first of 0.65% at 89–173°C assigned to adsorbed water. The second weight loss of 14.9% from 351°C to 542°C is attributed to 4,4′-bpy (Calcd 14.78%). The TG curve of **2** also has two stages. The first of 2.2% at 79–197°C corresponds to release of water (Calcd 2.12%). The second weight loss of 13.49% from 252°C to 566°C is attributed to 4,4′-bpy in **2** (Calcd 13.86%).

Decomposition temperature of **1** is 100°C higher than that of **2**, which should be due to the presence of different hydrogen-bonding interactions like O···O, C–H···O, and N–H···O in **1**.

4. Conclusion

Two new hydrogen-bonded high supramolecular compounds based on Keggin POMs and 4,4′-bpy have been synthesized and structurally characterized. Syntheses of **1** and **2** provide discrete inorganic building blocks (POMs) with various organic moieties or water extending to high-dimensional supramolecular networks through hydrogen bonds. The most striking feature of **2** is $(H_2O)_2$ water cluster linking adjacent POMs and 4,4′-bpy to a 2-D supramolecular layer which further connects 4,4′-bpy with 3-D networks through hydrogen bonds. Research revealing synthetic rules and exploring the properties of POM-based supramolecular materials is underway in our group.

Supplementary material

CCDC reference numbers 888558 for **1** and 888559 for **2** contain the crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif

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