



Two new transition-metal complexes (TMCs)-templated three-dimensional supramolecular networks based on tungstovanadophosphates

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ABSTRACT

Two new polyoxometalates $[\text{Ni}(\text{phen})_3][\text{Ni}(\text{en})_3][\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{en})_2]_{0.5}[\text{PW}^{\text{VI}}_7\text{W}^{\text{V}}_2\text{V}^{\text{IV}}_3\text{O}_{40}(\text{V}^{\text{IV}}\text{O}_2)] \cdot 6\text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{phen})_3]_2[\text{Ni}(\text{en})_2]\text{Na}[\text{PW}^{\text{VI}}_7\text{W}^{\text{V}}_2\text{V}^{\text{IV}}_3\text{O}_{40}(\text{V}^{\text{IV}}\text{O}_2)] \cdot 8\text{H}_2\text{O}$ (**2**) (en = ethylenediamine, phen = 1,10-phenanthroline) have been hydrothermally synthesized and structurally characterized by single-crystal X-ray diffraction, IR, EPR, XPS, elemental analysis and thermogravimetry. Their structures exhibit interesting 3D supramolecular networks, and contain new bicapped (pseudo-) Keggin-type tungsten–vanadium cluster and the template transition-metal complexes (TMCs) being generated *in situ* under mild hydrothermal conditions. Interestingly, compound **1** contains four different kinds of nickel complex counteranions.

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1. Introduction

The significant contemporary interest in the crystal engineering of inorganic–organic hybrid materials not only originates from their diverse structural flexibility, but also from their widely promising potential applications in catalysis, medicine, photochemistry and electromagnetism [1–3]. In the crystal engineering, a remarkable area is supramolecular chemistry, which has developed at a tremendous rate in the past 30 years [4,5]. In the construction of supramolecular materials, one important strategy is that low-dimensional building blocks extend to high-dimensional networks through intermolecular interactions, including hydrogen bonding, $\pi \cdot \cdot \pi$ stacking and van der Waals interactions, etc. [6]. Doubtless, the hydrogen bond is the most familiar organizing force in supramolecular assemblies by virtue of its unique strength and directionality that may control short-range packing [7].

Polyoxometalates (POMs) have attracted extensive attention for many years owing to their interesting structural diversity [8–20]. Supramolecular compounds based on POMs have been unexplored in the past decades, though the spherical surface of the POMs gives a better opportunity in forming hydrogen bonds with the organic/inorganic moieties. Recently, a promising approach toward the synthesis of this kind of supramolecular

material lies in the proper selection of POMs as building blocks and organic substrates as structure-directing agents [21–25]. However, there are only small amount of reports about transition-metal complexes (TMCs) as templates or structure-directing agents, and the relationship between POMs and TMCs has also been studied infrequently [26–28].

The study of heteropolyoxometalates is mainly focused on molybdovanadate system [29–32]. Up to now, owing to the kinetic sluggishness of tungsten relative to molybdates and vanadates, less attention has been paid to the tungstovanadate heteropoly complexes [33–40]. Keeping in mind that tungsten is kinetically inert, the great majority of them are synthesized under hydrothermal conditions. Consequently, we attempted to explore our research on the preparation of Keggin-type tungsten–vanadium clusters templated by TMCs formed *in situ*, and we succeed in doing so.

In this paper we report two novel TMCs-templated 3D supramolecular networks based on tungstovanadophosphates $[\text{Ni}(\text{phen})_3][\text{Ni}(\text{en})_3][\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{en})_2]_{0.5}[\text{PW}^{\text{VI}}_7\text{W}^{\text{V}}_2\text{V}^{\text{IV}}_3\text{O}_{40}(\text{V}^{\text{IV}}\text{O}_2)] \cdot 6\text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{phen})_3]_2[\text{Ni}(\text{en})_2]\text{Na}[\text{PW}^{\text{VI}}_7\text{W}^{\text{V}}_2\text{V}^{\text{IV}}_3\text{O}_{40}(\text{V}^{\text{IV}}\text{O}_2)] \cdot 8\text{H}_2\text{O}$ (**2**) (en = ethylenediamine, phen = 1,10-phenanthroline). Interestingly, compound **1** contains four different kinds of counteranions being coordination complexes of Ni. Based on the same heteropolyanion $[\text{PW}_9\text{V}_3\text{O}_{40}(\text{VO})_2]^{7-}$, the interesting hydrogen-bonded host networks are formed and employed to accommodate the *in situ* templates (TMCs). Furthermore, we also discuss, in the paper, the formation process of these two compounds and the function of each fragment in the crystallization process for the first time.

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2. Experimental section

2.1. Material and methods

All reagents are used of analytical grade and obtained from commercial sources without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR (KBr pellets) spectra were recorded in the 250–4000 cm^{-1} range using a Perkin-Elmer spectrum one spectrophotometer. Determinations of electron paramagnetic resonance (EPR) were carried out on Bruker ER 200D-SRC spectrometer. XPS analyses were performed on Thermo ESCALAB 250 spectrometer with an Mg-K α (1253.6 eV) achromatic X-ray source. Thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer TAG-7 instrument from room temperature to 800 °C with a heating rate of 10 °C/min.

2.2. Syntheses

2.2.1. Synthesis of $[\text{Ni}(\text{phen})_3][\text{Ni}(\text{en})_3][\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{en})_2]_{0.5}[\text{PW}^{\text{VI}}_7\text{W}^{\text{V}}_2\text{V}^{\text{IV}}_3\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2] \cdot 6\text{H}_2\text{O}$ (**1**)

The starting materials Na_2WO_4 (0.33 g, 1.0 mmol), $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ (0.20 g, 1.0 mmol), H_3PO_4 (0.25 mL, 3.65 mmol), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.15 g, 0.5 mmol), 1,10-phen (0.20 g, 1.0 mmol) and $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.12 g, 1.0 mmol) were added to 20 mL of distilled water at room temperature. After stirring for 2 h, the pH value of the reaction system was adjusted to 8.5 using ethylenediamine (4 mL). The mixture was sealed in a Teflon-lined autoclave, and heated at 180 °C for 72 h. Then the autoclave was cooled to room temperature slowly. The black hexagonal prism crystals were filtered, washed with distilled water and dried at ambient temperature. Yield: 59.3% based on W. Anal. Calcd. for $\text{C}_{48}\text{H}_{88}\text{N}_{18}\text{Ni}_{3.5}\text{O}_{50}\text{PV}_5\text{W}_9$ (3863.17): C, 14.92; H, 2.30; N, 6.53%. Found: C, 14.79; H, 2.21; N, 6.43%.

2.2.2. Synthesis of

$[\text{Ni}(\text{phen})_3]_2[\text{Ni}(\text{en})_2]\text{Na}[\text{PW}^{\text{VI}}_7\text{W}^{\text{V}}_2\text{V}^{\text{IV}}_3\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2] \cdot 8\text{H}_2\text{O}$ (**2**)

The same procedure as that for **1** was followed, except for that the pH value of the reaction system was adjusted to 7.5 using

Table 1

The crystallographic data for compounds **1** and **2**.

