

Two New Supramolecular Hybrids Based on Bi-capped Keggin {PMo₁₂V₂O₄₂} Clusters and Transition Metal Mixed-organic-ligand Complexes

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Abstract Two supramolecular compounds [Cu(imz)₂][Cu(phen)(imz)₂]{[Cu(phen)]₂[PMo₆^{VI}Mo₆^{IV}V₂^{IV}O₄₂]} (**1**) and [Co₂(2,2'-bpy)₄(C₂O₄)] [Co(2,2'-bpy)₃][PMo₇^{VI}Mo₅^VV₂^{IV}O₄₂](2,2'-bpy)_{0.5}·H₂O (**2**) (phen=1,10'-phenanthroline, imz=imidazole, 2,2'-bpy=2,2'-bipyridine) have been synthesized hydrothermally and characterized by elemental analyses, infrared spectrum, UV-Vis, X-ray photoelectron spectroscopy(XPS), electron spin resonance(ESR) spectra, thermogravimetry analyses and single crystal X-ray diffraction analyses. Single-crystal X-ray diffraction analyses revealed that both the compounds represent the examples of compounds based on the bi-capped Keggin polyoxoanion {PMo₁₂V₂O₄₂} and transition metal mixed-organic-ligand coordination complexes. Compound **1** consists of bi-capped Keggin polyoxoanion [PMo₁₂V₂O₄₂]⁵⁻ supported copper coordination groups, which are further interconnected with two types of copper complex fragments forming a 3D supramolecular framework *via* $\pi\cdots\pi$ stacking, C—H \cdots O and N—H \cdots O hydrothermal bonding interactions. Compound **2** is a new hybrid consisted of polyoxoanion [PMo₁₂V₂O₄₂]⁴⁻, [Co₂(2,2'-bpy)₄(C₂O₄)]²⁺ and [Co(2,2'-bpy)₃]²⁺. There are no direct interactions in compound **2**, but the polyoxoanions together with two different cobalt complex groups construct a 3D supramolecular network through C—H \cdots O hydrogen bonding interactions.

Keywords Transition metal mixed-organic-ligand complex; Keggin polyoxometalate; Hydrogen bond; $\pi\cdots\pi$ Stacking interaction

1 Introduction

In recent years, the design and synthesis of supramolecular assemblies have drawn more and more attention due to their fascinating properties and potential applications in the areas of molecular electronics, sensor design, catalysis and photochemistry^[1–4]. Currently, one important strategy in the field of supramolecular chemistry is to make 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, etc. Doubtless, the hydrogen bond plays a major role in supramolecular assemblies due to its unique strength and directionality that may control short-range packing^[5–10]. Poly-oxometalates (POMs), as one kind of ideal inorganic building block to construct coordination polymers, have attracted an extensive interest owing to their nano sizes, intriguing topological structures and numerous applications in analytical chemistry, magnetism, material science and medicine^[11–17]. However, supramolecular compounds based on Keggin-type POMs have been unexplored in recent years, though their spherical oxygen-rich surfaces can give a better opportunity in

forming various hydrogen bonds with the organic/inorganic moieties^[18–25].

Keggin POMs and their derivatives have become a major research focus in the field of POMs chemistry because of their nano size, intriguing topological structures and their potential application in catalysis, medicine, optic and magnetic materials^[11,26–29].

For the past ten years, a large number of hybrid compounds constructed from a combination of POMs with transition metal complexes(TMCs) have been obtained^[23,30–46]. These compounds can be mainly divided into two groups. First, POMs and TMCs linked into 1D, 2D and 3D extended structures with covalent bond interaction. Secondary, POMs linked up with TMCs to form high-dimensional supramolecular assembly through weak bond interactions, such as hydrogen bonding, $\pi\cdots\pi$ stacking and van der Waals interactions, etc.^[23,31–44].

On the other hand, Keggin POMs derivatives could be categorized into two groups: (I) substituted Keggin POMs^[45]; (II) capped Keggin POMs^[23,30–43], and the TMCs contains two parts: (I) the central metal anions used are always Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺ or some lanthanide ions; (II) organic ligands used

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are more diverse, including N-containing ligands and O-containing ligands. As we all known, the supramolecular compounds based on Keggin-type POMs and TMCs have been explored in recent years due to polyoxoanions spherical oxygen-rich surfaces which can give a better opportunity to form various hydrogen bonds with the organic/inorganic moieties. However, supramolecular compounds constructed from capped Keggin POMs and transition metal mixed-organic-ligand complexes have remained relatively unexplored. And to the best of our knowledge, only a few such hybrids were reported previously^[46–51].

Considering quite a limited number of supramolecular compounds based on POM and transition metal mixed-organic-ligand complexes compared to a large family of high-dimensional supramolecular coordination polymeric frameworks, we attempted to explore the preparation of hybrids based on POMs and transition metal mixed-organic-ligand complexes.

Fortunately, two new high-dimensional supramolecular compounds $[\text{Cu}(\text{imz})_2][\text{Cu}(\text{phen})(\text{imz})]_2 \cdot \{[\text{Cu}(\text{phen})]_2[\text{PMo}_6^{\text{VI}}\text{Mo}_6^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}]\}$ (**1**) and $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)] \cdot [\text{Co}(2,2'\text{-bpy})_3][\text{PMo}_7^{\text{VI}}\text{Mo}_5^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}](2,2'\text{-bpy})_{0.5}\text{H}_2\text{O}$ (**2**) have been synthesized hydrothermally. Compound **1** consists of bi-capped Keggin polyoxoanion $[\text{PMo}_{12}\text{V}_2\text{O}_{42}]^{4-}$ supported copper coordination groups, which are further interconnected with two types of cooper complex fragments, forming a 3D supramolecular framework *via* $\pi \cdots \pi$ stacking and hydrothermal bonding interactions. Compound **2** is a hybrid compound consisted of polyoxoanion $[\text{PMo}_{12}\text{V}_2\text{O}_{42}]^{4-}$, $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)]^{2+}$ and $[\text{Co}(2,2'\text{-bpy})_3]^{2+}$. There are no direct interactions in compound **2**, but the polyoxoanions together with two different cobalt complex groups construct a 3D supramolecular network through complex C—H \cdots O hydrogen bonding interactions.

