

## (4,4'-H<sub>2</sub>bipy)<sub>4</sub>[Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]·7H<sub>2</sub>O: A New Supramolecular Hybrid Based on 1D Cu-N Coordination Polymeric Chain and Wells-Dawson Type Polyoxometalate

RUI-LIAN LIN, WEN-QI SUN\*, JING-XIN LIU and XIANG-FENG CHU

College of Chemistry and Chemical Engineering, Anhui University of Technology, Maanshan 243002, P.R. China

\*Corresponding author: E-mail: sunwenqi@ahut.edu.cn

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The hydrothermal reaction of CuCl<sub>2</sub>·2H<sub>2</sub>O with K<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·15H<sub>2</sub>O and 4,4'-bipyridine (4,4'-bipy) gave a novel inorganic-organic hybrid (4,4'-H<sub>2</sub>bipy)<sub>4</sub>[Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]·7H<sub>2</sub>O, in which Cu(II) coordinated to [P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> polyanions, 4,4'-bipyridine and monoprotonated 4,4'-bipyridine ligands to form a 1D polyanionic chain. The 1D polyanionic chains stacked into a 3D supramolecular architecture consisting of numerous 1D open channels, in which water molecules are encapsulated. Additionally, thermal stability of the inorganic-organic hybrid materials has also been studied.

**Keywords:** Polymeric chain, Polyoxometalate, Crystal structure, Thermal analyses.

### INTRODUCTION

As a unique class of metal-oxide clusters, polyoxometalates (POMs) have attracted much attention not only because of their diverse structures and properties<sup>1-3</sup> but also because of their intriguing potential applications in catalysis<sup>4-6</sup>, medicine, biology<sup>7,8</sup> and functional material science<sup>9-13</sup>. Owing to their large number of potential coordination sites and different sizes and shapes, polyoxometalates are usually employed as excellent inorganic building blocks to construct inorganic-organic hybrids by combining with some transition metal coordination polymers. In this field, numerous 1D, 2D and 3D supramolecular assemblies based on some classical polyoxometalates, such as Keggin type anions, have been successfully synthesized<sup>14-21</sup>. By contrast, the number of observed examples of Wells-Dawson type polyoxometalate based on supramolecular assemblies is quite limited hitherto<sup>21-34</sup>. The main reason may rely on the large size, which may cause steric hindrance effect and the high charge of the Wells-Dawson type polyoxometalates. Therefore, the work of designing and assembling inorganic-organic hybrids based on Wells-Dawson type polyoxometalates is still a great challenge. In this work, we choose commonly used linear rigid ligand 4,4'-bipyridine as the organic component and obtain a novel Wells-Dawson polyoxometalate-based inorganic-organic supramolecular hybrid, (4,4'-H<sub>2</sub>bipy)<sub>4</sub>[Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]·7H<sub>2</sub>O (4,4'-bipy = 4,4'-bipyridine).

### EXPERIMENTAL

All the reagents employed were commercially available and used as received without further purification. K<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·15H<sub>2</sub>O was synthesized by published procedures<sup>35</sup>. The C, H and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer. The IR spectra were obtained on an Alpha Centaur FT/IR spectrometer with KBr pellets in the 4000-400 cm<sup>-1</sup> region. The thermal gravimetric analyses (TGA) were carried out on a NETZSCH STA 449 C instrument in flowing N<sub>2</sub> with a heating rate of 10 °C/min.

#### Synthesis

**(4,4'-H<sub>2</sub>bipy)<sub>4</sub>[Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]·7H<sub>2</sub>O:** A mixture of K<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·15H<sub>2</sub>O (0.235 g, 0.05 mmol), 4,4'-bipy (0.0384 g, 0.2 mmol), CuCl<sub>2</sub>·2H<sub>2</sub>O (0.0340 g, 0.2 mmol) and H<sub>2</sub>O (8 mL) in a molar ratio of about 1:4:4:2200 was adjusted to approximately pH = 5-6 with 1 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O, then transferred and sealed in a 20 mL Teflon-lined stainless steel container. The container was heated to 190 °C and held at that temperature for 3 days, then cooled to 120 °C at a rate of 5 °C h<sup>-1</sup> and held for 1000 min, followed by further cooling to 30 °C at the same rate. Oxford blue granules of the title compound were collected in 20 % yield (0.0480 g) based on K<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·15H<sub>2</sub>O. Anal. Calcd for C<sub>70</sub>H<sub>80</sub>CuN<sub>14</sub>O<sub>131</sub>P<sub>4</sub>W<sub>36</sub>: C, 8.39; H, 0.80; N, 1.96. Found: C, 8.36; H, 0.77; N, 1.94.