Compound	1	2
Empirical formula	$\text{C}_{48}\text{H}_{88}\text{N}_{18}\text{Ni}_{3.5}\text{O}_{50}\text{PV}_5\text{W}_9$	$\text{C}_{76}\text{H}_{80}\text{N}_{16}\text{NaNi}_3\text{O}_{50}\text{PV}_5\text{W}_9$
Formula weight	3863.17	4157.00
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/n$	$C2/c$
<i>a</i> (Å)	24.1898(6)	30.629(6)
<i>b</i> (Å)	13.2813(2)	13.760(3)
<i>c</i> (Å)	28.5790(6)	25.761(5)
β (°)	94.164(2)	100.93(3)
<i>V</i> (Å ³)	9157.4(3)	10660(4)
<i>Z</i>	4	4
ρ_{calc} (g cm^{-3})	2.802	2.590
Absorption coef. (mm^{-1})	12.553	10.713
θ range (°)	1.69–28.33	2.20–27.68
Reflections collected	66 121	49 718
Unique reflections (<i>R</i> _{int})	22 763 (0.0701)	12 395 (0.0886)
Completeness (%)	99.8	99.4
Goodness-of-fit on F^2	1.029	1.035
<i>R</i> indexes [$>2\sigma(I)$] ^a	<i>R</i> ₁ = 0.0505 <i>wR</i> ₂ = 0.1238	<i>R</i> ₁ = 0.0611 <i>wR</i> ₂ = 0.1482
<i>R</i> (all data) ^a	<i>R</i> ₁ = 0.0989, <i>wR</i> ₂ = 0.1430	<i>R</i> ₁ = 0.1230, <i>wR</i> ₂ = 0.1836
Largest diff. peak and hole ($e \text{ \AA}^{-3}$)	2.870, −3.064	1.913, −3.432

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.

ethylenediamine (3 mL). Yield: 43.2% based on W. Anal. Calcd. for $\text{C}_{76}\text{H}_{80}\text{N}_{16}\text{NaNi}_3\text{O}_{50}\text{PV}_5\text{W}_9$ (4157.00): C, 21.96; H, 1.94; N, 5.39%. Found: C, 21.85; H, 1.87; N, 5.26%.

2.3. X-ray crystallography

The crystal structures were determined by single-crystal X-ray diffraction analyses. The data were collected on a Bruker-AXS Smart CCD diffractometer (Mo K α , $\lambda = 0.71073 \text{ \AA}$) at room temperature with ω -scan mode. Empirical absorption corrections were applied. The structures were solved by direct methods and

Table 2

Selected bond lengths (Å) for **1–2**.

Compound 1					
W(1)–O(29)	1.711(8)	W(2)–O(39)	1.739(8)	W(3)–O(31)	1.708(8)
W(1)–O(1)	1.813(7)	W(2)–O(28)	1.827(7)	W(3)–O(15)	1.808(8)
W(1)–O(11)	1.815(7)	W(2)–O(12)	1.835(7)	W(3)–O(32)	1.821(8)
W(1)–O(5)	2.035(7)	W(2)–O(9)	2.044(7)	W(3)–O(13)	2.037(8)
W(1)–O(9)	2.045(7)	W(2)–O(13)	2.058(7)	W(3)–O(14)	2.053(7)
W(1)–O(26)	2.433(7)	W(2)–O(26)	2.431(7)	W(3)–O(24)	2.428(7)
M(4)–O(21)	1.711(8)	M(5)–O(34)	1.713(8)	W(6)–O(35)	1.714(9)
M(4)–O(20)	1.817(7)	M(5)–O(23)	1.826(7)	W(6)–O(41)	1.821(8)
M(4)–O(22)	1.834(8)	M(5)–O(2)	1.834(7)	W(6)–O(30)	1.824(8)
M(4)–O(5)	2.049(7)	M(5)–O(3)	2.039(7)	W(6)–O(7)	2.040(7)
M(4)–O(14)	2.063(7)	M(5)–O(7)	2.070(7)	W(6)–O(8)	2.051(7)
M(4)–O(24)	2.446(7)	M(5)–O(4)	2.440(7)	W(6)–O(25)	2.447(7)
W(7)–O(37)	1.724(7)	W(8)–O(17)	1.716(7)	M(9)–O(18)	1.670(8)
W(7)–O(10)	1.813(7)	W(8)–O(27)	1.805(8)	M(9)–O(2)	1.885(8)
W(7)–O(16)	1.836(7)	W(8)–O(19)	1.834(7)	M(9)–O(20)	1.899(7)
W(7)–O(8)	2.049(7)	W(8)–O(3)	2.036(7)	M(9)–O(19)	1.958(7)
W(7)–O(6)	2.053(7)	W(8)–O(6)	2.059(7)	M(9)–O(1)	1.974(8)
W(7)–O(25)	2.439(7)	W(8)–O(4)	2.449(7)	M(9)–O(4)	2.464(7)
M(10)–O(42)	1.636(8)	M(11)–O(38)	1.658(7)	M(12)–O(33)	1.660(8)
M(10)–O(28)	1.931(7)	M(11)–O(10)	1.902(7)	M(12)–O(23)	1.909(7)
M(10)–O(15)	1.936(7)	M(11)–O(27)	1.945(7)	M(12)–O(30)	1.948(8)
M(10)–O(41)	1.940(8)	M(11)–O(12)	1.950(7)	M(12)–O(22)	1.950(8)
M(10)–O(16)	1.969(7)	M(11)–O(11)	1.970(7)	M(12)–O(32)	1.979(8)
M(10)–O(25)	2.452(7)	M(11)–O(26)	2.474(6)	M(12)–O(24)	2.445(7)
V(13)–O(36)	1.621(9)	V(14)–O(40)	1.601(8)	P(1)–O(4)	1.532(7)
V(13)–O(7)	1.900(7)	V(14)–O(5)	1.910(7)	P(1)–O(26)	1.534(7)
V(13)–O(6)	1.912(8)	V(14)–O(13)	1.921(7)	P(1)–O(25)	1.538(7)
V(13)–O(3)	1.989(7)	V(14)–O(14)	1.986(8)	P(1)–O(24)	1.542(7)
V(13)–O(8)	2.001(8)	V(14)–O(9)	1.995(7)	Ni(3)–N(20)	1.86(2)
Ni(1)–N(1)	2.082(10)	Ni(2)–N(7)	2.136(10)	Ni(3)–N(19)	1.88(2)
Ni(1)–N(2)	2.074(10)	Ni(2)–N(8)	2.156(11)	Ni(4)–N(14)	2.076(13)
Ni(1)–N(3)	2.109(9)	Ni(2)–N(9)	2.146(11)	Ni(4)–N(15)	2.041(13)
Ni(1)–N(4)	2.092(9)	Ni(2)–N(10)	2.128(11)	Ni(4)–N(17)	2.184(15)
Ni(1)–N(5)	2.076(10)	Ni(2)–N(11)	2.151(11)	Ni(4)–O(44)	2.155(10)
Ni(1)–N(6)	2.090(10)	Ni(2)–N(12)	2.105(11)		
Ni(4)–N(18)	2.084(18)	Ni(4)–O(43)	2.153(10)		