2 Experimental

2.1 Reagents and Apparatuses

All the chemicals were purchased and used without further purification. Elemental analyses(C, H and N) were performed on a Perkin-Elmer 2400 Series II CHNS/O elemental analyzer. Analyses of Si, W and Cu were performed on a Perkin-Elmer Optima 3300DV spectrophotometer. Infrared(IR) spectra were obtained on a Perkin-Elmer spectrophotometer from 200 cm^{-1} to 4000 cm^{-1} with pressed KBr pellets. UV-Vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer in the saturated solution of *N,N*-dimethylformamide. The X-ray photoelectron spectroscopy(XPS) measurement was performed on a Thermo ESCALAS 250 spectrometer with a Mg $K\alpha$ (1253.6 eV) achromatic X-ray source. Electron spin resonance(ESR) spectra were recorded on a Bruke ER 200D-SRC spectrometer. The thermogravimetric(TG) analyses were taken on a Perkin-Elmer TGA-7000 thermogravimetric analyzer in flowing air at a temperature rate of 10 $^\circ\text{C}/\text{min}$. Variable temperature magnetic susceptibility measurement was performed on a Quantum Design MPMS XL-5 SQUID magnetometer in a temperature range of 2—300 K.

2.2 Syntheses

2.2.1 Synthesis of $[\text{Cu}(\text{imz})_2][\text{Cu}(\text{phen})(\text{imz})]_2 \cdot \{[\text{Cu}(\text{phen})]_2[\text{PMo}_6^{\text{VI}}\text{Mo}_6^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}]\}$ (**1**)

$(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (0.62 g, 0.33 mmol), V_2O_5 (0.13 g, 0.72 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.17 g, 1 mmol), phen(0.18 g, 0.9 mmol), imz(0.12 g, 1.8 mmol), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.47 g, 3.7 mmol) and distilled water(20 mL) were mixed, stirred for 60 min, and the pH of the mixture was necessarily adjusted to 5 with $\text{NH}_3 \cdot \text{H}_2\text{O}$. The mixture was transferred to a Teflon-lined autoclave(35 mL) and heated to 160 $^\circ\text{C}$ within 90 min, kept at 160 $^\circ\text{C}$ for 3 d, and then cooled gradually to room temperature at a rate of about 4 $^\circ\text{C}/\text{h}$. Black block crystals of compound **1** suitable for X-ray diffraction were isolated in a yield of 78%(based on Mo). Elemental anal.(%) calcd. for $\text{C}_{60}\text{H}_{48}\text{N}_{16}\text{Mo}_{12}\text{V}_2\text{Cu}_5\text{O}_{42}\text{P}$ (3267.21): C 22.06, H 1.48, N 6.86, Mo 35.24, V 3.12, Cu 9.73, P 0.95; found: C 22.03, H 1.51, N 6.92, Mo 35.19, V 3.13, Cu 9.76, P 0.93.

2.2.2 Synthesis of $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)] \cdot [\text{Co}(2,2'\text{-bpy})_3][\text{PMo}_7^{\text{VI}}\text{Mo}_5^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}](2,2'\text{-bpy})_{0.5} \cdot \text{H}_2\text{O}$ (**2**)

$(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40} \cdot x\text{H}_2\text{O}$ (0.62 g, 0.33 mmol), V_2O_5 (0.13 g, 0.72 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.24 g, 1 mmol), 2,2'-bpy(0.28 g, 1.8 mmol), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.47 g, 3.7 mmol) and distilled water(20 mL) were mixed, stirred for 60 min, and the pH of the mixture was necessarily adjusted to 3 with $\text{NH}_3 \cdot \text{H}_2\text{O}$. The mixture was transferred to a Teflon-lined autoclave(35 mL) and heated to 160 $^\circ\text{C}$ within 90 min, kept at that temperature for 3 d, and then cooled gradually to room temperature at a rate of about 4 $^\circ\text{C}/\text{h}$. Black block crystals of compound **2** suitable for X-ray diffraction(XRD) were isolated in a yield of 66%(based on Mo). Elemental anal.(%) calcd. for $\text{C}_{77}\text{H}_{62}\text{N}_{15}\text{Mo}_{12}\text{V}_2\text{Co}_3\text{O}_{47}\text{P}$ (3410.56): C 27.12, H 1.83, N 6.16, Mo 33.76, V 2.99, Co 5.18, P 0.91; found: C 27.15, H 1.81, N 6.18, Mo 33.73, V 3.01, Co 5.16, P 0.89.

2.3 X-Ray Crystallography

Reflection intensity data of compound **1** were collected on a Rigaku R-AXIS RAPID IP diffractometer with graphite monochromated Mo $K\alpha$ ($\lambda=0.071073$ nm) radiation, and those of compound **2** were measured on a Bruker Smart CCD diffractometer at room temperature with graphite monochromated Mo $K\alpha$ ($\lambda=0.071073$ nm) radiation. Neither the crystal showed the evidence of crystal decay during data collections. Both the structures were solved by the direct method and refined with full-matrix least squares on F^2 with the help of SHELXTL-97 crystallographic software^[52]. In final refinements, all the atoms were refined anisotropically; hydrogen atoms were included in their ideal positions, while those of water and disorder 2,2'-bpy in compound **2** were not added. A summary of the crystallographic data and structure refinements for compounds **1** and **2** is given in Table 1. Selected bond lengths of compounds **1** and **2** are listed in Tables S1 and S2(see the Electronic Supplementary Material of this paper).

