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Supramolecular assembly of organic bicapped Keggin polyoxometalate

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Abstract

Two novel supramolecular assemblies of organic bicapped Keggin polyoxometalates $(pbpy)_8H_3[PW_{12}O_{40}] \cdot 2H_2O$ (1) and $(pbpy)_4H[PMo_{12}O_{40}(VO)]$ (2) (pbpy = 5-phenyl-2-(4-pyridinyl)pyridine) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction. Crystallographic data for compound (1), $C_{128}H_{103}N_{16}O_{42}PW_{12}$, triclinic, space group $P\bar{1}$: $a = 13.4759(8)$ Å, $b = 14.6395(11)$ Å, $c = 16.5743(10)$ Å, $\alpha = 95.764(2)°$, $\beta = 102.166(2)°$, $\gamma = 92.9870(10)°$, $Z = 1$, $V = 3171.1(4)$ Å^3; for compound (2), $C_{64}H_{49}N_8O_{41}PMo_{12}V$, triclinic, space group $P\bar{1}$: $a = 11.5377(11)$ Å, $b = 12.7552(8)$ Å, $c = 14.9599(10)$ Å, $\alpha = 72.270(4)°$, $\beta = 88.916(2)°$, $\gamma = 67.865(4)°$, $Z = 1$, $V = 1931.0(3)$ Å^3. X-ray analyses show that both 1 and 2 represent rare organic bicapped Keggin structures and are supported by supramolecular interactions to extend into a 3D framework. In particular, the unusual structure feature of compound 2 contains a simultaneously organic and inorganic capped structure.
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Keywords: Supramolecular compound; Organic capped Keggin structures; 5-phenyl-2-(4-pyridinyl)pyridine

1. Introduction

Crystal engineering of assemblies of inorganic and/or organic molecules has shown spectacular advances in the last couple of decades as a consequence of their unusual physicochemical properties, and interesting structural chemistry [1]. Solid-state supramolecular chemistry plays an important role in this field. Supramolecular compounds of polyoxometalates (POMs) have been intensively investigated in many important aspects of chemistry such as catalysis, non-linear optical materials, and medicine [2]. A current development in this area is to explore novel lattice architectures resulting from the association of organic molecules with POM anions. Supramolecular structures of POMs with organic molecules such as TTF type [3], organic amines [4], and crown ethers [5] have been successfully constructed.

Among those interactions in fabricating supramolecular structures, hydrogen bonding is more attractive because of its highly directional nature and relatively high bonding energy, and is most commonly used as the supramolecular cement in constructing this kind of structure assemblies [6]. Usually, aromatic–aromatic interactions of organic molecules are also used to design and synthesize hybrid materials with coexistence of novel structure characteristics and physical properties [7]. As versatile organic molecules, derivatives of pyridine have been extensively used to functionalize POMs [8]. The 5-phenyl-2-(4-pyridinyl)pyridine (pbpy) has a straight and planar structure with a very good π-electron conjugated system that is an indispensable factor for the construction of π−π stacking-supported supramolecular structure. Benzene, which is the archetypal of all aromatic systems, has no dipole moment, but has a substantial, permanent quadrupole moment [9]. This quadrupole provides an important force in controlling the solid-state architecture of molecules having phenyl rings. Our strategy in this research work

is to choose the conjugated pbpy molecule as a supramolecular synthon to assemble POMs. Although many organic–inorganic hybrid complexes are reported, inorganic–organic hydrogen bonding and $\pi-\pi$ stacking-supported 3D assemblies of POMs containing Keggin moieties are still sparse [10]. We present here two novel supramolecular compounds: $(pbpy)_8H_3[PW_{12}O_{40}] \cdot 2H_2O$ (**1**) and $(pbpy)_4H[PMo_{12}O_{40}(VO)]$ (**2**). Both **1** and **2** have 3D networks constructed from inorganic Keggin POM anions and organic pbpy molecules via supramolecular interaction forces. An interesting structural feature is that both compounds contain a rare organic capped structure of α-Keggin polyanion. In particular, compound **2** presents a simultaneously organic and inorganic capped structure. To our knowledge, this unusual structure feature has not been reported to date.

