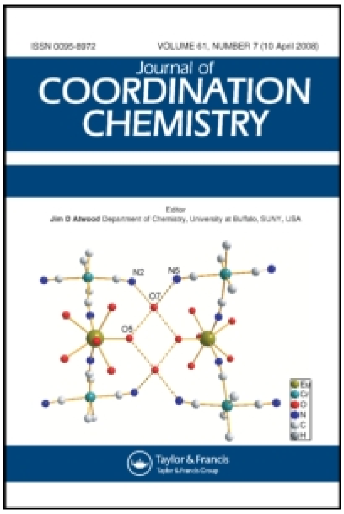

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Hydrothermal syntheses and characterizations of two compounds assembled from tungstates and bpy (bpy = 4,4'-bipyridine)

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Hydrothermal syntheses and characterizations of two compounds assembled from tungstates and bpy (bpy = 4,4′-bipyridine)

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Two compounds based on polyoxometalates, $(4,4'\text{-H}_2\text{bpy})_7(4,4'\text{-Hbpy})[\text{BW}^{\text{VI}}_{12}\text{O}_{40}]_2[\text{BW}^{\text{VI}}_{12}\text{O}_{40}]\cdot 10\text{H}_2\text{O}$ (**1**) and $(4,4'\text{-H}_2\text{bpy})_6(4,4'\text{-bpy})[\text{P}_2\text{W}^{\text{VI}}_{18}\text{O}_{62}]_2\cdot 18\text{H}_2\text{O}$ (**2**), have been prepared under hydrothermal conditions and characterized by IR, XPS spectra, TG analyses, and single crystal X-ray diffraction. Both compounds consist of 4,4′-bipyridine units and polyoxometalates: $[\text{BW}^{\text{VI}}_{12}\text{O}_{40}]^{5-}$ for **1** and $[\text{P}_2\text{W}^{\text{VI}}_{18}\text{O}_{62}]^{6-}$ for **2**. In addition, **1** contains both Keggin-type and disordered Keggin-type anions, while **2** contains a $(\text{H}_2\text{O})_{10}$ water cluster.

Keywords: Polyoxometalate; Hydrothermal synthesis; Keggin; Wells–Dawson POMs; Hydrogen bonding; Water cluster

1. Introduction

Growth in supramolecular chemistry has been driven by increased synthetic and characterization methods for complex structures [1–3]. Directed assembly of supramolecular arrays from discrete molecular building blocks has applications in catalysis, molecular electronics, sensor design, and optics [4–6]. In construction of supramolecular materials, discrete molecular building blocks generally extend to high-dimensional supramolecular arrays through hydrogen bonding, $\pi\cdots\pi$ stacking, and van der Waals interactions; hydrogen bonding is the most important organizing force in supramolecular assemblies by virtue of its unique strength and directionality that may control short-range packing [7].

4,4′-Bipyridine (4,4′-bpy) is a rod-like ligand extensively employed as the rigid organic building block for the construction of infinite 1-D, 2-D, and even 3-D coordination polymers [8–11]. Several coordination modes or existing forms of 4,4′-bpy in previously reported metal complexes are summarized as follows: (a) bridging mode in polymeric complexes [12]; (b) dimeric linker serving as only a short bridge [13];

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(c) unidentate mode [14]; and (d) protonated mode [15]. We are interested in employing 4,4′-bpy as organic building blocks to construct multidimensional supramolecular networks.

The spherical surface of the polyoxometalates (POMs) gives an opportunity for forming hydrogen bonds with organic or inorganic moieties. Extensive efforts have been made to design and assemble such supramolecular architectures and a few high-dimensional supramolecular architectures have been synthesized [16, 17].

Recently, we have synthesized supramolecular architectures based on POMs [18]. However, examples of such organic–inorganic hybrids built from POMs and 4,4′-bpy are still rare [17a, 18b]. We have prepared $(4,4'\text{-}H_2bpy)_7(4,4'\text{-}Hbpy)[BW^{VI}_{12}O_{40}]_2[BW^{VI}_{12}O_{40}] \cdot 10H_2O$ (**1**) and $(4,4'\text{-}H_2bpy)_6(4,4'\text{-}bpy)[P_2W^{VI}_{18}O_{62}]_2 \cdot 18H_2O$ (**2**).

2. Experimental

2.1. *Material and measurement*

All reagents were purchased commercially and used without purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer. B, P, 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. A Perkin-Elmer TGA7 thermogravimetric (TG) analyzer was used to obtain TGA curves. XPS measurements were performed on single crystals with ESCALAB MARK II apparatus using the Mg-Kα X-ray radiation as the excitation source (1253.6 eV).