Compound 2					
W(1)–O(18)	1.667(10)	M(4)–O(15)	1.691(10)	V(7)–O(11)	1.591(10)
W(1)–O(9)	1.790(11)	M(4)–O(16)	1.783(13)	V(7)–O(1)	1.937(11)
W(1)–O(8)	1.793(10)	M(4)–O(10)	1.804(13)	V(7)–O(2)	1.943(10)
W(1)–O(2)	2.037(10)	M(4)–O(2)	2.039(11)	V(7)–O(3)	1.950(10)
W(1)–O(3)	2.038(9)	M(4)–O(1)	2.058(11)	V(7)–O(4)	1.960(9)
W(1)–O(21)	2.431(16)	M(5)–O(19)	1.625(10)	P(1)–O(22)#1	1.460(15)
W(2)–O(12)	1.689(10)	M(5)–O(6)	1.872(11)	P(1)–O(20)	1.485(14)
W(2)–O(7)	1.793(11)	M(5)–O(10)#1	1.880(11)	P(1)–O(21)	1.523(15)
W(2)–O(6)	1.806(10)	M(5)–O(5)	1.951(11)	P(1)–O(23)#1	1.683(16)
W(2)–O(4)	2.016(10)	M(5)–O(9)#1	1.967(11)	Ni(1)–N(4)	2.068(11)
W(2)–O(3)	2.022(10)	M(5)–O(21)#1	2.454(16)	Ni(1)–N(5)	2.081(11)
W(2)–O(20)#1	2.430(14)	M(6)–O(13)	1.649(10)	Ni(1)–N(2)	2.088(12)
W(3)–O(14)	1.669(10)	M(6)–O(16)#1	1.887(13)	Ni(1)–N(3)	2.101(11)
W(3)–O(17)	1.767(14)	M(6)–O(7)	1.907(12)	Ni(1)–N(1)	2.104(11)
W(3)–O(5)	1.812(11)	M(6)–O(17)#1	1.968(13)	Ni(1)–N(6)	2.106(10)
W(3)–O(1)	2.018(10)	M(6)–O(8)	1.974(11)	Ni(2)–N(8)	1.88(2)
W(3)–O(4)	2.036(10)	M(6)–O(23)#1	2.389(16)	Ni(2)–N(7)	1.98(3)

Symmetry codes for compound **1**: #1–*x*+2, −*y*, −*z*+2.

The M positions are crystallographically disordered occupied by W and V.

refined by full-matrix least squares on F^2 using SHELXTL 97 software [41]. In compounds **1** and **2**, the metal positions for M of the Keggin unit are disorderedly occupied by W and V. All non-hydrogen atoms were refined anisotropically except for six lattice water molecules of **1** and C38, eight lattice water molecules of **2**, respectively. A summary of crystal data and structure refinement for compounds **1** and **2** are provided in Table 1. Selected bond lengths of **1** and **2** are listed in Table 2. Some of the data for hydrogen bonding are listed in Table S1.

3. Results and discussion

3.1. Syntheses

The synthesis of such controlled assembly based on tungsten-containing building units is generally difficult at room temperature (in contrast to corresponding molybdovanadate system) due to the kinetic sluggishness of tungsten. Consequently, two compounds were successfully prepared with good yields through hydrothermal reactions at the pH values of 8.5 and 7.5, respectively. The hydrothermal method has been proved to be very effective for the syntheses of POMs [11–13,15–17]. It is well known that small changes in one or more of the reaction factors, such as pH value [42], temperature [43], reaction time, molar ratio of the reactants, etc., may result in profound influence on final reaction products. No title compounds were obtained when the pH value of reaction system is larger than 8.5 and less than 7.5. This shows that preparation of **1** and **2** needs strictly controlled pH value of the reaction system. In order to study the influence of TMCs on the structures of POMs, we selected two different types of ligands, phen and en. The quantity of en not only influences pH values of the systems, but also influences the crystal structures of the compounds. We tried to synthesize **1** and **2** under the same conditions without oxalic acid, no desired crystal was found. So we speculate, in the synthesis reactions, oxalic acid acts as reducing agent reducing W^{VI} to W^V .

3.2. Crystal structures

3.2.1. Structure description of **1**

Single-crystal X-ray diffraction study reveals that compound **1** is composed of a novel bicapped α -Keggin tungsten–vanadium cluster anion $[PW^{VI}_7W^V_2V^{IV}_3O_{40}(V^{IV}O_2)]^{7-}$ and four different kinds of counteranions, $[Ni(1)(phen)_3]^{2+}$, $[Ni(2)(en)_3]^{2+}$, $[Ni(4)(en)_2(H_2O)_2]^{2+}$ and $[Ni(3)(en)_2]^{2+}$ cations, and lattice water molecules. The polyanion unit $[PW^{VI}_7W^V_2V^{IV}_3O_{40}(V^{IV}O_2)]^{7-}$ is

based on the well-known α -Keggin structure $\{XM_{12}O_{40}\}^{n-}$ with two additional (VO) units (V1 and V2) capping two opposite square holes (see Fig. 1). Each bicapped α -Keggin tungsten–vanadium polyanion unit contains a distorted PO_4 tetrahedron and 12 coordination distorted octahedra including six $\{WO_6\}$ and six $\{MO_6\}$ octahedra. In the $\{MO_6\}$ octahedra, M position is crystallographically disordered with occupancies of 0.86 and 0.14 (M4), 0.86 and 0.14 (M5), 0.36 and 0.64 (M9), 0.26 and 0.74 (M10), 0.25 and 0.75 (M11), 0.39 and 0.61 (M12) for W and V, respectively. The PO_4 tetrahedron has P–O distances of 1.532(7)–1.542(7) Å and bond angles in the range of 109.1(4)°–109.9(4)°. According to the kind of oxygen atoms bonded to the M (W, W/V and V) atoms, the distances of M–O bonds are divided into three groups: W–Oc 2.428(7)–2.449(7) Å, W/V–Oc 2.440(7)–2.474(6) Å (Oc, center O atoms); W–Ob 1.805(8)–2.059(7) Å, W/V–Ob 1.817(7)–2.070(7) Å, V–Ob 1.900(7)–2.001(8) Å (Ob, bridge O atoms); M–Ot 1.708(8)–1.739(8) Å, W/V–Ot 1.636(8)–1.713(8) Å, V–Ot 1.601(8)–1.621(9) Å (Ot, terminal O atoms) (Table 2).