**X-ray crystallography:** Diffraction intensity data for the title compound were collected at 298(2) K on a Bruker Apex-

2000 CCD diffractometer using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) with  $\omega/2\theta$  scan mode. Lorentz-polarization and absorption corrections were applied. Structural solution and full matrix least-squares refinement based on  $F^2$  were performed with the SHELXS-97 and SHELXL-97 program package<sup>36,37</sup>, respectively. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically [(C-H) 0.93  $\text{\AA}$ ]. All the hydrogen atoms were assigned the same isotropic temperature factors and included in the structure factor calculations.

A summary of the crystallographic data, data collection and refinement parameters for the title compound is given in Table-1.

TABLE-1  
SUMMARY OF CRYSTALLOGRAPHIC  
DATA FOR THE TITLE COMPOUND

Empirical formula	C <sub>70</sub> H <sub>80</sub> CuN <sub>14</sub> O <sub>131</sub> P <sub>4</sub> W <sub>36</sub>
Formula weight	10019.50
Crystal system	Orthorhombic
Space group	Pccn
a/ $\text{\AA}$	47.305(7)
b/ $\text{\AA}$	15.314(2)
c/ $\text{\AA}$	21.867(3)
Volume ( $\text{\AA}^3$ )	15840(4)
Z	4
Crystal size (mm)	0.31 $\times$ 0.21 $\times$ 0.20
D <sub>calcd.</sub> (Mg/m <sup>3</sup> )	4.201
Temperature (K)	296(2)
Reflection measured	77163
Unique reflections	15453
R(int)	0.0777
R1/wR2 (I > 2 $\sigma$ (I))	0.0560/0.1055
R1/wR2 (all data)	0.0765/0.1129
GOF on F <sup>2</sup>	1.178

## RESULTS AND DISCUSSION

**Crystal structures:** Hydrothermal reaction of K<sub>6</sub>P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>·15H<sub>2</sub>O with 4,4'-bipyridine and CuCl<sub>2</sub>·2H<sub>2</sub>O in water solution gave the title compound. Single-crystal X-ray diffraction analysis reveals that the title compound crystallizes in the orthorhombic single system with the space group *Pccn*. In the asymmetric unit of the title compound there exist two diprotonated 4,4'-bipy guest, three and half lattice water molecules and half a [Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]<sup>8-</sup> unit. According to bond valence sum calculations<sup>38</sup>, all tungsten atoms in the title compound are in +VI oxidation states and copper atoms are in +II oxidation states. The P-O and W-O lengths for [P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> cluster are in the normal ranges<sup>39,40</sup>. In the [Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]<sup>8-</sup> unit, the Cu(II) center lies in a distorted octahedral geometry. As can be seen in Fig. 1, the Cu(II) ion is coordinated by two terminal oxygen atoms of different [P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>]<sup>6-</sup> cluster at the apical positions and four nitrogen atoms at the basal plane with two from the monoprotonated 4,4'-bipy ligands and two from the 4,4'-bipy ligands. The corresponding bond lengths and angles are 2.442(2)  $\text{\AA}$  (Cu1-O25), 1.97(2)  $\text{\AA}$  (Cu1-N7), 2.077(15)  $\text{\AA}$  (Cu1-N6), 180.000(3) $^\circ$  (N7-Cu1-N8A), 94.4(4) $^\circ$  (N7-Cu1-N6), 85.6(4) $^\circ$  (N8A-Cu1-N6), 171.3(8) $^\circ$  (N6B-Cu1-N6). The letters "A" and "B" in the atom labels indicate symmetry