2.2. *Synthesis*

2.2.1. Preparation of $(4,4'\text{-}H_2bpy)_7(4,4'\text{-}Hbpy)[BW^{VI}_{12}O_{40}]_2[BW^{VI}_{12}O_{40}] \cdot 10H_2O$ (1). **Compound 1** was synthesized hydrothermally by reacting $Na_2WO_4 \cdot 2H_2O$ (0.5 g, 1.5 mmol), H_3BO_3 (0.1 g, 1.6 mmol), $CdCl_2 \cdot 2.5H_2O$ (0.3 g, 1.3 mmol), 4,4′-bpy (0.3 g, 1.56 mmol), and distilled water (15 mL) in a 18 mL Teflon-lined autoclave. The pH was adjusted to 4 with $NH_3 \cdot H_2O$ solution. The mixture was heated under autogenous pressure at 160°C for 6 days and then left to cool to room temperature. Yellow crystals were isolated in 55% yield (based on W). Anal. Calcd for $C_{80}H_{99}B_3N_{16}O_{130}W_{36}$: W, 66.08; B, 0.32; C, 9.59; H, 0.98; N, 2.24%. Found: W, 66.01; B, 0.23, C, 9.63; H, 0.89; N, 2.37%.

2.2.2. Preparation of $(4,4'\text{-}H_2bpy)_6(4,4'\text{-}bpy)[P_2W^{VI}_{18}O_{62}]_2 \cdot 18H_2O$ (2). Compound 2 was synthesized hydrothermally by reacting $Na_2WO_4 \cdot 2H_2O$ (0.5 g, 1.5 mmol), H_3PO_4 (0.3 mL), $CdCl_2 \cdot 2.5H_2O$ (0.3 g, 1.3 mmol), 4,4′-bpy (0.3 g, 1.56 mmol), and distilled water (15 mL) in a 18 mL Teflon-lined autoclave. The pH was adjusted to 5 with $NH_3 \cdot H_2O$ solution. The mixture was heated under autogenous pressure at 160°C for 6 days and then left to cool to room temperature. Black crystals were isolated in 45% yield (based on W). Anal. Calcd for $C_{70}H_{104}P_4N_{14}O_{142}W_{36}$: W, 65.17; P, 1.22; C, 8.29; H, 1.02; N, 1.93%. Found: W, 65.26; P, 1.25; C, 8.41; H, 0.79; N, 1.87%.

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

Compound	**1**	**2**
Empirical formula	$C_{80}H_{99}B_3N_{16}O_{130}W_{36}$	$C_{70}H_{104}P_4N_{14}O_{142}W_{36}$
Formula weight	10075.78	10156.16
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit Cell dimensions (Å,°)		
a	11.821(2)	13.313(3)
b	19.154(4)	14.113(3)
c	20.895(4)	26.951(5)
α	63.44(3)	78.36(3)
β	73.91(3)	83.91(3)
γ	79.83(3)	68.28(3)
Volume (Å^3), Z	4058.4(14), 1	4604.6(16), 2
Calculated density		
D_c (mg/m^3)	4.098	3.663
Absorption coefficient (mm^{-1})	25.506	22.521
θ range for data collection (°)	3.03–27.48	2.99–27.48
Completeness	95.8%	94.8%
$F(000)$	4410	4482
Reflection collected	39883/17843	43453/20007
R(int)	0.0661	0.0788
Goodness-of-fit on F^2	1.020	1.023
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0576$, $wR_2 = 0.1425$	$R_1 = 0.0542$, $wR_2 = 0.1320$

${}^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR = [\Sigma w(F_o^2 - F_c^2)_2/\Sigma w(F_o^2)^2]^{1/2}$.