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

Compound	1	2
Empirical formula	C ₆₀ H ₄₈ Cu ₅ N ₁₆ O ₄₂ PMo ₁₂ V ₂	C ₇₇ H ₆₂ Co ₃ N ₁₅ O ₄₇ PMo ₁₂ V ₂
Formula weight	3267.21	3410.56
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
<i>a</i> /nm	1.2949(3)	1.65509(8)
<i>b</i> /nm	1.3053(3)	2.84089(8)
<i>c</i> /nm	1.4063(3)	2.29185(1)
α (°)	94.92(3)	90
β (°)	90.09(3)	94.926(3)
γ (°)	115.86(3)	90
Volume/nm ³	2.1291(3)	10.7363(8)
<i>Z</i>	1	4
<i>D_c</i> /(Mg·m ⁻³)	2.548	2.110
Absorption coefficient/mm ⁻¹	3.246	2.071
θ range for data collection/(°)	3.14—27.48	1.43—28.28
<i>F</i> (000)	1565	6604
Reflection collected	9533/643	36955/13153
Goodness-of-fit on <i>F</i> ²	1.050	1.058
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ ^a =0.0520, <i>wR</i> ₂ ^b =0.1601	<i>R</i> ₁ ^a =0.0846, <i>wR</i> ₂ ^b =0.2691
Largest diff. peak and hole/(e·nm ⁻³)	1533 and -2272	3623 and -4419
CCDC No.	1042344	1042345

$$a. R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; b. wR_2 = \left\{ \frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right\}^{1/2}.$$

3 Results and Discussion

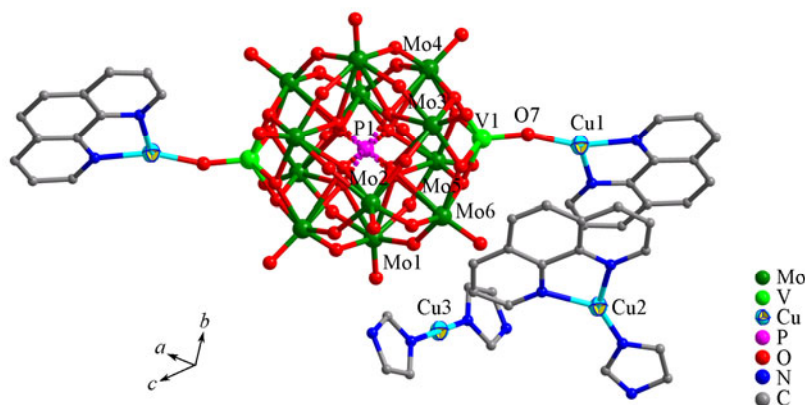
3.1 Synthesis

Hydrothermal synthesis has been proven to be a perfect technique to prepare organic-inorganic hybrids based on POMs and transition metal mixed-organic-ligand complexes^[53]. Compounds **1** and **2** were successfully isolated from the reaction of (NH₄)₃PMo₁₂O₄₀·*x*H₂O and CuCl₂·2H₂O/CoCl₂·6H₂O in the presence of two or more different organic ligands as structural-directing agent by hydrothermal method. Some strategies are crucial for the formation of the two compounds. (I) Adding the metal as center together with two or more different organic ligands is significant in the self-assembly of the transition metal mixed-organic-ligand complexes. As we know, transition metal center atoms can efficiently influence the formation of hybrid structure. If CuCl₂·2H₂O was substituted by CoCl₂·6H₂O in compound **1** and replaced CoCl₂·6H₂O with CuCl₂·2H₂O in the preparation of compound **2**, only unidentified amorphous powders were obtained. (II) The pH

value is significant. When the pH value was 5, compound **1** can be formed, and only when the pH was 3, was compound **2** formed. On the other hand, oxalic acid has three main advantages for the preparation of compounds **1** and **2**. (I) It is a moderate acid; with the addition of H₂C₂O₄·2H₂O, the solution of the starting material has a lower pH value, which is advantageous for the formation of POM anions. (II) It is a bidentate ligand in compound **2**. (III) It is also a reducing reagent under the hydrothermal conditions, Cu²⁺, Mo⁶⁺ and V⁵⁺ in reagent were reduced in the presence of H₂C₂O₄·2H₂O. Relevant research revealing the synthetic rules is underway in our group.

3.2 Crystal Structure of Compound **1**

Crystal structure analysis reveals that the asymmetric unit of compound **1** consists of a [PMo₆^{VI}Mo₆^VV₂^{IV}O₄₂]⁵⁻ anion, a [Cu(phen)]⁺ cation, two [Cu(phen)(imz)]⁺ cations and a [Cu(imz)₂]⁺ cation. As shown in Fig.1, the bi-capped Keggin polyoxoanion [PMo₆^{VI}Mo₆^VV₂^{IV}O₄₂]⁵⁻ is based on a typical Keggin core [PMo₁₂O₄₀]³⁻ with two [VO₂]²⁺ cations capping its two opposite pits. The anion [PMo₁₂O₄₀]³⁻ can be described as

**Fig.1** Crystal structure of compound **1**

Several hydrogen atoms are omitted for clarity.