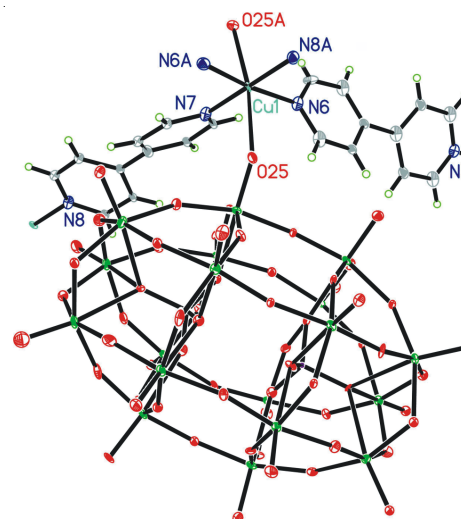


Fig. 1. ORTEP plot showing the [Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]<sup>8-</sup> unit and the coordination environment of Cu(II) ions in the title compound. Symmetry codes: A x, -y + 3/2, z + 1/2

operations "x, -y + 3/2, z + 1/2" and "-x + 1/2, -y + 3/2, z" respectively.

The most remarkable feature of the crystal structure of the title compound is that adjacent Cu(II) ions are connected together through the coordination of two terminal nitrogen atoms of the same 4,4'-bipy ligand. The bridging behaviour of the 4,4'-bipy ligand gives rise to the formation of a 1D polyanionic chain of [Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]<sup>8n-</sup> along the crystallographic c-axis direction, as illustrated in Fig. 2. Interestingly, two adjacent 1D polyanionic chains are parallel to each other and extend in opposite directions.

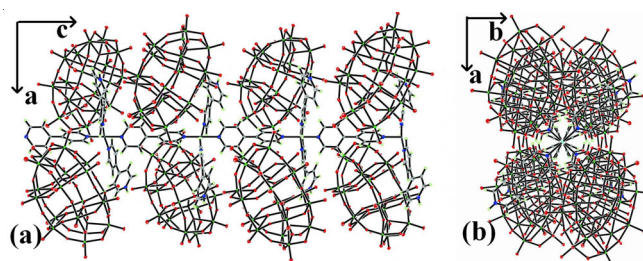


Fig. 2. ORTEP plot showing 1D polyanionic chain of [Cu(4,4'-Hbipy)<sub>2</sub>(4,4'-bipy)(P<sub>2</sub>W<sub>18</sub>O<sub>62</sub>)<sub>2</sub>]<sup>8n-</sup> in the title compound (a) viewed down the b axis and (b) viewed down the c axis. Hydrogen atoms, solvate water molecules and the diprotonated 4,4'-bipy guests are omitted for clarity

Careful crystal structure analysis of the title compound revealed that each 1D polyanionic chain strongly interacts with eight nearest neighbors by the hydrogen bonding between the Wells-Dawson type polyanion and the diprotonated 4,4'-bipy guests (or the lattice water molecules). Hydrogen bonds for the title compound are shown in Table-2. In such a way, the 1D polyanionic chains further joined each other to generate an interesting 3D inorganic-organic hybrid. It is noteworthy that such a 3D supramolecular structure possesses numerous 1D channels along the c-axis, which are filled with the water molecules (Fig. 3). The solvent accessible volume of these channels, calculated with the PLATON program<sup>41</sup>, is 884.2  $\text{\AA}^3$  or 5.6 % of the total unit cell volume (15841.0  $\text{\AA}^3$ ).