2.3. *X-ray crystallography*

Reflection intensity data for **1** and **2** were measured at 293 K 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 collections. 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 **1** and **2**, hydrogens were included in their ideal positions, while those of water were not added. It should be noted that one water in **2** is disordered over two positions (O6W and O7W) with occupancy factors of 0.5, respectively. 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. *Synthesis*

The supramolecular compounds were prepared by conventional hydrothermal methods [19, 20], which are applied to isolation of POMs [21]. **1** and **2** were obtained from reactions of $Na_2WO_4 \cdot 2H_2O$, H_3BO_3 (or H_3PO_4) and $CdCl_2 \cdot 2.5H_2O$ in the presence of 4,4′-bpy as a structure-directing agent, with pH adjusted to 4 or 5 with $NH_3 \cdot H_2O$. The pH is crucial for formation of **1** and **2. 1** could be formed only when the pH was 4 and **2** could be formed only when the pH was 5. **1** and **2** were synthesized with the same molar ratios of $Na_2WO_4 \cdot 2H_2O/CdCl_2 \cdot 2.5H_2O$/4,4′-bipy, only H_3BO_3

was replaced by H_3PO_4. We also tried to synthesize **2** at pH 4 and to synthesize **1** at pH 5, but were not successful. Parallel experiments demonstrated that it is not possible to synthesize **1** or **2** without addition of $CdCl_2 \cdot 2.5H_2O$, although the role of $CdCl_2 \cdot 2.5H_2O$ is elusive. If $NH_3 \cdot H_2O$ was replaced by solution of KOH or NaOH, only microcrystalline materials could be isolated.

3.2. *Crystal structure of 1*

The asymmetric unit of **1** consists of a Keggin anion $[BW^{VI}_{12}O_{40}]^{5-}$ (**POM A**), half of a disordered Keggin anion $[BW^{VI}_{12}O_{40}]^{5-}$ (**POM B**) [22], 3.5 bi-protonated 4,4′-bpy, half of a monoprotonated 4,4′-bpy and five water molecules. **1** contains two different Keggin anions, the first such example reported.

As shown in figure 1, the anion of **POM A** is a typical Keggin molecule. The structure of the **POM A** may be viewed as a shell of $\{W_{12}O_{36}\}$ encapsulating a $\{BO_4\}$ moiety, responsible for the local tetrahedral geometry. Each oxygen of $\{BO_4\}$, covalently bonded to three different tungsten centers of the shell, is in a bridging mode with B–O distances in the 1.47(2)–1.56(3) Å range. Alternatively, **POM A** may be described as being constructed from 12 $\{WO_6\}$ octahedra, present in four $\{W_3O_{13}\}$ tri-octahedra. The three $\{WO_6\}$ octahedra in each $\{W_3O_{13}\}$ unit are fused with each other by edge-sharing. Each $\{W_3O_{13}\}$ unit is joined with the central $\{BO_4\}$ group and with two other $\{W_3O_{13}\}$ units through corner sharing. According to coordination environment, the oxygens can be divided into three groups: O_t (terminal oxygen atoms connecting to one W atom) with W–O_t 1.684(16)–1.738(14) Å, O_b (atoms located at the shared corners between two W_3O_{13} units) with W–O_b 1.850(14)–1.953(12) Å, O_c (oxygen atoms connecting edge sharing WO_6 octahedra in the W_3O_{13} unit) with W–O_c 2.315(14)–2.406(12) Å. Bond angles at tungsten range from 73.8(5) to 127.7(6)°.

In contrast to **POM A**, **POM B** is a disordered Keggin molecule (figure 1), consisting of a disordered BO_4 tetrahedron at its center surrounded by a cube of eight oxygens with each oxygen site half-occupied surrounded by 12 WO_6 octahedra. The B–O distances and W–O distances are all similar to that of **POM A**.

Analysis shows that there are two kinds of hydrogen bonds in **1** through oxygen from water and oxygen from POMs and oxygens from water and nitrogens from bpy. As shown in figure S1, O2W, and O5W form a $(H_2O)_2$ water cluster. O2W is connected

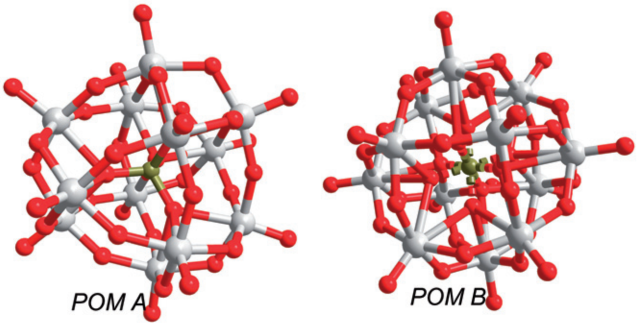

Figure 1. The ball-and-stick representation of the Keggin POM A and the pseudo-Keggin POM B in **1**.