four internally edge-shared tri-octahedra Mo_3O_{13} corner-shared to each other, which are disposed tetrahedrally around a central PO_4 unit. The P—O distances vary from 0.1499(7) nm to 0.1624(8) nm. According to the coordination mode, there are three kinds of oxygen atoms in the $[\text{PMo}_{12}\text{V}_2\text{O}_{42}]^{5-}$: terminal oxygen(O_t), bridging oxygen(O_b) and central oxygen(O_c). The Mo— O_t distances are 0.1640(6)—0.1666(5) nm, V— O_t distances are 0.1611(5) nm, Mo— O_b distances are 0.1805(6)—0.2061(5) nm, V— O_b distances are 0.1932(5)—0.1938(6) nm and Mo— O_c distances are 0.2450(8)—0.2515(8) nm, respectively (Table S1, see the Electronic Supplementary Material of this paper). These results show that the bond lengths in compound **1** are comparable to the reported values^[41]. The bond valence sum calculation (BVS) values^[54] for the six crystallographically independent molybdenum atoms of compound **1** are 5.47, 5.50, 5.59, 5.56, 5.54 and 5.58, respectively, with the average value of 5.54 (the expected for $\text{Mo}_6^{\text{V}}\text{Mo}_6^{\text{VI}}$ being 5.50), and those of two vanadium atoms are both 4.14. The above-calculated results are consistent with the formula $[\text{PMo}_6^{\text{VI}}\text{Mo}_6^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}]^{5-}$.

According to the coordinated environments, there are three different types of copper cations in compound **1**. The Cu1 in the Cu-phen complex cation is coordinated by two nitrogen atoms from a phen molecule with Cu—N bond distances of 0.1974(5) and 0.2122(7) nm. As illustrated in Fig.1, two copper complexed cations $\{[\text{Cu1}(\text{phen})]^+\}$ and $[\text{Cu1A}(\text{phen})]^+$, symmetry code A, $1-x$, $2-y$, $1-z$ are connected with $[\text{PMo}_6^{\text{VI}}\text{Mo}_6^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}]^{5-}$ anion through the two covalent bonds Cu1—O7 and Cu1A—O7A with a Cu—O distance of 0.1866(5) nm, respectively, forming one new bi-supported $\{[\text{Cu}(\text{phen})]_2[\text{PMo}_6^{\text{VI}}\text{Mo}_6^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}]\}^{3-}$ cluster, which is different from these bi-supported compounds constructed from copper complexes and capped-Keggin clusters reported by our group^[31,37]. The Cu2 in the Cu-phen-imz complex cation is coordinated by two nitrogen atoms belonging to the phen and one nitrogen atom belonging to imidazole ligand with Cu—N bond distances of 0.1862(8)—0.2075(8) nm, exhibiting an irregular triangle geometry. The Cu3 in the Cu3-imz complex

cation receives the contributions from the two nitrogen atoms belonging to the two imidazole ligands with Cu—N bond distances of 0.1879(7) nm, exhibiting a regular rod-like geometry. To our knowledge, compound **1** contains three different kinds of copper complex with mixed-organic-ligand, which has not been observed before.

The most unusual structural feature of compound **1** is that $\pi\cdots\pi$ stacking and hydrogen bonds play important roles in stabilizing the crystal structure. Detailed analysis reveals that there exists three kinds of $\pi\cdots\pi$ stacking interaction in compound **1**. As shown in Fig.2, the bi-supported $\{[\text{Cu}(\text{phen})]_2[\text{PMo}_6^{\text{VI}}\text{Mo}_6^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}]\}^{3-}$ cluster anions are stacked into some 1D supramolecular chains by the $\pi\cdots\pi$ stacking interaction between the coordinating phen molecules [0.3686 nm, ring(N1, C1—C4, C12) from a copper-phen complex to ring(N2, C7—C11) from a neighbouring copper-phen complex]. These 1D chains are further stacked along *b* axis into 2D supramolecular layers by $\pi\cdots\pi$ stacking interaction between the phen ligands bonded to Cu1 atom and those bonded to Cu2 [0.3585 nm, ring(N1, C1—C4, C12) from a copper-phen complex to ring(N4, C19—C23) from a copper-phen-imz complex; 0.3683 nm, ring(C4—C7, C11—C12) from a copper-phen to ring(N3, C13—C16, C24) from copper-phen-imz], and the $\pi\cdots\pi$ stacking interaction between the phen ligands bonded to Cu2 atom and the imidazole ligands bonded to Cu2 [0.3686 nm, ring(N4, C19—C23) to ring(N5, N6, C25—C27)]. There also exist strong C—H \cdots O and N—H \cdots O hydrogen bond interactions in compound **1**. The 2D supramolecular layers are extended into a novel 3D supramolecular network *via* hydrogen-bonding interactions between the coordinating imidazole ligand bonded to Cu3 atom and the terminal oxygen atoms of POMs with the N6—H \cdots O13 and C28—H \cdots O12 distances of 0.3023(1) and 0.3239(1) nm, as shown in Fig.S1 (see the Electronic Supplementary Material of this paper). This strong hydrogen bonding interactions in compound **1** are listed in Table 2.