In the compensating cations, the Ni1 atom is surrounded by six N atoms from three 1,10-phen ligands with the Ni–N distances of 2.074(10)–2.109(9) Å, and N–Ni–N angles varying from 80.4(4)°–173.0(4)°; the Ni2 center completes its octahedron configuration by six N atoms from three en ligands with the Ni–N distances of 2.105(11)–2.156(11) Å, and N–Ni–N angles in the range of 79.2(4)°–172.3(5)°; the Ni3 atom is defined by four nitrogen donors from two en ligands with the Ni–N distances of 1.86(2)–1.88(2) Å, and N–Ni–N angles in the range of 87.5(10)°–180.0(6)°; the coordination geometry of Ni4 is described as a distorted octahedron formed by four N atoms from two en ligands with the Ni–N distances of 2.041(13)–2.184(15) Å and two water molecules with the distances of 2.153(10) and 2.155(10) Å, and N(O)–Ni–N(O) angles varying from 80.4(6)° to 179.2(10)°, respectively. The heteropolyanions are linked via hydrogen bonding $[O6W \cdots O39a, 2.828 \text{ \AA}; O6W \cdots O40, 2.927 \text{ \AA}; (a) 0.5-x, -0.5+y, 1.5-z]$, giving rise to a 1D infinite supramolecular helical chain with a pitch of 13.28 Å along *b* axis (Fig. S1a). Adjacent helical chains are connected by $[Ni(en)_2(H_2O)_2]^{2+}$ fragments to form 2D supramolecular layered structure along *ab* direction through hydrogen bonds (Fig. S1b), $[O43 \cdots O36b, 2.818 \text{ \AA}; O43 \cdots O34b, 2.932 \text{ \AA}; O44 \cdots O22c, 2.793 \text{ \AA}; O44 \cdots O37a, 2.922 \text{ \AA}; (a) 0.5-x, -0.5+y, 1.5-z; (b) 1+x, y, z; (c) 0.5-x, 0.5+y, 1.5-z]$ (Table S1). It is worth noting that templates $[Ni(2)(en)_3]^{2+}$ fragments are generated *in situ* and uniformly filled in the holes (Fig. 2).

Adjacent supramolecular layers are interlinked by $[Ni(3)(en)_2]^{2+}$ fragments through robust hydrogen bonding $[N(19) \cdots O(31), d = 3.10(2) \text{ \AA}]$ (Table S1) to form a host supramolecular network (Fig. 3a). Each POMs center connecting with

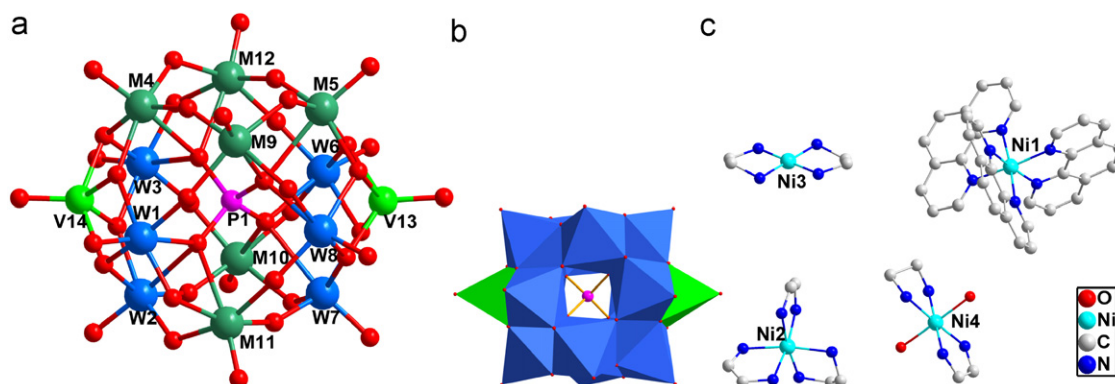


Fig. 1. (a) View of crystal structure of $[PW^{VI}_7W^V_2V^{IV}_3O_{40}(V^{IV}O_2)]^{7-}$ for **1**, (b) polyhedral representation of the polyanion for **1** and (c) four different kinds of counteranions in compound **1**.

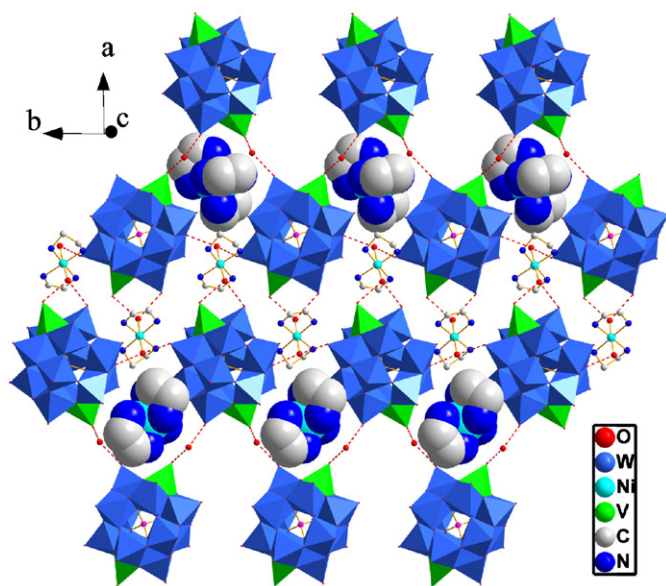


Fig. 2. View of the 2D supramolecular layer of compound **1** along *c* axis showing the *in situ* template $[\text{Ni}(\text{en})_3]^{2+}$ as space filling presentation.

three $[\text{Ni}(4)(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ fragments, two O6W and one $[\text{Ni}(3)(\text{en})_3]^{2+}$ is viewed as a six-connected node, correspondingly, each $[\text{Ni}(4)(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ fragment connecting with three POMs centers is regarded as a three-connected node, then the two different kinds of nodes in the ratio 1:1 interconnect each other to form a 3D (3, 6)-connected network with the Schläfli symbol $(4^3)(4^5 \cdot 6^9 \cdot 8)$ (Fig. 3b). The most striking feature of the host supramolecular network is that there exist large dimension channels running along *b* axis. The approximate dimension of the channels is 8.34×18.59 Å (Fig. 3a).