to O(9)a from a **POM A** and N(4) from a 4,4′-bpy unit through hydrogen bonds with distances of 2.8908(12) Å and 2.7146(6) Å, respectively; O5W is connected to O(1)a from a **POM A** and O(61) from a **POM B** through hydrogen bonds with distances of 2.9487(8) Å and 2.9574(14) Å, respectively. Alternatively, the $(H_2O)_2$ water cluster links **POM A**, **POM B**, and 4,4′-bpy as a cluster bridge. In addition, there also exist hydrogen bonds between O1W and two **POM A** anions (figure S2), O3W and a **POM A**, a **POM B** and a 4,4′-bpy unit (figure S3) as well as O4W and a **POM A**, a **POM B** and a 4,4′-bpy (figure S4). These hydrogen bonds are listed in table 2. Water, POMs, and 4,4′-bpy are constructed into a 3-D supramolecular network (figure 2) through synergistic interactions of these hydrogen bonds.

1 is constructed from POMs and 4,4′-bpy containing phenyl rings. However, no $\pi \cdots \pi$ stacking interactions exist in **1**, confirmed by Platon software [23]. The lack of $\pi \cdots \pi$ stacking interaction may be attributed to steric hindrance of the POMs.

Table 2. The hydrogen bonds between the oxygens of the $(H_2O)_{10}$ water cluster and the oxygens from the $(H_2O)_{10}$ and oxygens from the $[P_2W^{VI}_{18}O_{62}]^{6-}$.

Hydrogen bond D···A	Bond lengths d(D···A)	Hydrogen bond D···A	Bond lengths d(D···A)
O2W···O5W	2.8991(7) Å	O3W···O(10)d	3.0881(14) Å
O1W···O(18)b	3.0843(11) Å	O3W···N(1)e	2.7906(6) Å
O1W···O(5)c	2.9781(12) Å	O4W···O(4)f	2.9414(9) Å
O2W···O(9)a	2.8908(12) Å	O4W···O(60)g	3.0482(8) Å
O2W···N(4)	2.7146(6) Å	O4W···N(6)h	2.6262(9) Å
O3W···O(54)	3.1804(8) Å	O5W···O(1)a	2.9487(8) Å
O3W···O(45)	3.0237(12) Å	O5W···O(61)	2.9574(14) Å

Symmetry codes for the generated atoms: a $(1-x,1-y,-z)$, b $(1-x,1-y,1-z)$, c $(-x,1-y,1-z)$, d $(1-x,-y,1-z)$, e $(x,-1+y,z)$, f $(x,y,1+z)$, g $(-x,1-y,1-z)$, h $(-1+x,y,1+z)$.

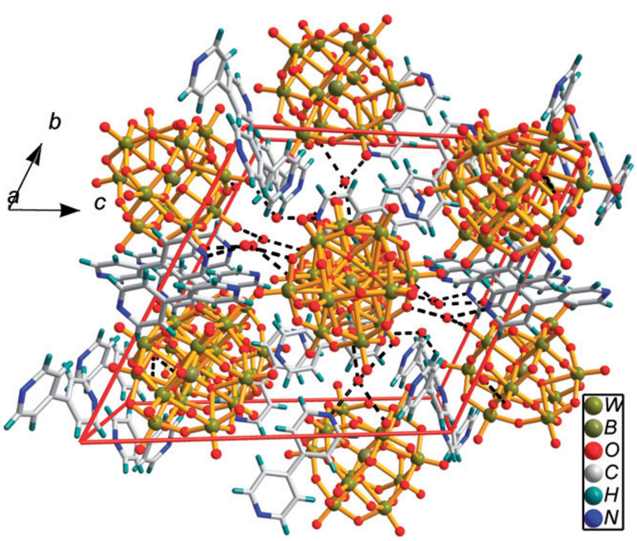

Figure 2. The combined wire and ball-and-stick representation of the crystal packing diagram of **1**.

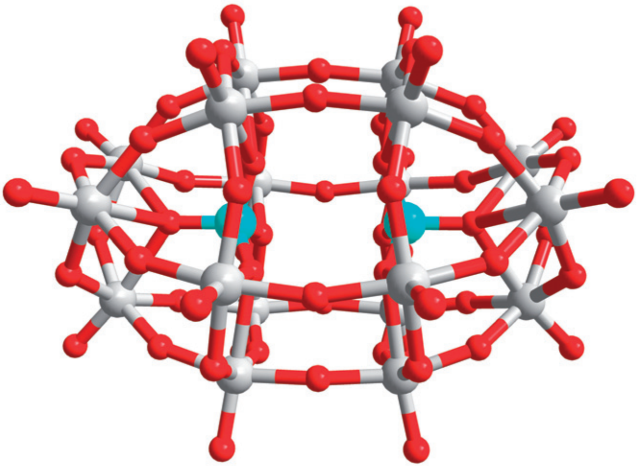

Figure 3. The ball-and-stick representation of the $[P_2W^{VI}_{18}O_{62}]^{6-}$ anion in **2**.