Several compounds based on bi-capped Keggin POMs and TMCs have been reported^[23,33—35,38—40]. However, it is strange that the compounds based on bi-capped Keggin POMs and

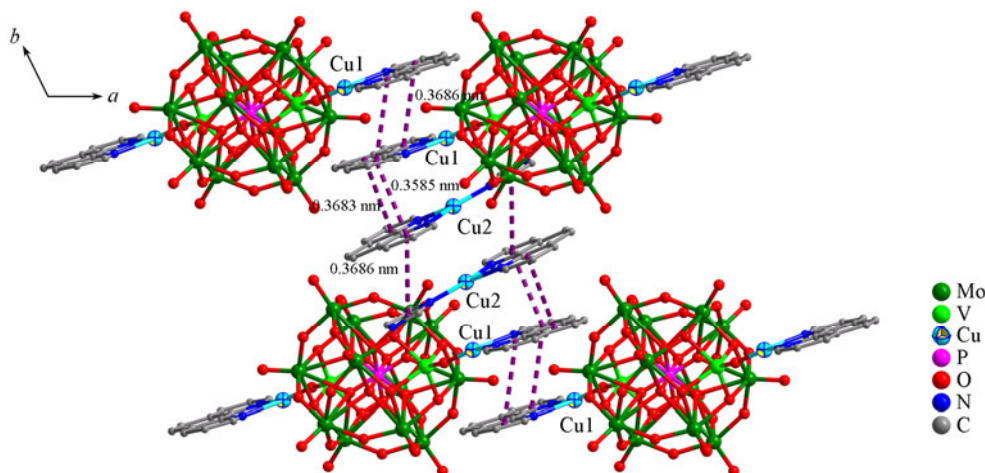


Fig.2 Ball-and-stick representation of the 2D supramolecular layer constructed from the bi-supported POMs and $[\text{Cu2}(\text{phen})(\text{imz})]^+$ TMCs through $\pi\cdots\pi$ stacking interaction on the *ab* plane in compound **1**

Several hydrogen atoms are omitted for clarity.

Table 2 Lengths of hydrogen bonds in compounds **1** and **2***

Compound	D—H···A	d(D—H···A)/nm	Compound	D—H···A	d(D—H···A)/nm
1	C3—H···O20#1	0.3241(9)	2	C10—H···O12#2	0.3279(1)
	C6—H···O7#2	0.3216(8)		C11—H···O10#2	0.3160(1)
	C13—H···O21	0.3142(1)		C13—H···O3#3	0.3271(1)
	C14—H···O21	0.3100(7)		C14—H···O7#3	0.3280(1)
	C20—H···O10#3	0.3282(1)		C17—H···O13#3	0.3181(1)
	C22—H···O21#4	0.3206(1)		C18—H···O13	0.3096(1)
	C27—H···O7#4	0.3143(9)		C20—H···O17#4	0.3196(1)
	C28—H···O12#5	0.3293(1)		C20—H···O22	0.3191(1)
	C29—H···O19#6	0.3292(8)		C21—H···O9#5	0.3297(1)
	C30—H···O18	0.3209(8)		C27—H···O6#6	0.3269(1)
	N6—H···O9#7	0.3265(3)		C33—H···O5#7	0.3211(1)
	N6—H···O13#7	0.3023(1)		OW1···O5#3	0.3204(1)
	N8—H···O14#8	0.3023(1)		OW1···O15#3	0.3240(1)
	2	C8—H···O9#1		0.3264(1)	OW1···C24#4
C9—H···O11#2		0.3241(1)			

* Symmetric codes for compound **1**: #1. $-1+x, y, z$; #2. $-x, 2-y, -z$; #3. $1-x, 2-y, -z$; #4. $-x, 1-y, -z$; #5. $-x, 1-y, 1-z$; #6. $x, -1+y, z$; #7. $-1/2+x, 1/2-y, -1/2+z$; #8. $1-x, -1-y, 1-z$; symmetric codes for compound **2**: #1. $-1+x, -1/2-y, 1/2+z$; #2. $1-x, y, 1/2-z$; #3. $1/2-x, 1/2+y, 1/2-z$; #4. $x, 1-y, -1/2+z$; #5. $-x, y, 1/2-z$; #6. $1/2-x, 1/2-y, 1-z$; #7. $1/2+x, 1/2+y, z$.

transition metal mixed-organic-ligand complexes are rather rare^[41]. Compound **1** not only gives a new example of such compounds, but also shows features unobserved before with three different TMCs including a kind of transition metal mixed-organic-ligand complex.

3.3 Crystal Structure of Compound **2**

The asymmetric unit of compound **2** is composed of a bi-capped Keggin polyanion $[\text{PMo}_7\text{V}_5\text{V}_2\text{O}_{42}]^{4-}$, one $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)]^{2+}$ cation, one $[\text{Co}(2,2'\text{-bpy})_3]^{2+}$ cation, half a disorder $2,2'\text{-bpy}$ and one water molecule. As shown in Fig.3, the $[\text{PMo}_7\text{V}_5\text{V}_2\text{O}_{42}]^{4-}$ polyanion in compound **2** is identical to that in compound **1**, but the differences are bond distances, bond angles and negative charges of the two polyanions. The bond valence sum(BVS) values for the six crystallographically independent molybdenum atoms in compound **2** are 5.56, 5.62, 5.63, 5.56, 5.53 and 5.53, respectively, with an average value of 5.57(the expected for Mo_7Mo_5 , being 5.58), and also a value

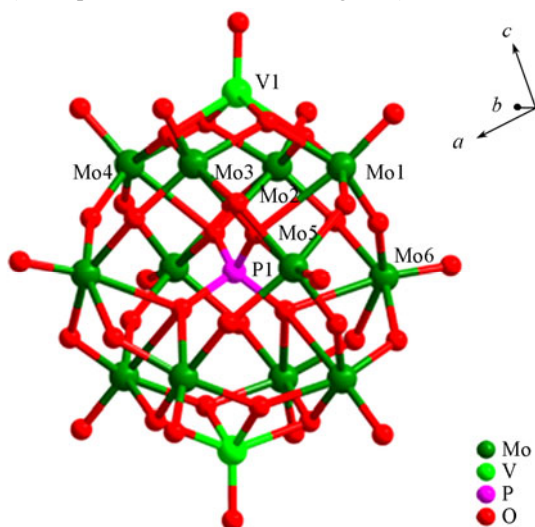


Fig.3 Combined ball-and-stick representation of the polyoxoanion $[\text{PMo}_7\text{V}_5\text{V}_2\text{O}_{42}]^{4-}$ showing the bi-capped Keggin structure in compound **2**

Several hydrogen atoms are omitted for clarity.

of 4.01 for V1. The above-calculated results are consistent with the formula $[\text{PMo}_7^{\text{VI}}\text{Mo}_5^{\text{V}}\text{V}_2\text{O}_{42}]^{4-}$.