2. Experimental section

2.1. General methods

All chemicals purchased were of reagent grade and used without further purification. Organic molecule pbpy was synthesized in the laboratory. Elemental analyses were carried on a MOD 1106 elemental analyzer. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a MgKα (1253.6 eV) achromatic X-ray source. The vacuum inside the analysis chamber was maintained at 6.2×10^{-6} Pa during analysis. FTIR spectra were recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FTIR spectrophotometer using a KBr pellet. The ESR spectrum was recorded on BRUKER ER 200D spectrometer. DPPH (α,α-diphenyl-β-picrylhydrazyl) was used for determination of *g* factors. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N$_2$ at a heating rate of 10°C min^{-1}. Cyclic voltammograms (CV) were recorded on a 384B polarographic analyzer. A typical three-electrode cell having a glassy carbon working electrode, a platinum counter electrode, and a silver/silver chloride reference electrode was used for the voltammetry experiments.

2.2. Hydrothermal syntheses

$(pbpy)_8H_3[PW_{12}O_{40}] \cdot 2H_2O$ (**1**): A reaction mixture of Na$_2$WO$_4 \cdot$ 2H$_2$O (2.1 mmol), H$_3$PO$_4$ (ca. 0.7 mmol), pbpy (0.2 mmol) and H$_2$O (10 mL) was sealed in an 18 mL Teflon-lined reactor under autogenous pressure at 155°C for 4 days, followed by slowly cooling (10°C h^{-1}) to room temperature. Yellow block crystals were obtained along with amorphous powder. The crystals were picked out, washed with distilled water, and air-dried at 50°C (yield: 63%). Elemental anal.

found: C, 31.9; H, 2.4; N, 4.7%; calcd. for C$_{128}$H$_{103}$N$_{16}$O$_{42}$PW$_{12}$: C, 32.2; H, 2.2; N, 5.0%.

$(pbpy)_4H[PMo_{12}O_{40}(VO)]$ (**2**): Compound **2** was synthesized from the reaction mixture of Na$_2$MoO$_4 \cdot$2H$_2$O (2.5 mmol), H$_3$PO$_4$ (ca. 1.0 mmol), NH$_4$VO$_3$ (1.2 mmol), pbpy (0.2 mmol) and H$_2$O (10 mL) in an 18 mL Teflon-lined reactor under autogenous pressure at 165°C for 4 days, followed by slowly cooling (10°C h^{-1}) to room temperature. Red prism crystals were obtained together with amorphous powder. The crystals were collected, washed with distilled water, and air-dried at 50°C (yield: 46%). Elemental anal. found: C, 26.9; H, 1.9; N, 3.7%; calcd. for C$_{64}$H$_{49}$N$_8$O$_{41}$PMo$_{12}$V: C, 27.2; H, 1.7; N, 4.0%.

2.3. X-ray crystallography

Single crystals of **1** and **2** with dimensions $0.252 \times 0.151 \times 0.142$ and $0.412 \times 0.134 \times 0.112$ mm, respectively, were glued on glass fibers. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer with MoKα monochromated radiation ($\lambda = 0.71703$ Å) at 293 K. An empirical absorption correction was applied. The structures were refined by the full-matrix least-squares method on F^2, using the SHELXTL crystallographic software package [11]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. The crystal data and structure refinement of compounds **1** and **2** are summarized in Table 1.

The CCDC has assigned reference numbers 224563 for **1** and 224564 for **2**.

3. Results and discussion

3.1. Crystal structures $(pbpy)_8H_3[PW_{12}O_{40}] \cdot 2H_2O$ (**1**)

The crystal structure analysis reveals that compound **1** consists of one $PW_{12}O_{40}^{3-}$ unit, two types of water molecules, and eight pbpy molecules divided into four sets of crystallographically independent molecules in a unit cell.

The anion shows a structure typical of disordered 'α-Keggin' molecules [12]. The central atom P is located at the inversion center 0, 1/2,1/2 and is surrounded by a cube of eight oxygen atoms, with each oxygen site half-occupied. P–O bonds range from 1.466(18) to 1.51(3) Å (mean 1.492 Å). The W–Od (Od = terminal oxygen) bonds are in the usual range of 1.641(8)–1.677(10) Å. All W–W distances are nearly equal, ranging from 3.501 to 3.544 Å.