Several compounds based on Keggin POMs and 4,4′-bpy coordination fragments have been reported [24]. However, it is strange that compounds based on Keggin POMs directly combined with 4,4′-bpy are rather rare [17a, 18b]. Compound **1** not only gives a new example of such compounds, but also shows features unobserved before with two different Keggin POMs.

3.3. *Crystal structure of 2*

The asymmetric unit of **2** consists of one Wells–Dawson $[P_2W^{VI}_{18}O_{62}]^{6-}$ anion, three bi-protonated 4,4′-bpy, half of a 4,4′-bpy and nine waters. The polyoxoanion in **2** is a classical Wells–Dawson structure (figure 3), described as two $[PW_9O_{31}]^{3-}$ units, generated from the well-known $[PW_{12}O_{40}]^{3-}$ by removal of a set of three corner-sharing WO_6 octahedra and fused into a cluster of virtual D_{3h} symmetry. In the polyoxoanion, the two central P are tetrahedrally coordinated by four bridging oxygens, forming two $\{PO_4\}$ clusters. The O–P–O bond angles are 106.1(6)°–112.0(6)°, indicating a distorted tetrahedral geometry around P. The P–O average distance of 1.545 Å in the Dawson model is longer than the corresponding bond distance of 1.499 Å in the Keggin model [25], indicating different coordination between the Keggin and Wells–Dawson systems. The anion contains only two structurally distinct types of W: six polar W on vertical mirror planes grouped in two sets of three, and 12 equatorial W that do not lie on mirror planes grouped in two sets of six [26]. The W–O bond distances are: W–O_t: 1.683(10)–1.725(12) Å, W–O_b: 1.859(11)–1.967(11) Å, W–O_c: 2.344(9)–2.401(11) Å.

The most striking feature of **2** is a $(H_2O)_{10}$ water cluster (figure 4), which could be viewed as a decorated rhombic water cluster. The rhombic water cluster exhibits a four-core rhombus motif which is formed from OW3a, OW4, and their symmetry-related ones through hydrogen bonds with distances of 3.18(9) Å and 3.01(13) Å, respectively. The OW4 and OW4b of the rhombus are decorated with two $(H_2O)_2$ water clusters through hydrogen bonds as shown in figure 4, OW1a (or its

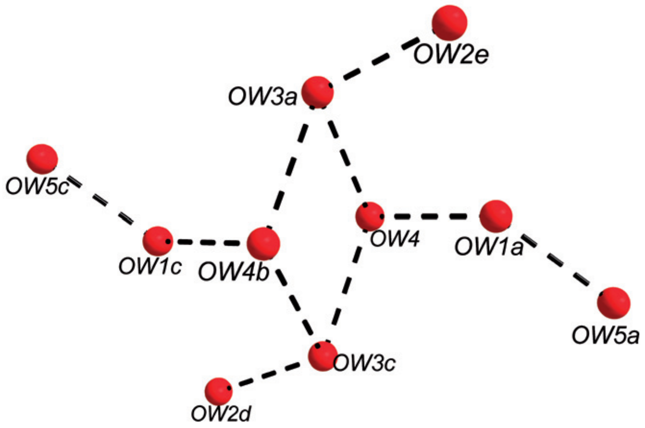

Figure 4. The representation of the $(H_2O)_{10}$ water cluster. Symmetry code; a $(2-x, 1-y, -z)$; b$(1-x, 1-y, -z)$; c$(-1+x, y, z)$; d$(1-x, 2-y, -z)$; e $(x, -1+y, z)$.

symmetry equivalent OW1c) performs as a bridge-site and links OW4 (or its symmetry equivalent OW4b) and OW5a (or its symmetry equivalent OW5c) via hydrogen bonds, 2.98(7) Å and 2.78(8) Å, respectively. OW3a and OW3c were decorated with OW2d and OW2e molecules via 2.85(8) Å hydrogen bonds. In the $(H_2O)_{10}$ water cluster, the average OW ··· OW distance is 2.956 Å, which is slightly longer than those observed in liquid water (2.854 Å) [27].