According to the coordinated environments, there are two different types of cobalt cations in compound **2**. It is noteworthy that the Co1 cation in the Co1- $2,2'\text{-bpy}$ -oxalic complex cation $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)]^{2+}$ exhibits an unprecedented structural feature. In contrast to the one in compound **1**, the metal mixed-organic-ligand complex contains not only N-containing ligands but also one O-containing ligand. To the best of our knowledge, only three examples of hybrids of POMs and metal mixed-organic-ligand complexes which are constructed from both N-containing and O-containing ligands have been reported^[41,47,50]. The crystal structure analysis reveals that compound **2** is the first hybrid of POMs and cobalt coordination complex with one N-containing and one O-containing organic ligand. As shown in Fig.4(A), $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)]^{2+}$ is constructed from two Co coordination complexes connected by an oxalate anion. Each Co ion is coordinated by four nitrogen atoms from two $2,2'\text{-bpy}$ molecules with Co—N bond distances in a range of 0.2113(8)—0.2146(1) nm, and two oxygen atoms from one oxalic acid molecule with Co—O bond distances of 0.2113(8) and 0.2117(8) nm. It should be noted that there exist two such distorted octahedra in compound **2**, and oxalate anion acts as an organic bridge connecting the two distorted octahedra into a novel metal mixed-organic-ligand complex. The Co2 cation in compound **2** is coordinated with six nitrogen atoms from three $2,2'\text{-bpy}$ molecules to form a distorted octahedron with Co—N bond distances in a range of 0.2080(8)—0.2127(8) nm [Fig.4(B)]. According to a number of references^[23,33–35,38–40], neither bi-capped Mo/V Keggin type is decorated by the $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)]^{2+}$ and $[\text{Co}(2,2'\text{-bpy})_3]^{2+}$ cations.

A striking feature of compound **2** is that it exhibits an unusual 3D supramolecular network structure constructed from $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)]^{2+}$ cations, $[\text{Co}(2,2'\text{-bpy})_3]^{2+}$ cations and POMs anions through C—H···O hydrogen bonds, as shown in Fig.5. The $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)]^{2+}$ cation joins six adjacent anions together through hydrogen-bonding interactions of

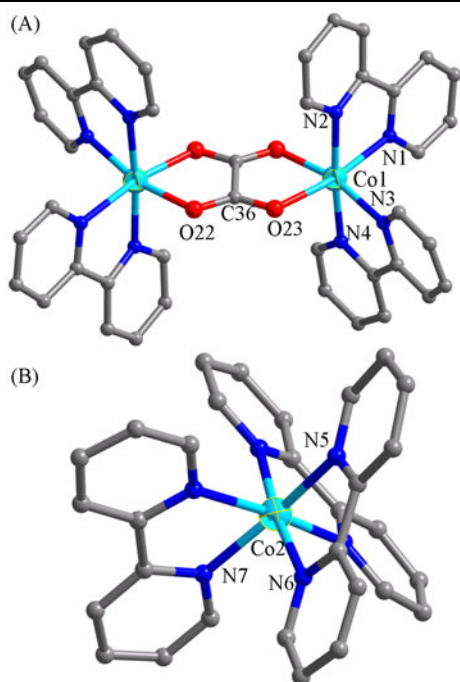


Fig.4 Ball-and-stick representations of two different cations in compound **2**

(A) Co1-2,2'-bpy-oxalic complex; (B) Co2-2,2'-bpy complex. Several hydrogen atoms are omitted for clarity.

C8—H \cdots O9(-1/2+x, 1/2-y, -1/2+z), C9—H \cdots O11(1-x, y, 1/2-z), C11—H \cdots O10(1-x, y, 1/2-z), C20—H \cdots O17(x, 1-y, -1/2+z), C13—H \cdots O3(1/2-x, 1/2+y, 1/2-z), C17—H \cdots O13(1/2-x, 1/2+y, 1/2-z) and C18—H \cdots O13(1/2-x, 1/2+y, 1/2-z) with the distances of 0.3264(1), 0.3241(1), 0.3160(1), 0.3196(1), 0.3271(1), 0.3181(1) and 0.3096(1) nm, respectively. The [Co(2,2'-bpy) $_3$] $^{2+}$ cation joins five adjacent anions through hydrogen-bonding interactions of C21—H \cdots O9(-x, y, 1/2-z), C27—H \cdots O6(1-x, y, 1/2-z), C27—H \cdots O13, C27—H \cdots O6(1/2-x, 1/2-y, 1-z) and C33—H \cdots O5(-1/2+x, 1/2+y, z) with distances of 0.3297(1) 0.3269(1), 0.3230(1), 0.3269(1) and 0.3211(1) nm, respectively. Alternatively, each POM links six [Co $_2$ (2,2'-bpy) $_4$ (C $_2$ O $_4$)] $^{2+}$ cations together through C—H \cdots O hydrogen-bonding interactions. These hydrogen bonds play important roles in stabilizing the crystal structure of compound **2**. [PMo $^{VI}_7$ Mo V_5 V $_2$ O $_42$] $^{4-}$ anion and the different cobalt cations are linked by complex hydrogen bonds(C—H \cdots O) to give the complex a 3D supramolecular network structure. Disordered 2,2'-bpy molecules(Fig.S2, see the Electronic Supplementary Material of this paper) are located in the holes of the 3D supramolecular network. This strong hydrogen bonding interaction in compound **2** is listed in Table 2.