TABLE-2  
HYDROGEN BONDS FOR THE TITLE COMPOUND (Å AND deg)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WB)...O(15)	0.85	2.48	3.29(2)	158.8
O(1W)-H(1WB)...O(26)	0.85	2.53	3.15(2)	130.3
O(2W)-H(2WA)...O(30)	0.85	2.11	2.79(2)	136.2
O(2W)-H(2WA)...O(9)	0.85	2.57	3.33(2)	151.0
O(3W)-H(3WA)...O(7)	0.85	2.42	3.06(3)	132.8
O(3W)-H(3WB)...O(23) #4	0.85	2.65	3.12(4)	115.9
O(4W)-H(4WA)...O(44) #5	0.85	2.38	3.080(13)	139.5
O(4W)-H(4WA)...O(2W) #6	0.85	2.41	2.92(5)	119.6

Symmetry transformations used to generate equivalent atoms: #4 -x, y + 1/2, -z + 1/2; #5 x, -y + 5/2, z-1/2; #6 -x + 1/2, -y + 5/2, z

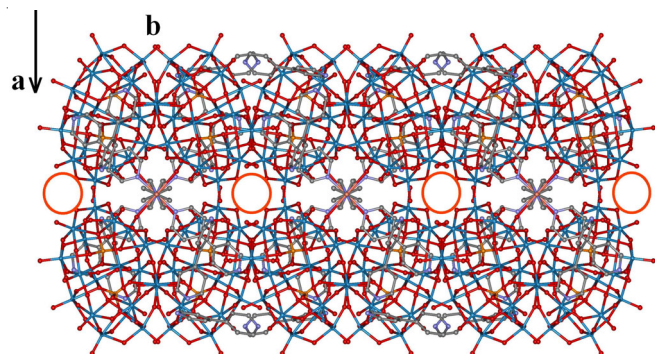


Fig. 3. Structure of the title compound showing the 1D channels along the *c* axis. Hydrogen atoms and solvate water molecules are omitted for clarity

It must be noted that the present compound contain three kinds of 4,4'-bipy molecules and all of them experience some twist. The first kind is the normal 4,4'-bipy ligands serving as bidentate ligands and bridging adjacent Cu(II) ions into linear chain, in which the torsion angel of neighboring pyridine aromatic rings is 36.81° (Fig. 4a). The second kind is the mono-protonated 4,4'-bipy ligands serving as monodentate ligands and coordinating only one Cu(II) ion each, in which the torsion angel of neighboring pyridine aromatic rings is 34.17° (Fig. 4b). The last one kind is the two diprotonated 4,4'-bipy guests, in which the torsion angel of neighboring pyridine aromatic rings are 39.29° and 27.13°, respectively (Fig. 4c).

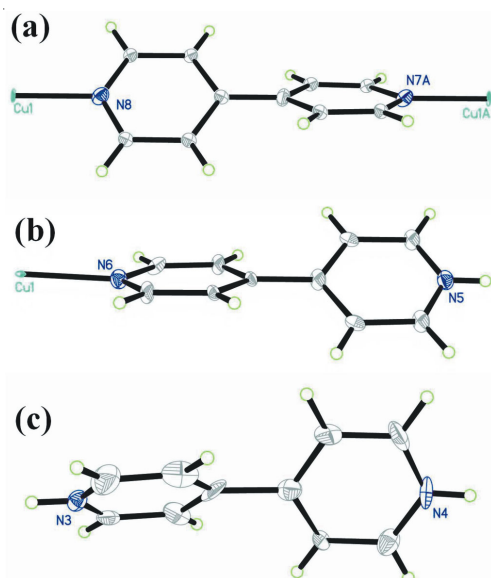


Fig. 4. ORTEP plot showing three kinds of 4,4'-bipy molecules

**IR spectrum:** In the IR spectrum of the title compound (Fig. 5), characteristic bands at 1092, 959, 914, 780 cm<sup>-1</sup> can be attributed to  $\nu(\text{P-O}_a)$ ,  $\nu(\text{W-O}_c)$ ,  $\nu(\text{W-O}_b\text{-W})$  and  $\nu(\text{W-O}_e\text{-W})$ , respectively, which indicates that the polyanion in the title compound still retains Wells-Dawson type structure. Additionally, bands in the region of 1631-1491 cm<sup>-1</sup> can be regarded as the characteristic vibration of 4,4'-bipy ligands.