Two types of water molecules serve as nodes in constructing the supramolecular compound. The first

Table 1
Crystal data and structure refinement of **1** and **2**

Molecular formula	$C_{128}H_{103}N_{16}O_{42}PW_{12}$	$C_{64}H_{49}N_8O_{41}PMo_{12}V$
M	4774.43	2819.29
T (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Space group	Triclinic	Triclinic
Cryst syst	$P\bar{1}$	$P\bar{1}$
a (Å)	13.4759(8)	11.5377(11)
b (Å)	14.6395(11)	12.7552(8)
c (Å)	16.5743(10)	14.9599(10)
α (deg)	95.764(2)	72.270(4)
β (deg)	102.166(2)	88.916(2)
γ (deg)	92.9870(10)	67.865(4)
V (Å^3)	3171.1(4)	1931.0(3)
Z; calcd. density (mg/m^3)	1; 2.500	1; 2.424
μ (mm^{-1})	10.937	2.116
$F(000)$	2222	1358
Limiting indices	$-17 \leqslant h \leqslant 17$,	$-12 \leqslant h \leqslant 12$,
	$-18 \leqslant k \leqslant 18$,	$-14 \leqslant k \leqslant 14$,
	$-21 \leqslant l \leqslant 21$	$-17 \leqslant l \leqslant 17$
Reflns. collected	22,939	9389
Indep. reflns.	14187 (R_{int} = 0.0697)	5772 (R_{int} = 0.0451)
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0675, wR_2 = 0.1259	R_1 = 0.0883, wR_2 = 0.2080
R indices (all data)	R_1 = 0.1363, wR_2 = 0.1443	R_1 = 0.1106, wR_2 = 0.2217

Table 2
Short intermolecular distances (Å) in **1** and **2**

1		**2**	
O(10)–OW(1)	2.979	N(1)–N(4)	2.845
N(6)–OW(1)	3.033	N(1)–C(20)	3.197
N(3)–N(5)	2.779	N(1)–O(7)	3.171
O(6)–OW(2)	2.779	N(2)–O(5)	3.102
O(14)–OW(2)	2.965	O(14)–C(1)	3.182
N(7)–OW(2)	2.907	O(19)–C(7)	3.137
N(1)–O(4)	3.056	O(21)–C(10)	3.255
N(1)–O(13)	2.894	N(3)–O(11)	3.008
N(1)–O(15)	2.926	N(3)–O(9)	3.124
N(1)–O(17)	3.082	N(3)–O(20)	3.154
C(47)–C(49)	3.389	N(3)–O(4)	3.083
C(35)–C(64)	3.374	O(4)–C(21)	3.146
C(4)–O(9)	3.116	O(21)–C(14)	3.204
N(2)–C(33)	3.138	O(20)–C(17)	3.101
O(8)–C(61)	3.355	C(18)–C(29)	3.334

type is OW(2) molecules bridging adjacent $PW_{12}O_{40}^{3-}$ units via hydrogen bonding into one-dimensional inorganic chains that run along the c-axis. The shortest intermolecular distances between OW(2) and POM anions are 2.779 Å (OW(2)⋯O(6)) and 2.965 Å (OW(2)⋯O(14)), respectively. The second type is OW(1) molecules, which behave as junctions to link pbpys and polyanions and together fulfill space filling. Some typical intermolecular interactions are shown in Table 2.

The four crystallographically independent organic molecules are named A(N(1), N(2)), B(N(3), N(4)), C(N(5), N(6)) and D(N(7), N(8)) for clarity (see Fig. 1). The A of pbpy is very near to the polyanion, with the distances: N(1)⋯O(4) = 3.056, N(1)⋯O(13) = 2.894, N(1)⋯O(15) = 2.926 and N(1)⋯O(17) = 3.082 Å (mean value = 2.990 Å), all of which fall into the range of hydrogen bond interactions. Therefore, two As of pbpys cap over the two opposite surface windows of a polyanion (see Fig. 2a), introducing an organic-bicapped structure. It is noted that this kind of Keggin anions capped by two organic molecule fragments is rare, to say nothing of Keggin heteropolytungstates. Therefore, compound **1** represents the first example of capped structure containing Keggin $PW_{12}O_{40}^{3-}$.

The B of pbpy is parallel to A in the bc plane with an angle of about $-132.09°$ between the long axes of the two molecules (including C(11)–C(9) and C(27)–C(25)). In addition, molecules B and C are close to each other, with N(3)⋯N(5) = 2.779 Å.