The $(H_2O)_{10}$ shows strong interactions with the POMs via hydrogen bonds (figure S5) of OW5a ··· O53b, OW1c ··· O36, OW1c ··· O59, OW4 ··· O42, OW2e ··· O16e, OW2 ··· O59b (and their symmetry equivalents) with distances of 2.92(9) Å, 3.19(8) Å, 2.92(6) Å, 2.8(7) Å, 2.91(11) Å, and 3.07(13) Å, respectively. Thus the POMs and the $(H_2O)_{10}$ water clusters connect into a 3-D supramolecular structure (figure 5) via the hydrogen bonds.

2 is constructed from POMs and 4,4′-bpy units; however, no $\pi \cdots \pi$ stacking interactions exist in **2**, confirmed by Platon software [23]. The lack of $\pi \cdots \pi$ stacking interaction again is attributed to steric hindrance of the POMs.

3.4. *Characterization of the compounds*

The IR spectrum of **1** exhibits the characteristic Keggin anion peaks at 986 cm^{-1} associated with the ν(W–O$_t$), 929 cm^{-1} to ν(W–O$_b$–W), 809 and 803 cm^{-1} to ν(W–O$_c$–W). Bands at 1047 cm^{-1} can be ascribed to B–O stretching in **1**. Bands in the 1613–1221 cm^{-1} region are due to vibrations of the 4,4′-bpy (figure S6(a)). In the IR spectrum of **2**, bands at 1089 cm^{-1} are ascribed to ν(P–O). Strong bands at 957, 907, and 780 cm^{-1} are attributed to ν(W–O$_t$), ν(W–O$_b$–W), and ν(W–O$_c$–W), respectively. A series of bands from 1214–1611 cm^{-1} are characteristic vibrations of 4,4′-bpy (figure S6(b)).

Figure S7(a) shows the XPS spectrum of **1** as two overlapped peaks at 35.7 and 37.4 eV ascribed to W^{6+} $4f_{7/2}$ and W^{6+} $4f_{5/2}$. The XPS spectrum for **2** (figure S7(b)) gives two peaks at 35.7 and 37.6 eV attributed to W^{6+} $4f_{7/2}$ and W^{6+} $4f_{5/2}$, respectively.

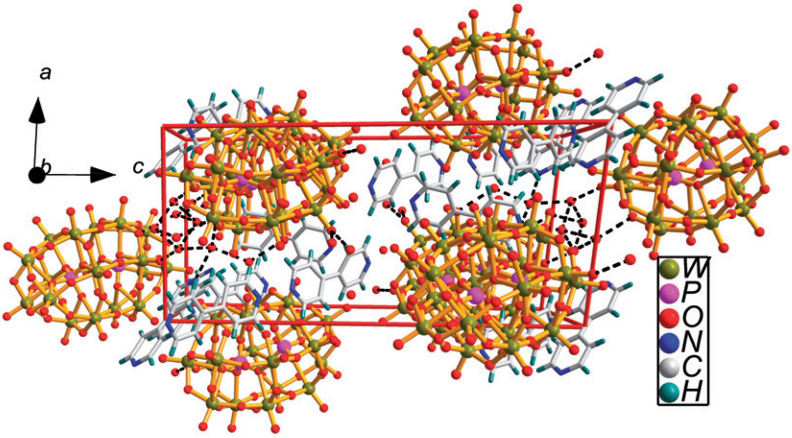

Figure 5. The combined wire and ball-and-stick representation of the crystal packing diagram of **2**.

The XPS estimation of the valence is in reasonable agreement with those calculated from bond valence sum calculations.

TG analyses (Supplementary material) in the temperature range 35°C–800°C show that **1** loses its crystal water and 4,4′-H_2bpy and 4,4′-Hbpy from 202°C–774°C with weight loss of 16.12%, in accord with the calculated value (15.98%). From 236°C–688°C, **2** loses its crystal water and 4,4′-H_2bpy and 4,4′-Hbpy molecules, 14.41%, in good accord with the calculated value (14.06%).

4. Conclusion

Two hydrogen-bonded compounds have been synthesized and structurally characterized. The asymmetric unit of **1** consists of a Keggin $[BW_{12}^{VI}O_{40}]^{5-}$ and half a disordered Keggin $[BW_{12}^{VI}O_{40}]^{5-}$. The most striking feature of **2** is a $(H_2O)_{10}$ water cluster. Continuing research is underway to reveal the synthetic rules and explore their attractive properties.

Supplementary material

CCDC reference numbers: 734777 for **1** and 734778 for **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Acknowledgments

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