Compound **2** is constructed from POMs and two different TMCs. Compared with those of compound **1**, no $\pi\cdots\pi$ stacking

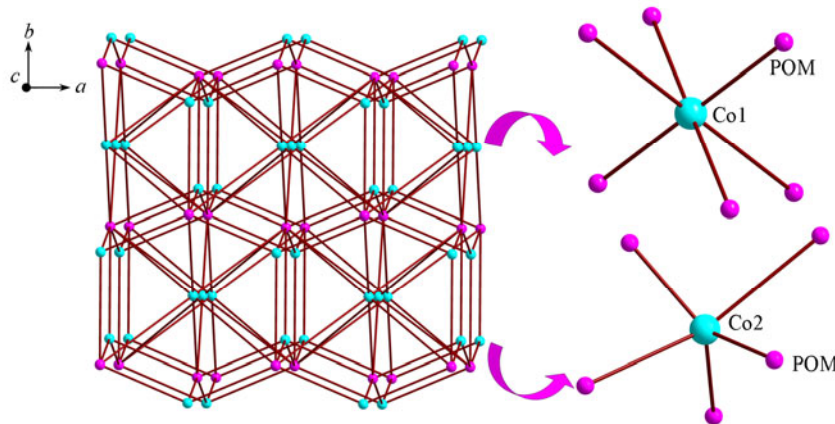


Fig.5 Schematic representation of the 3D topological network constructed from POMs, [Co $_2$ (2,2'-bpy) $_4$ (C $_2$ O $_4$)] $^{2+}$ and [Co(2,2'-bpy) $_3$] $^{2+}$ fragments through C—H \cdots O hydrogen bonding interactions along *c* axis in compound **2**

interactions exist in compound **2**. The lacking of $\pi\cdots\pi$ stacking interaction may be attributed to steric hindrance of the POMs.

3.4 Characterization

3.4.1 IR Spectra

The IR spectra of compounds **1** and **2** are shown in Fig.S3(see the Electronic Supplementary Material of this paper). Three characteristic peaks in the low-wavenumber region($\tilde{\nu}<1000$ cm $^{-1}$) at 947, 834 and 769 cm $^{-1}$ for compound **1**, and 965, 937 and 760 cm $^{-1}$ for compound **2** are attributed to the ν (Mo—O $_t$), ν (Mo—O $_b$ —Mo), and ν (Mo—O $_c$) frequencies, respectively^[55]. The peaks at 714 cm $^{-1}$ for compound **1** and at 727 cm $^{-1}$ for compound **2** are attributed to the ν (O—V—O) frequencies^[41]. The peaks at 1066 cm $^{-1}$ for compound **1** and at 1048 cm $^{-1}$ for compound **2** are attributed to the ν (P—O $_c$)

frequencies^[41]. The peaks in the regions of 1141—1622 cm $^{-1}$ for compound **1** and 1109—1642 cm $^{-1}$ for compound **2** are due to vibrations of phen and imidazole ligands in compound **1**, and those of 2,2'-bpy in compound **2**. The strong broad bands around 3450 cm $^{-1}$ for compound **2** could be due to the stretching vibration of water molecules.

3.4.2 UV-Vis Spectra

The UV-Vis spectra of compounds **1** and **2**, in a range of 250—400 nm, are presented in Fig.S4(see the Electronic Supplementary Material of this paper). Characteristic bands at 284 nm for compound **1**, and 274 nm for compound **2** are attributed to the charge transfer band of O \rightarrow Mo in the polyanion of the compounds^[41]. It should be noted that the spectra for compounds **1** and **2** are very similar to each other, indicating that compounds **1** and **2** contain similar Keggin type POMs.

3.4.3 XPS and ESR Spectra

The XPS spectra of compounds **1** and **2** are similar to each other. Fig.S5(see the Electronic Supplementary Material of this paper) shows the XPS spectrum of compound **1** with four overlapped peaks at 232.4, 233.2, 235.0 and 236.2 eV ascribed to $\text{Mo}_{3d_{5/2}}^{5+}$, $\text{Mo}_{3d_{5/2}}^{6+}$, $\text{Mo}_{3d_{5/2}}^{5+}$ [Fig.S5(A)], and $\text{Mo}_{3d_{5/2}}^{6+}$, and a peak at 516.1 eV attributed to $\text{V}_{2p_{3/2}}^{4+}$ [Fig.S5(B)], respectively. The XPS spectrum of compound **2** shows four overlapped peaks at 232.2, 233.0, 235.4 and 236.2 eV ascribed to $\text{Mo}_{3d_{5/2}}^{5+}$, $\text{Mo}_{3d_{5/2}}^{6+}$, $\text{Mo}_{3d_{5/2}}^{5+}$, and $\text{Mo}_{3d_{5/2}}^{6+}$ [Fig.S6(A), see the Electronic Supplementary Material of this paper], and a peak at 515.9 eV attributed to $\text{V}_{2p_{3/2}}^{4+}$ [Fig.S6(B), see the Electronic Supplementary Material of this paper], respectively^[43]. The XPS estimation of valence is in reasonable agreement with those calculated from bond valence sum calculations.