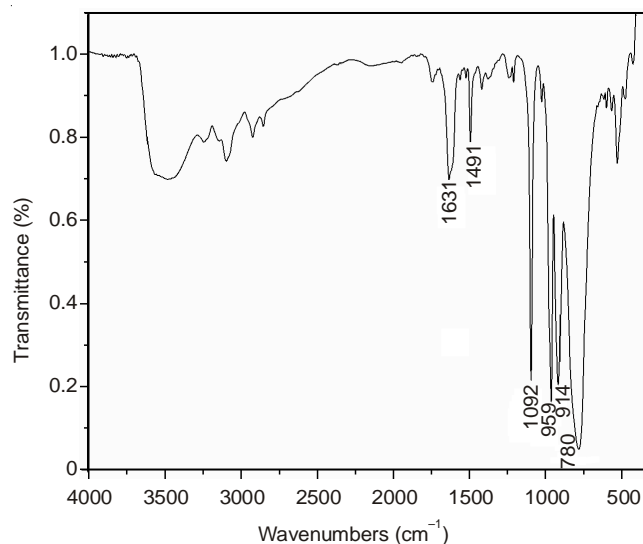


Fig. 5. IR spectra of the title compound

**Thermal analyses:** The title compound is highly stable in air at ambient temperature and almost insoluble in common solvents such as water, alcohol, acetonitrile, chloroform and acetone. To examine thermal stability of this title compound, thermogravimetric analysis were carried out. Thermogravimetric curves (Fig. 6) have been obtained under a flow of N<sub>2</sub> gas for crystalline samples of the title compound in the temperature range 35-900 °C. The thermogravimetric analysis of the title compound revealed two distinct steps of weight losses. Obviously, the first weight loss of 1.23 % in the range of 35-200 °C corresponds to the removal of the lattice water molecules (calculated value, 1.26 %) in each formula unit. No further weight loss was observed until the temperature reached 420 °C, which suggests that the frameworks of the inorganic-organic hybrid materials are highly stable. In the second weight loss (above 420 °C), 4,4'-bipy ligands began to decompose gradually and the resulting white unknown residues can be found after decomposing completely.

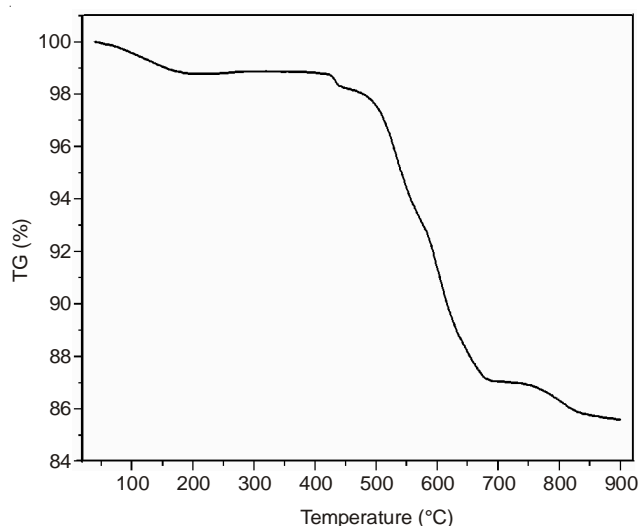


Fig. 6. Thermogravimetric analysis curve of the title compound

## Conclusion

In summary, a novel inorganic-organic hybrid  $(4,4'\text{-H}_2\text{bipy})_4[\text{Cu}(4,4'\text{-Hbipy})_2(4,4'\text{-bipy})(\text{P}_2\text{W}_{18}\text{O}_{62})_2]\cdot 7\text{H}_2\text{O}$  has been hydrothermally synthesized and characterized. X-ray diffraction analysis reveals that Cu(II) coordinated to  $[\text{P}_2\text{W}_{18}\text{O}_{62}]^{6-}$  polyanions, 4,4'-bipy and monoprotonated 4,4'-bipy ligands to form a 1D polyanionic chain. Connection of adjacent 1D polyanionic chains through the hydrogen bonding between the Wells-Dawson type polyanion and the diprotonated 4,4'-bipy guests (or the lattice water molecules) forms 3D supramolecular assembly with parallel channels and the free dimensions of these channels occupy 5.6 % of the crystal volume. Thermal gravimetric analysis indicates that the frameworks of the inorganic-organic hybrid materials are highly stable.

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