The C and D of pbpy molecules are approximately parallel to each other and stack along the b-axis in a CC–DD–CC–DD⋯style (see Fig. 3). The nearest interplanar spacings are 3.373 Å between a couple of C molecules, 3.561 Å between a couple of D molecules and 3.374 Å between C and D, respectively. The distances between two benzene rings coming from two neighbor D molecules are in the range of 3.561–3.742 Å (mean value = 3.633 Å), further showing that the two D molecules are nearly parallel. All the above-mentioned distances demonstrate strong $\pi-\pi$ stacking interactions in compound **1**, arising from their close stacking sequence that serves to stabilize the whole structure. Furthermore, the C is attached to the polyanion through OW(1); the D is linked through OW(2) into a part of inorganic anion chains. These pbpys are held together by hydrogen bonding and $\pi-\pi$ stacking interactions including edge-to-face aromatic C–H⋯π and face-to-face aromatic interactions [13].

Seen from the c-axis direction, these pbpys give rise to regular chambers surrounding inorganic polyanions. Therefore, the packing arrangement of the whole molecule can be described as follows: organic moieties form a netlike structure via supramolecular interactions, into which infinite columns of inorganic polyanions are posed.

3.2. (pbpy)$_4$H[PMo$_{12}$O$_{40}$(VO)] (**2**)

Compound **2** consists of one unusual single {VO} capped discrete Keggin polyoxoanion [PMo$_{12}$O$_{40}$(VO)]$^-$ and four pbpy molecules. More recently, the introduction of the hydrothermal technique and suitable templates has led to the appearance of various inorganic capped Keggin ion derivatives. These capped compounds mainly pertain to several systems: X/Mo/O [14],
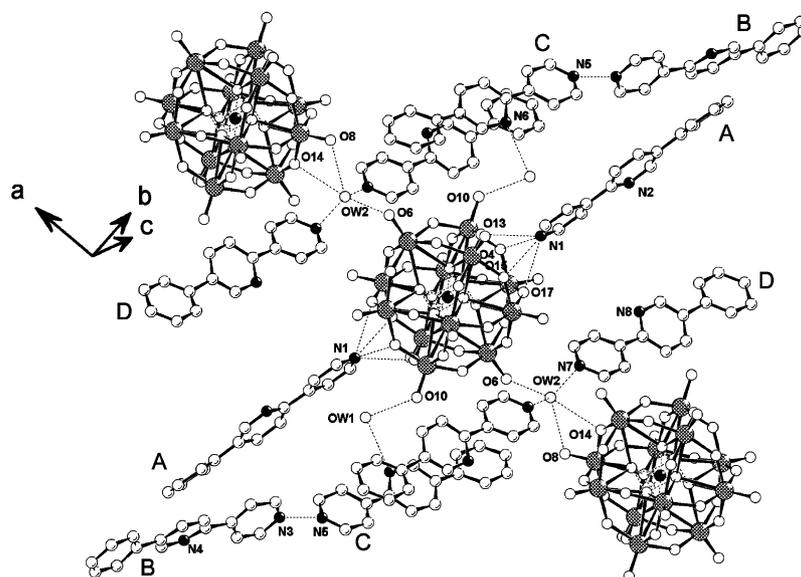
Fig. 1. A representation showing the linkages of hydrogen bonding among pbpys, crystal waters and Keggin POM clusters in compound **1**. A, B, C and D represent four categories of pbpy molecules with different packing modes, respectively.
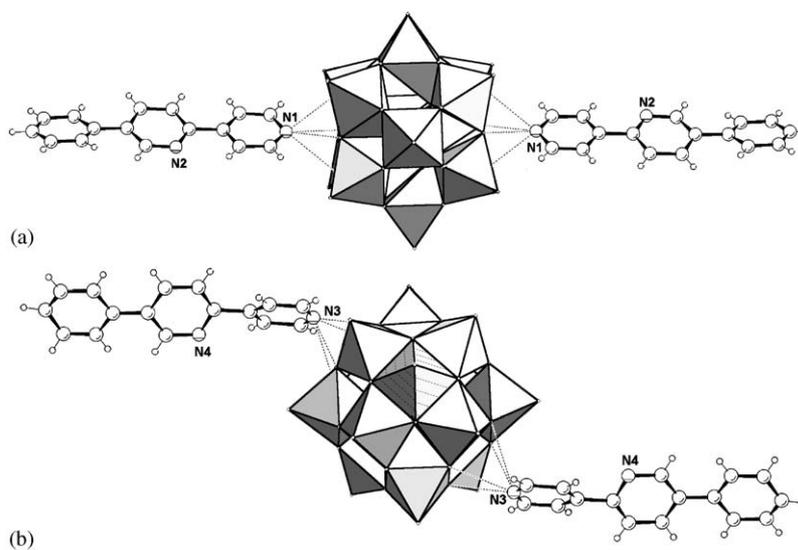
Fig. 2. Polyhedral representations of the interesting organic bicapped structure: (a) compound **1**; (b) compound **2**, and the gray polyhedron hatched lines (dots) represent the vanadium square pyramid.