A large number of facts have demonstrated that the $[\text{Ni}(\text{en})_2]^{2+}$ fragment is a good candidate for linker in the formation of polymer of POM clusters [11–13,44]. Why the $[\text{Ni}(3)(\text{en})_2]^{2+}$ fragments cannot link the polyanions to generate supported POMs or polymer of the polyoxoanion clusters through the terminal oxygen atoms? We speculate that the template $[\text{Ni}(1)(\text{phen})_3]^{2+}$ with more large volume filled in channels handicap that the four-coordinated Ni3 atoms link heteropolyanions to generate a high-dimensional covalent compound (Fig. 4). If the templates $[\text{Ni}(1)(\text{phen})_3]^{2+}$ are absent, the polyanions should be covalently linked through $[\text{Ni}(\text{en})_2]^{2+}$ linkers to form a polymer of polyanion clusters [11–13]. The $[\text{Ni}(3)(\text{en})_2]^{2+}$ fragments are restricted in the biggish spaces constructed by $[\text{Ni}(1)(\text{phen})_3]^{2+}$ fragments and the heteropolyanions, and the shortest distance of Ni(3) and the terminal oxygen atoms of the heteropolyanions is 3.463 Å being obviously larger than covalently binding distance. In contrast to the POMs employed to construct the 3D hydrogen-bonded host networks, the guest TMCs $[\text{Ni}(\text{phen})_3]^{2+}$ were incorporated into the host networks through hydrogen-bonding interactions with their nearest polyanion neighbors (Table S1). To sum up, the generated *in situ* TMCs, $[\text{Ni}(\text{phen})_3]^{2+}$ and $[\text{Ni}(\text{en})_3]^{2+}$, play a crucial part in the formation of compound **1** displaying above-mentioned crystal 3D supramolecular structure.

3.2.2. Crystal structure of compound 2

The structure of **2** consists of heteropolyanion $[\text{PW}^{\text{VI}}_7\text{W}^{\text{V}}_2\text{V}^{\text{IV}}_3\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_2]^{7-}$ (Fig. S2a), cations, Na^+ , $[\text{Ni}(1)(\text{phen})_3]^{2+}$ and $[\text{Ni}(2)(\text{en})_2]^{2+}$ cations, as well as lattice water molecules. The polyanion in **2** possesses a pseudo-Keggin-type structure capping with two additional (VO) units. In the {MO₆} octahedra, M position is crystallographically disordered with occupancies of

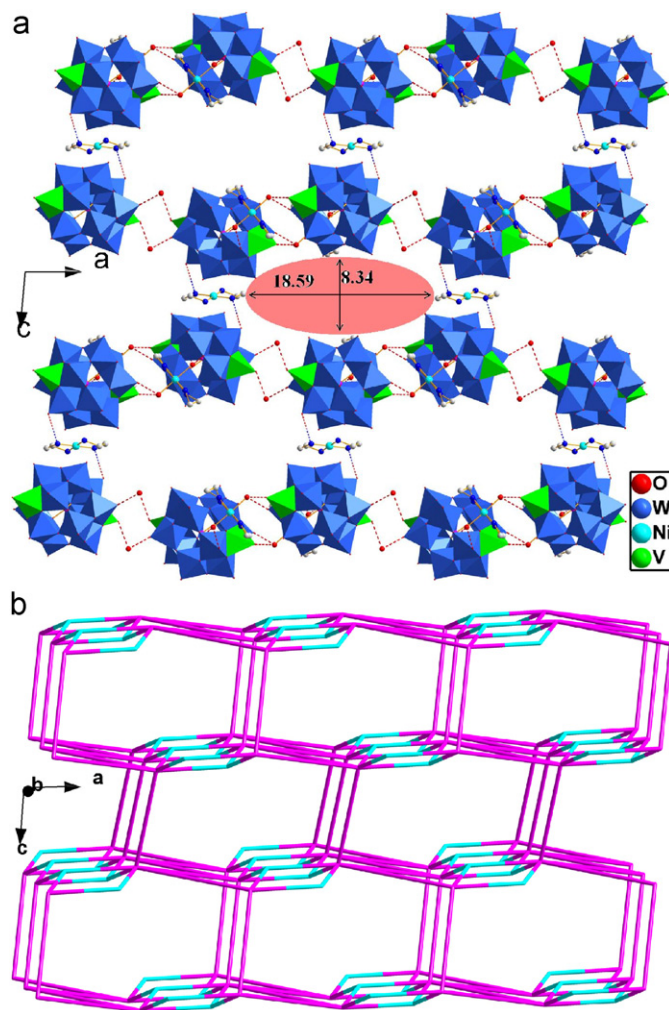


Fig. 3. (a) Views of the 3D hydrogen-bonded host supramolecular framework constructed by POMs, $[\text{Ni}(\text{en})_2]^{2+}$ and $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ fragments along *b* axis and the dimension of channel. (b) Schematic representation of the (3, 6)-connected supramolecular topological network with the Schläfli symbol $(4^3)(4^5 \cdot 6^9 \cdot 8)$ of **1** (six-connected nodes (POMs) are depicted in purple and three-connected nodes ($[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ fragments) in cyan).

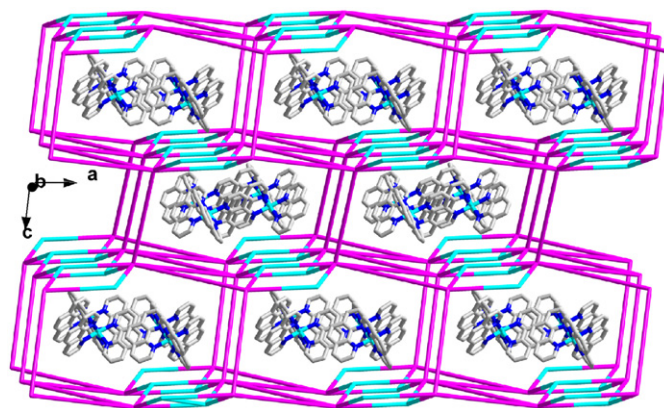


Fig. 4. View of the 3D host supramolecular framework of compound **1** along *b* axis showing the guest *in situ* templates $[\text{Ni}(\text{phen})_3]^{2+}$ fragments as space filling presentation.

0.89 and 0.11 (M4), 0.35 and 0.65 (M5), 0.33 and 0.67 (M6) for W and V, respectively. The P–O, W–O, M–O and V–O bond lengths [P–Oc, 1.460(15)–1.683(16) Å; W/V–Ot, 1.625(10)–1.691(10) Å;