The ESR spectrum of compound **2** shows the signal of V^{4+} with $g_{\parallel}=1.997$ and $g_{\perp}=2.066$ for compound **2** (Fig.S7, see the Electronic Supplementary Material of this paper), respectively. The XPS and ESR estimation of valence is in reasonable agreement with those calculated from bond valence sum calculations.

3.4.4 XRD Analysis

The XRD analyses have already been done to confirm the phase purity of compounds **1** and **2** (Fig.S8, see the Electronic Supplementary Material of this paper). The experimental patterns of compounds **1** and **2** are in good agreement with the simulated patterns, respectively, indicating that the phase purities of compounds **1** and **2** are good. The differences in reflection intensity are probably due to preferred orientations in the powder samples of compounds **1** and **2**.

3.4.5 Thermogravimetric Analysis

The TG analysis curves for compounds **1** and **2** are shown in Fig.S9(see the Electronic Supplementary Material of this paper). The curve of compound **1** shows one-step of mass loss, giving a total loss of 30.51% of its initial mass in a range of 225–650 °C, which corresponds to the release of four phen and four imidazole molecules (calcd. 30.40%) per formula unit of compound **1**. The TG curve of compound **2** is divided into two stages. The first mass loss is 0.56% in a temperature range of 48–166 °C, corresponding to the release of one water molecule in compound **2** (calcd. 0.53%). The second mass loss of 37.03% from 166 °C to 630 °C is attributed to the release of 2,2'-bpy and oxalate ligands in compound **2** (calcd. 37.0%).

3.4.6 Magnetic Property

The temperature dependence of the magnetic susceptibility χ_M of compound **1** was investigated in a range of 2–300 K at 398089 A/m on a Quantum Design MPMS-VSM magnetometer, with χ_M versus T plot shown in Fig.S10(A) (see the Electronic Supplementary Material of this paper). There are six Mo^{5+} ions, six Mo^{6+} ions and two V^{4+} ions in the discrete $[\text{PMo}_6^{\text{VI}}\text{Mo}_6^{\text{V}}\text{V}_2^{\text{IV}}\text{O}_{42}]$ cluster units. The average formal oxidation state of Mo is +5.50. However, the unpaired electron is delocalized over 12 Mo ions in the POM cluster unit and only

the unpaired electron is located in the V^{4+} 3d orbitals. The result is one $S=1/2$ magnetic moment on each Mo_{12} cluster in the POM. This cluster can then replace an atom as the basic building block of a magnetic system^[56,57]. There may be magnetic exchange contribution from isolated $\text{Mo}_{12}^{5.50+}-\text{O}-\text{V}^{4+}$ in the POMs. The temperature dependent magnetic data were fitted over the high temperature range with Curie-Weiss law, $\chi=C/(T-\theta)$, where C is Curie constant, θ is Weiss constant. The fit yields the values of $C=1.44 \text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ and $\theta=-14.6 \text{ K}$, which indicates the antiferromagnetic behavior of the compound. However, no separation was found between ZFC and FC curves in the whole temperature range, which indicates the short range exchange and consists with the magnetic structure as discussion above. For compound **2**, no separation was found between ZFC and FC curves in the whole temperature range [Fig.S10(B), see the Electronic Supplementary Material of this paper]. The χ_M-T was fitted over the high temperature range with Curie-Weiss law. The fit yields the values of $C=2.41 \text{ cm}^3\cdot\text{K}\cdot\text{mol}^{-1}$ and $\theta=-2.98 \text{ K}$, which also indicates the short range antiferromagnetic behavior of the compound. In the magnetic structure of compound **2**, there are isolated Co^{2+} , $\text{Co}^{2+}-\text{O}\cdots\text{O}-\text{Co}^{2+}$ dimers (weak super super-exchange) and $\text{Mo}_{12}^{5.58+}-\text{O}-\text{V}^{4+}$ from $[\text{PMo}^{\text{VI}}_7\text{Mo}^{\text{V}}_5\text{V}_2\text{O}_{42}]$ in the magnetic structure. The discrete magnetic ions and units are well separated, which leads to the lack of magnetic long range order. Since there are paramagnetic and short range antiferromagnetic contribution coexisted in the magnetic susceptibilities of compounds **1** and **2**, it is hard to directly calculate the effective magnetic moment of the magnetic ions in the systems.

4 Conclusions

Two new high dimensional supramolecular compounds based on bi-vanadium-capped Keggin polyoxoanion $\{\text{PMo}_{12}\text{V}_2\text{O}_{42}\}$ and transition metal mixed-organic-ligand coordination fragments have been isolated by hydrothermal method and structurally characterized. Compound **1** exhibits three different coordination complexes of cooper, and the complex $[\text{Co}_2(2,2'\text{-bpy})_4(\text{C}_2\text{O}_4)]^{2+}$ in compound **2** shows a novel structure feature. The $\{\text{PMo}_{12}\text{V}_2\text{O}_{42}\}$ and transition metal mixed-organic-ligand coordination fragments are linked *via* $\pi\cdots\pi$ stacking and hydrothermal bonding interactions, forming 3D supramolecular architectures for the two compounds. The combination of POMs with metal mixed-organic-ligand complex will not only significantly affect the chemistry of POMs but also significantly affect transition metal complexes. Relevant researches revealing the synthetic rules and exploring the properties of POM-based supramolecular materials are underway in our group.

Electronic Supplementary Material

Supplementary material is available in the online version of this article at <http://dx.doi.org/10.1007/S40242-015-5033-2>.

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