X/Mo/V/O [15,16], Mo/V/O [17], X/V/O [18] and V/O [19] ($X=$ P, As or Si). Nevertheless, capped Keggin derivatives reported are relatively limited because of the lack of good-quality single crystals. To our knowledge, the compound **2** represents a novel single-capped pseudo-Keggin structure, formed from a disordered VO_5 prism, 12 MoO_6 octahedra and two half-occupied PO_4 tetrahedra. In the X/Mo/V system, the double-capped Keggin anion of $[PMo_6^V Mo_6^{VI}(V^{IV}O)_2]^{5-}$ has been reported, which is highly reduced [15]. In compound **2**, however, the capping vanadium {VO} with an occupancy of 0.5 is disordered, being distributed at two opposite $\{Mo_4O_4\}$ faces in a distorted pyramidal arrangement, and bonded to one terminal oxygen atom and four triply bridging oxygen atoms. The introduction of electrophilic $\{VO\}^{2+}$ capping groups serves to stabilize the $PMo_{12}O_{40}^{3-}$ anion. The V–O distances vary from 1.66(5) to 1.97(3) Å. Another remarkable structural feature for **2** is that the square-pyramidal vanadium forms four Mo^{VI}–V^{IV} pairs with short Mo–V distances (2.815–2.935 Å, mean value = 2.884 Å), resulting in a 'metal-bonded' framework.

Bond valence sum calculations (BVS) [20] indicate that the Mo centers are in the highest oxidation state.
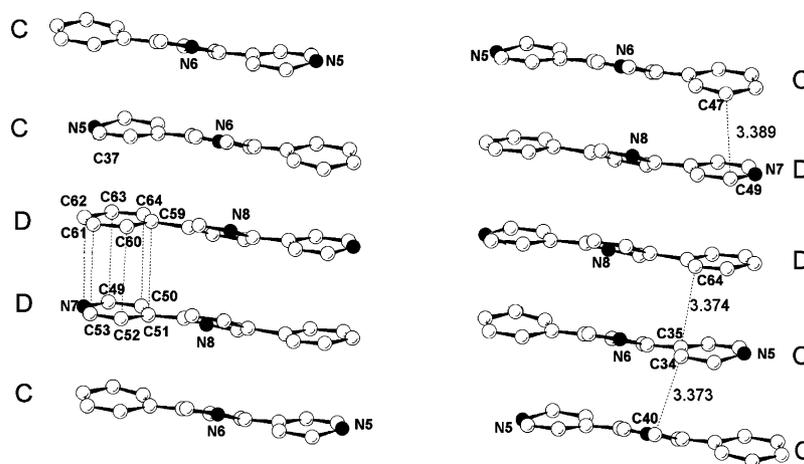
Fig. 3. A view of the parallel arrangement of C and D pbpy molecules in **1**. The short distances of two adjacent molecules show strong $\pi-\pi$ stacking interactions among them.
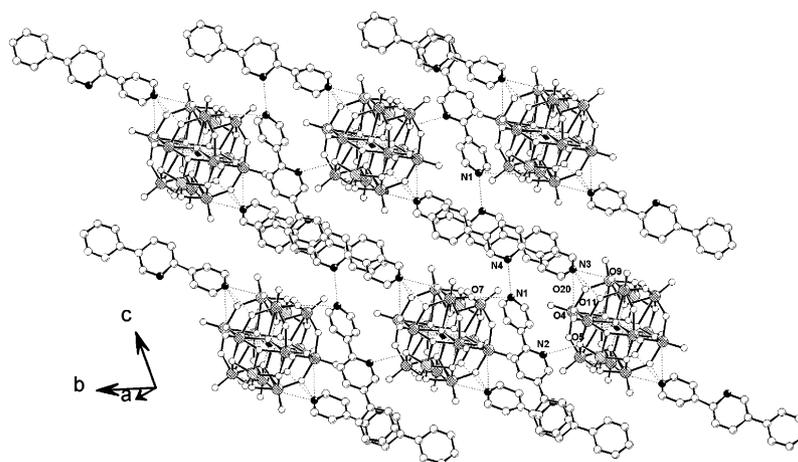
Fig. 4. A representation showing the linkages of hydrogen bonding among pbpys and Keggin POM anions in compound **2**.