W/V–Ob, 1.767(14)–2.058(11) Å; W/V–Oc, 2.344(17)–2.470(15) Å; W–Ot, 1.667(10)–1.689(10) Å; W–Ob, 1.767(14)–2.038(9) Å; W–Oc, 2.352(14)–2.437(14) Å; V–Ot, 1.591(10) Å; V–Ob, 1.937(11)–1.960(9) Å are within the normal ranges (Table 2). The coordination mode of Ni1 and Ni2 atoms in **2** is identical with Ni1 and Ni3 atoms in compound **1**, exhibiting a distorted octahedron and square geometry, respectively. The Ni–N distances and the N–Ni–N angles are in the range of 1.88(2)–2.106(10) Å and 79.4(4)°–180.0(4)°, respectively. All these bond distances and bond angles are within the normal ranges and in close agreement with those described in the relevant literatures. The polyanions are linked by sodium cations to form 1D inorganic chains along *c* axis through Na–O weak bonding (Fig. S2b). The occupancy factor of Na⁺ is 0.5. As in the compound **1**, the 1D inorganic chains and [Ni(en)₂]²⁺ fragments are further connected together via hydrogen bonding [N(7)···O(10) and N(8)···O(16)] with the

distance of 3.09(3) and 3.16(2) Å, thus resulting in an interesting 2D supramolecular layer (Fig. 5). The large volume templates [Ni(phen)₃]²⁺ generated *in situ* under mild hydrothermal conditions are sandwiched between the adjacent layers (Fig. 6). The [Ni(phen)₃]²⁺ fragments restrain that the 1D inorganic chains and the [Ni(en)₂]²⁺ fragments are covalently linked each other to form high-dimensional structure. The guest TMCs [Ni(phen)₃]²⁺ fragments are incorporated into the hydrogen-bonded host POMs lattice through extensive multi-point C–H···O hydrogen bonding interactions with their nearest polyanions (Table S1). So compound **2** shows an interesting 3D supramolecular TMCs-sandwich structure (Fig. 6b and d). According to the above-mentioned structure descriptions for compounds **1** and **2**, we speculate that the polyanions will be linked by [Ni(en)₂]²⁺ linkers in the absence of phen. The results of experiment have been demonstrated our inference [45]. So the TMCs [Ni(phen)₃]²⁺ act as structure-directing agents and guests in the construction of the 3D supramolecular networks based on tungstovanadophosphates.

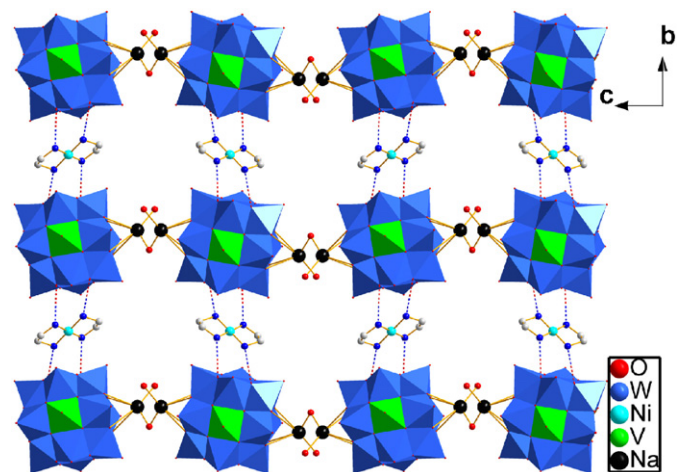


Fig. 5. View of the hydrogen-bonded sheet constructed with inorganic chain and [Ni(en)₂]²⁺ fragment in **2** along *a* axis.

3.3. Characterization of compounds

3.3.1. Bond valence sum (BVS) and XPS characterizations

The BVS for the W and V atoms were calculated by using parameters given by Brown [46]. For compound **1**, the result gives the average value 5.79 for W, 4.00 for the disordered V atoms and 4.15 for the capped V atoms, which reveal that there exist two W (V) atoms, seven W (VI) atoms and five V (IV) atoms. The XPS gives a peak at 516.5 eV attributed to V^{IV}2p_{3/2} and four partially overlapped peaks, and the fit of curve gives positions of these four peaks at 35.0, 36.3, 37.2 and 38.4 eV being attributed to W^V4f_{7/2}, W^{VI}4f_{7/2}, W^V4f_{5/2} and W^{VI}4f_{5/2} (Fig. 7), respectively, which is in agreement with the bond valence analysis. These results further confirm the composition of compound **1**.

According to the structure determination, elemental analysis, BVS calculations, XPS and charge balance, compound **2** is formulated as [Ni(phen)₃]₂[Ni(en)₂]Na[PW^{VI}₇W^V₂V^{IV}₃O₄₀(V^{IV}O)₂]₂·8H₂O. The BVS calculations show that the valence states of both the capped and disordered V atoms are all +4 (average calculated

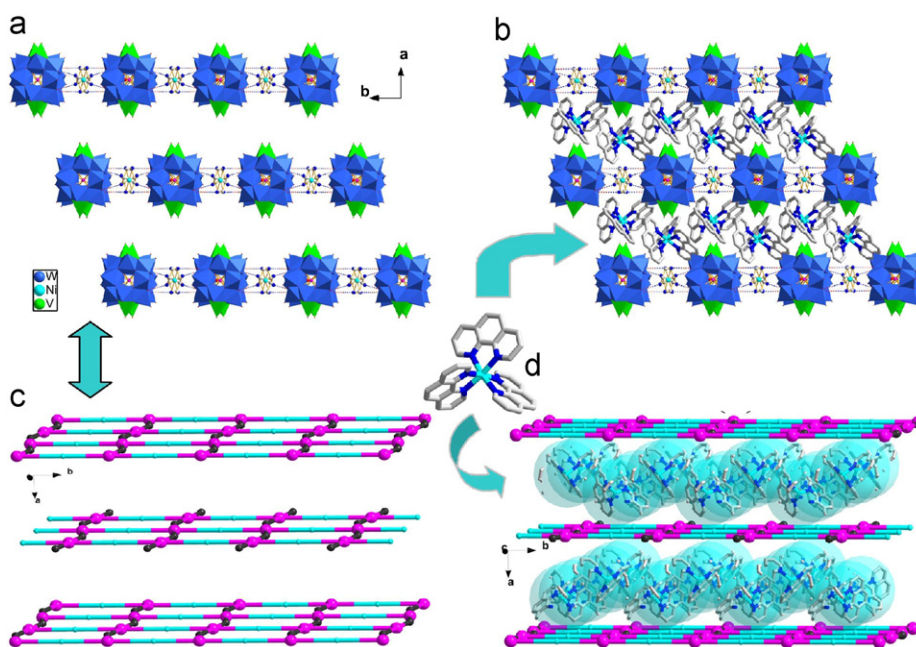


Fig. 6. (a)/(c) View of the 2D hydrogen-bonded host POMs layers of compound **2** along *c* axis. (b)/(d) View of the 3D sandwich structure constructed from POMs layers and guest template layers generated *in situ*.

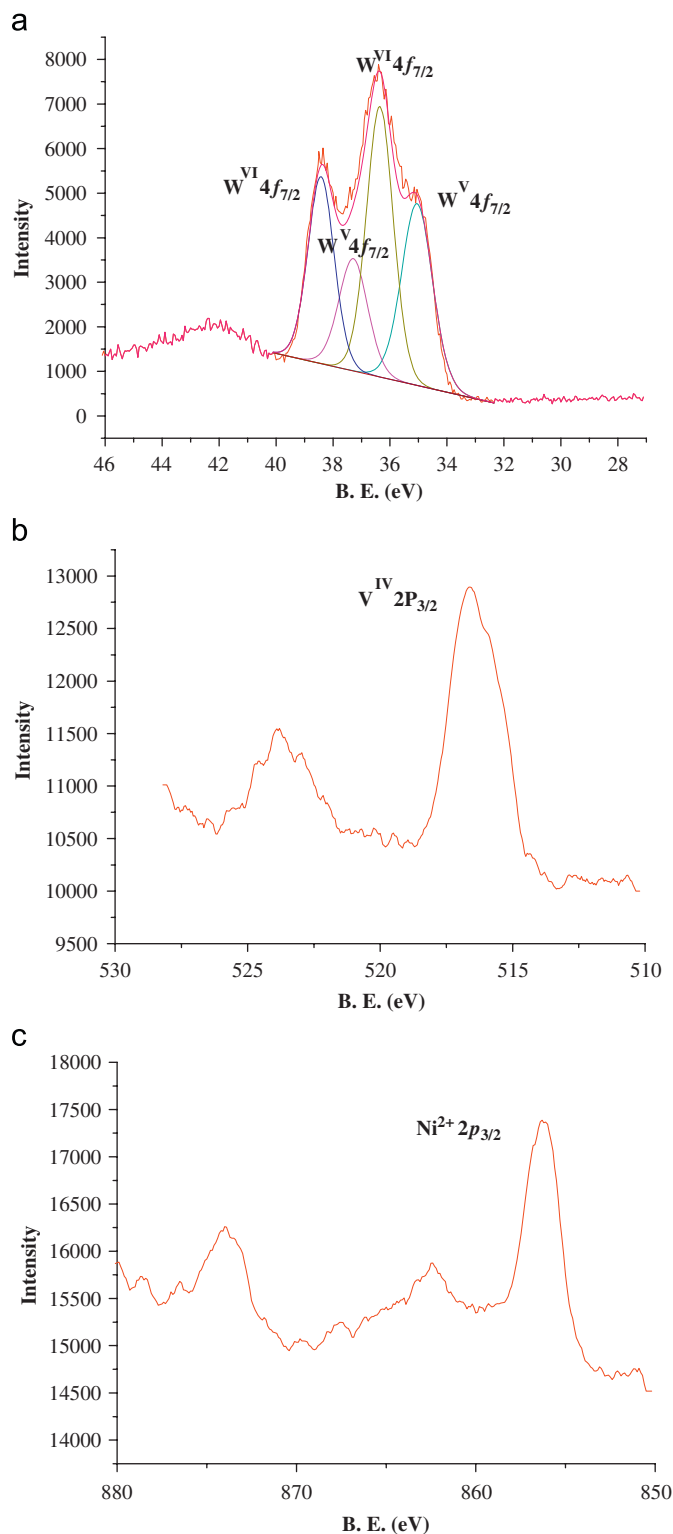


Fig. 7. The XPS for W (a), V (b) and Ni (c) in compound 1.

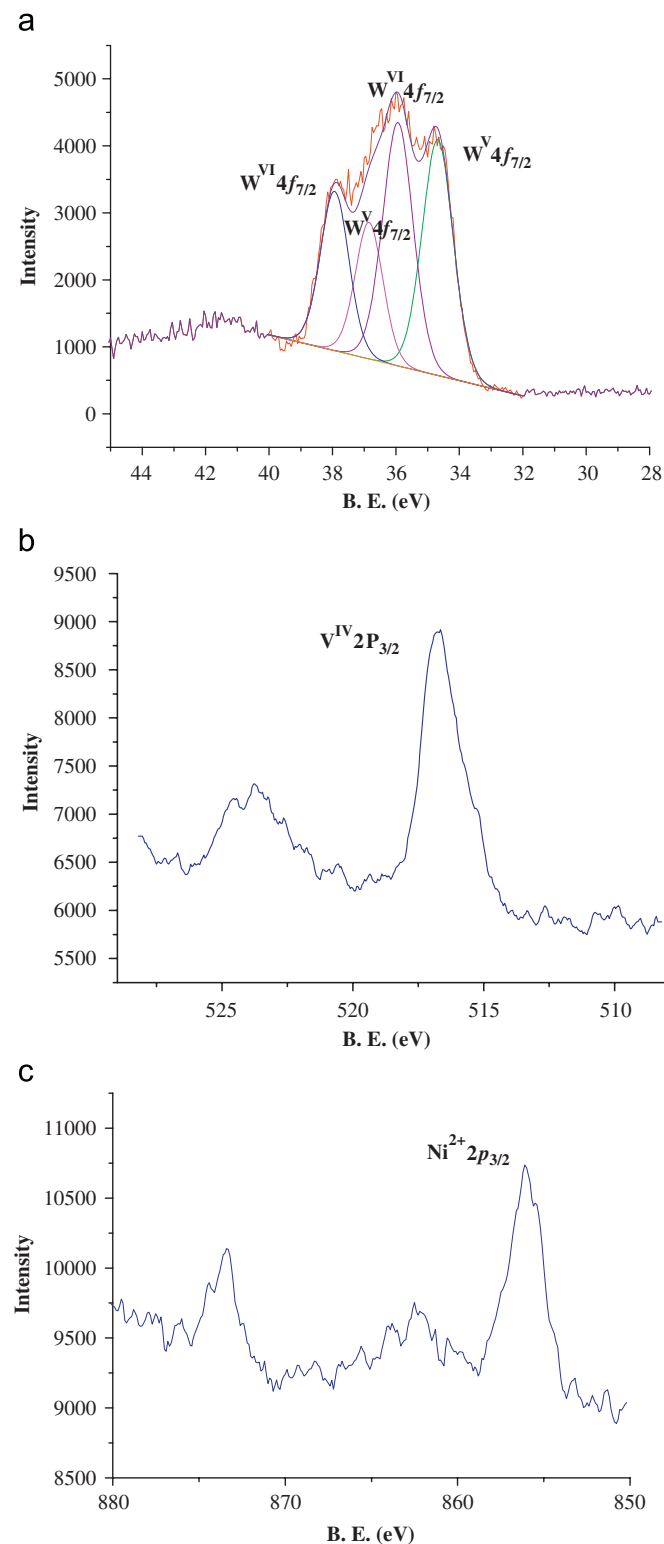


Fig. 8. The XPS for W (a), V (b) and Ni (c) in compound 2.

values are 4.33 and 4.25, respectively). The calculated results of all W atoms (average calculated value = 6.17), however, do not identify the reduced two W^V sites. This is due to the possible delocalization of the d electrons of the reduced tungsten centers over the polyanion framework involving all W as found in heteropolyblues [47–50] and hexatungstates [51]. The XPS of 2 (Fig. 8) show four partially

overlapped peaks, and the fit of curve provides with positions of these four peaks at 34.6, 35.9, 36.8 and 37.9 eV attributing to $W^V4f_{7/2}$, $W^{VI}4f_{7/2}$, $W^{VI}4f_{5/2}$ and $W^V4f_{5/2}$, respectively, and one peak at 516.6 eV attributed to $V^{IV}2p_{3/2}$ [52]. The XPS of compounds 1 and 2 give the same peaks at 856.2 eV attributed to $Ni^{2+}2p_{3/2}$. All these results further confirm the structure analyses.