Photoelectron spectrum (XPS) measurement gives peaks at 232.8 eV ($3d_{5/2}$) and 236 eV ($3d_{3/2}$) for **2**, which further confirms the valence of Mo^{6+} atoms. By BVS, it is established that the capping V atom possesses 3.94 of the formal oxidation state in compound **2**. The ESR spectrum of compound **2** at room temperature shows a paramagnetic signal of V^{4+} at 273 K with $g = 1.966$, which is consistent with the calculation result.

Another important structural feature is that the interesting organic bicapped structure also appears in compound **2**. The distances between N(3) and bridging oxygen atoms are as follows: N(3)···O(11) = 3.008, N(3)···O(9) = 3.124, N(3)···O(20) = 3.154 and N(3)···O(4) = 3.083 Å (mean value = 3.092 Å). An infrequent result is that compound **2** possesses a simultaneously organic and inorganic capped structure (see Fig. 2b). To date, this unusual structure feature has not been observed. The difference between compound **1** and **2** is that two capping pbpys lie in the same line for the former, while they lie in two parallel lines for the latter

(see Fig. 2), which may originate from bigger dipole moment of capped core of polyanion and/or from influence concerted with hydrogen bonds of other molecules.

The supramolecular interactions in the structure of **2** are shown in Fig. 4. The fact is that the twists of organic molecules are large. The torsion angles are 141.67° for C(18)–C(19)···C(22)–N(4), 156.71° for C(4)–C(3)···C(6)–C(7), 129.11° for C(4)–C(3)···C(11)–C(12) and 155.28° for C(8)–C(9)···C(11)–C(16), respectively. There are a number of significant contacts between oxo groups of anions and organic molecules (as shown in Table 2). As illustrated in Fig. 5, the layers of inorganic anions and organic molecules array alternately. The organic molecules are staggered arrangements and stack along the a-axis direction to form strips for separating different inorganic cores. Then, a 3D structure of **2** is fabricated by supramolecular interactions.

In view of the structure, we deduce, there exist two possible reasons that facilitate the formation of
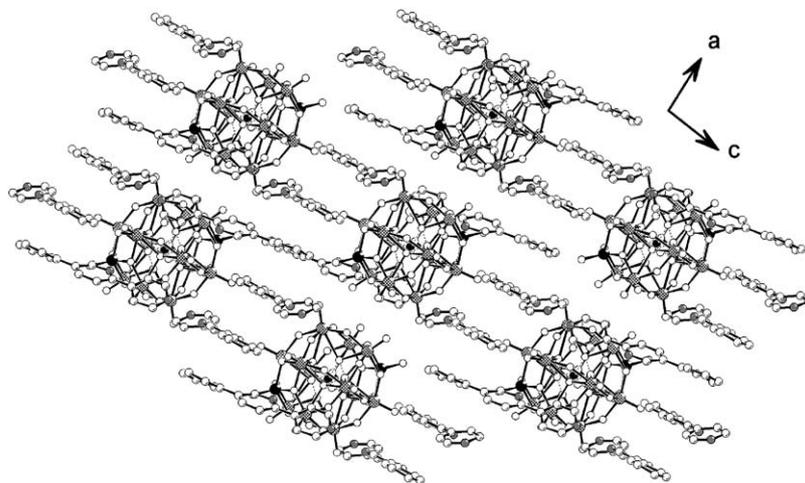
Fig. 5. A packing drawing of compound **2** showing that the layers of inorganic anions and organic molecules array alternatively.

supramolecular compounds containing organic capped structure of Keggin polyanions. One is that the rigid linear organic molecule possesses a coordination N atom located at the terminal to extend its connection. Another is the acidic condition of reaction. In an acidic system, N atoms are protonated, which prevents it from covalently bonding to other atoms or groups.

The two products are highly insoluble in common organic solvents and water, but slightly soluble in dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), where original supramolecular interactions in the compounds are broken to a certain degree.