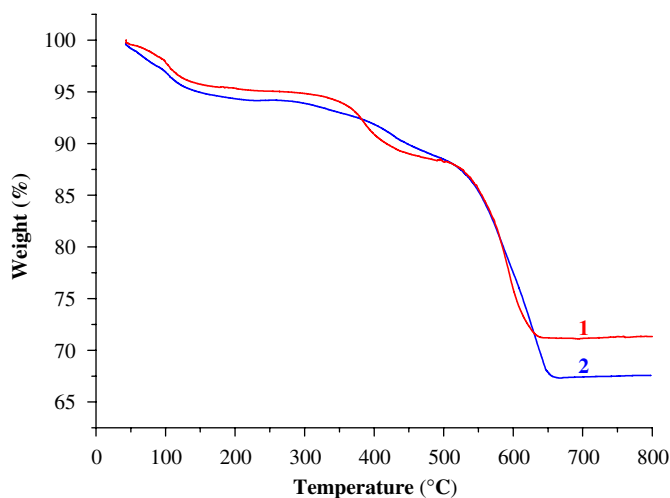


Fig. 9. Thermogravimetric patterns for two compounds.

3.3.2. EPR spectra

The EPR spectra for both compounds **1** and **2** recorded at room temperature (298 K) on a crystalline samples show the V^{IV} signal with $g = 1.929$ for compound **1**, and $g = 1.964$ for compound **2** (Fig. S3), being consistent with the results of valence sum calculations of compounds **1** and **2**.

3.3.3. Infrared spectra

As shown in Fig. S4, the IR spectra of **1** and **2** exhibit the characteristic bands of the tungstovanadophosphates with little differences between these two compounds. The bands at $945\text{--}644\text{ cm}^{-1}$ in compound **1** and $971\text{--}643\text{ cm}^{-1}$ in compound **2** should be attributed to $\nu(M\text{--}Ot)$ and $\nu(M\text{--}Ob\text{--}M)$ ($M = W$ or V), respectively. The strong bands at $1045, 1035\text{ cm}^{-1}$ in compound **1** and 1053 cm^{-1} in compound **2** are due to $\nu(P\text{--}O)$. The broad bands of $3433\text{--}3275\text{ cm}^{-1}$ for compound **1** and 3415 cm^{-1} for compound **2** characterize water molecules in the structures, although this band may contain weak C–H stretching vibration. The characteristic peaks at $1623, 1585, 1519, \text{ and } 1427\text{ cm}^{-1}$ for compound **1** and $1624\text{--}1578, 1518 \text{ and } 1425\text{ cm}^{-1}$ for compound **2** are attributed to stretching vibrations of C=N and C–N bonds. The weak bands at $1339\text{--}1105\text{ cm}^{-1}$ in compound **1** and $1341\text{--}1106\text{ cm}^{-1}$ for compound **2** could be due to absorption of ligand en.

3.3.4. Thermogravimetric analyses

Thermogravimetric curves (Fig. 9) of two compounds support their chemical composition. It exhibits three steps of weight loss for compound **1**. The first weight loss of 3.82% (calculated, 3.73%) from $43\text{--}119\text{ }^{\circ}\text{C}$ is ascribed to the release of six lattice water and two coordinated water molecules. The second weight loss is 9.05% (calculated, 9.33%) in the temperature range $119\text{--}530\text{ }^{\circ}\text{C}$, corresponding to the decomposition of six en molecules. The third step occurring between 530 and $640\text{ }^{\circ}\text{C}$ is assigned to the decomposition process of three phen molecules (Found: 14.71%; Calcd: 13.98%). The whole weight loss (27.58%) is in good agreement with the calculated value (27.04%). Thermal analysis of compound **2** reveals the involvement of two steps in weight loss. The weight loss amounts to 3.73% ($43\text{--}110\text{ }^{\circ}\text{C}$) and 29.02% ($110\text{--}660\text{ }^{\circ}\text{C}$), respectively. The calculated weight losses for eight crystallizing water molecules (3.47%), and six phenanthroline molecules and two en molecules (28.90%) are in agreement with the results of the TG experiment).

4. Conclusion

In summary, we have reported syntheses and characterizations of two novel TMCs-templated 3D supramolecular networks based on tungstovanadophosphates, $[\text{Ni}(\text{phen})_3][\text{Ni}(\text{en})_3][\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2][\text{Ni}(\text{en})_2]_{0.5}[\text{PW}_9\text{V}_3\text{O}_{40}(\text{VO})_2] \cdot 6\text{H}_2\text{O}$ (**1**) and $[\text{Ni}(\text{phen})_3]_2[\text{Ni}(\text{en})_2]\text{Na}[\text{PW}_9\text{V}_3\text{O}_{40}(\text{VO})_2] \cdot 8\text{H}_2\text{O}$ (**2**). The 3D supramolecular networks contain bicapped (pseudo-) Keggin-type heteropolyanions and the templates transition metal complexes generated *in situ* under mild hydrothermal conditions. Based on the same $[\text{PW}_9\text{V}_3\text{O}_{40}(\text{VO})_2]^{7-}$ POMs, the interesting hydrogen-bonded host networks are formed and employed to accommodate the *in situ* templates (TMCs). Furthermore, we also discuss the formation process of these two compounds and the function of each component in the crystallization process. In order to understand and master the influences of different ligands and transition-metal centers constructing *in situ* templates on the structures and performances of synthesized POMs-based compounds, further relevant research is underway in our group.

Acknowledgment

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Appendix A. Supporting information available

X-ray crystallographic files of compounds **1** and **2** in CIF format, selected bond lengths (\AA) and angles (deg.) of N(C)–H \cdots O hydrogen bonding for compounds **1** and **2**, the single-helix chain with a pitch of 13.28 \AA along b axis in compound **1**, view of 2D supramolecular layered structure constructed from single-helix chains and $[\text{Ni}(\text{en})_2(\text{H}_2\text{O})_2]^{2+}$ fragments through hydrogen bonding in compound **1**, view of the bicapped α -Keggin tungsten–vanadium cluster anion unit in compound **2**, polyhedron-and-stick representation of the 1D chain structure constructed from α -Keggin tungsten–vanadium polyanion and Na^+ of compound **2**, EPR spectra of **1** and **2**, IR spectra of two compounds, CCDC reference numbers: 697346, 697347 for compounds **1** and **2**, respectively.

Appendix B. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2008.12.005.

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