3.3. IR spectra, cyclic voltammetry and TG analysis

The IR spectra exhibit the characteristic peaks of the α-Keggin structure for compound **1** at 803, 880, 957 and 1062 cm^{-1}, attributed to ν(W–Oc–W), ν(W–Ob–W), ν(W–Od) and ν(P–O), respectively. The peaks at 3000–1080 cm^{-1} are characteristic for pbpy; and for compound **2** at 790, 875, 950 and 1058 cm^{-1}, respectively. The peaks at 3000–1080 cm^{-1} are characteristic for pbpy.

The cyclic voltammetric and polarographic behaviors (as shown in Fig. 6) of compounds **1** and **2** were measured in DMSO (0.1 M Bu$_4$NClO$_4$). The CV data of compound **1** show both redox waves of the heteropolyanion in $E_{1/2} = -0.36$ V and the organic moiety in $E_{1/2} = -1.36$ V and $E_{1/2} = -1.74$ V. For compound **2**, the redox wave of heteropolyanion appears in $E_{1/2} = 0.20$ V and that of organic moiety in $E_{1/2} = -1.74$ V.

The TG curve of compound **1** shows four stages of weight loss in the temperature range 22–620°C. The whole weight loss (39.90%) is in good agreement with the calculated value (39.67%). The TG curve of compound **2** also exhibits four steps of weight losses in
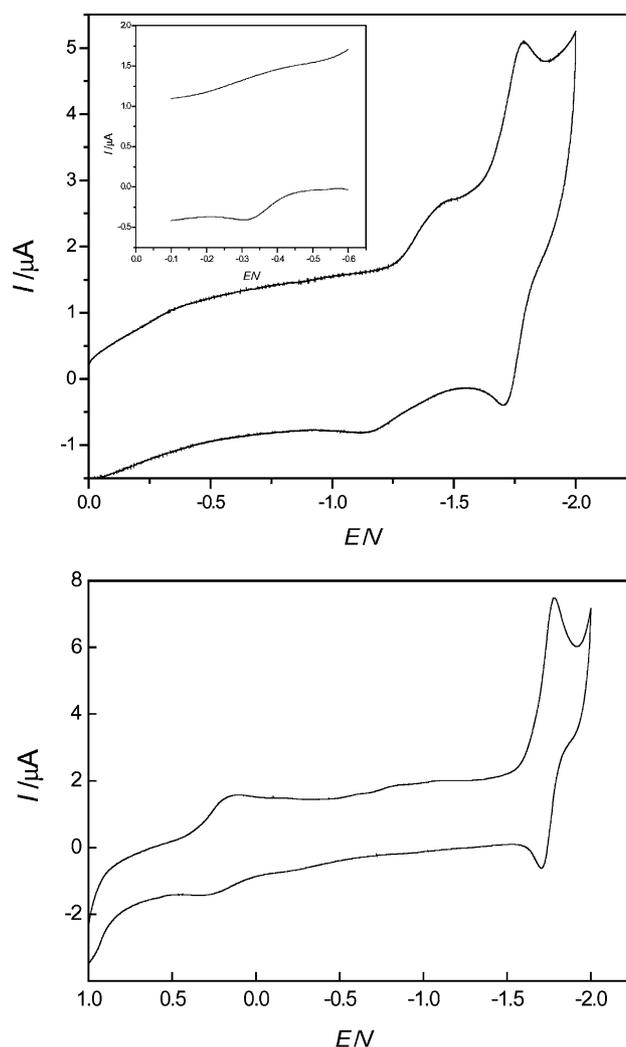
Fig. 6. Cyclic voltammetry of compound **1** (top) and **2** (bottom).

the temperature range 22–670°C. The whole weight loss (32.64%) is consistent with the calculated value (32.95%).

4. Conclusion

In this paper, two novel supramolecular assemblies of organic bicapped Keggin POMs have been successfully synthesized. It verifies that the conjugated pbpy molecule can be used as a supramolecular synthon to assemble POMs. Compound **1** represents the first example of capped structure containing heteropolytungstates; compound **2** exists with a simultaneously organic and inorganic capped structure in one molecule. These unusual structure features are reported for the first time. Supramolecular interactions among the organic molecules and inorganic polyanions play a significant role in stabilization of the supramolecular assemblies of organic bicapped Keggin POM. It shows that such large assembly may be designed and synthesized according to the inherent stereo and interactive information stored in the organic molecules and inorganic anions. Further research is underway to get more novel compounds with these kind of supramolecular frameworks and explore their valuable properties.

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