Hydrothermal synthesis and characterization of two new bicapped Keggin heteropoly tungstovanadated derivatives

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Abstract

Two new heteropoly tungstovanadate derivatives, $[Fe(phen)_3]_2[W_{10.5}V_{4.5}O_{42}] \cdot 3H_2O$ (1) and $[Fe(phen)_3]_2[W_{10}V_5O_{42}].6H_2O$ (2) (phen $=$ 1,10′-phenanthroline), have been synthesized under hydrothermal conditions by using different starting materials, and characterized by elemental analysis, IR, ESR, XPS, TGA and single-crystal X-ray diffraction analysis. Crystal data for compound 1: $C_{72}H_{54}Fe_2N_{12}O_{45}V_{4.5}W_{10.5}$, monoclinic, space group $C2/c$, $a = 30.244(9)$ Å, $b = 13.586(3)$ Å, $c = 24.707$ Å, $\beta = 99.882(8)°$, $V = 10002(5)$ Å^3, $Z = 4$; for compound 2, $C_{72}H_{60}Fe_2N_{12}O_{48}V_5W_{10}$, monoclinic, space group $C2/c$, $a = 30.246(6)$ Å, $b = 13.909(3)$ Å, $c = 25.329(5)$ Å, $\beta = 100.34(3)°$, $V = 10483(4)$ Å^3, $Z = 4$. The crystal structure analysis reveals that both polyoxoanions are decorated with the $[Fe(phen)_3]^{2+}$ cations, and that they have analogous structure to each other with slightly different packing modes of the polyoxoanions, $[Fe(phen)_3]^{2+}$ cations and water molecules. They are further linked to form two-dimensional (2D) supramolecular networks through extensive hydrogen bonding.

1. Introduction

In recent years, because of structural diversity and potential applications in many areas such as catalysis, magnetism, electric conductivity and medicine [1], polyoxometalates (POMs) containing Keggin moieties and derivatives have a prominent place in the forefront of polyoxometalatic chemistry. One of the challenges in this field is the design and synthesis of novel solid materials based on POMs [2]. Several successful synthesis strategies of the bicapped Keggin structure have been reported, such as discrete clusters $[V_{15}O_{42}]^{9-}$ [3], $[PMo_{12}V_2O_{42}]^{5-}$ [4] and $[SiMo_{12}V_2O_{42}]^{4-}$ [5]; 1D chain compound $Na_{0.5}K_{6.5}[Mo_8^{VI}V_4^{IV}O_{36}(V^VO_4)(V^{IV}O)_2] \cdot 12.5H_2O$ [6]; and 2D layer compound $[Cu(en)_2(H_2O)]$ $\{[PMo_8^{VI}V_6^{IV}O_{42}Cu(en)_2][Cu_{0.5}(en)_3]_3 \cdot 5.5H_2O$ [7] and 3D framework compound $H_3\{V^VMo_8^{VI}V_6^{IV}O_{42}[Cu(en)_2]_4\}[MoO_4] \cdot 14H_2O$ [8]. Because

the formation rates of heteropolytungstates are generally slower than those of heteropolymolybdates, and the control of their formation conditions is rather difficult, heteropolytungstates structurally characterized by crystallography are rare among previously reported polyoxometalates [9]. Considering the quite limited number of hydrothermal syntheses of heteropolytungstates compared to the large family of hybrid organic–inorganic materials of the heteropolymolybdates, we attempted to explore our research on the preparation of Keggin tungsten–vanadium clusters using simple reactants, and we succeed in doing so.

In this paper, we describe the hydrothermal syntheses, structures and properties of two new bicapped Keggin heteropoly tungstovanadates derivatives: $[Fe(phen)_3]_2[W_{10.5}V_{4.5}O_{42}] \cdot 3H_2O$ (1) and $[Fe(phen)_3]_2[W_{10}V_5O_{42}] \cdot 6H_2O$ (2) (phen $=$ 1,10′-phenanthroline). This is that capping Keggin mixed W/V metal–oxygen clusters possessing discrete structure from the view point of covalent bond are reported for the first time.

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2. Experimental

2.1. Materials and measurements

All reagents used were of analytical grade and obtained from commercial sources without further purification. The elemental analysis (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR (KBr pellets) spectra were recorded in the $225–4000\,cm^{-1}$ range using a Perkin-Elmer Spectrum One spectrophotometer. XPS analysis was performed on an VG ESCALAB MK II spectrometer with an Mg-$K\alpha$ (1253.6 eV) achromatic X-ray source. Determination of electron spin resonance (ESR) carried out on Bruker ER 200D-SRC spectrometer. The thermogravimetric analysis (TGA) were carried out on a Perkin-Elmer TAG-7000 instrument from room temperature to 800 °C, with a heating rate of 20 °C/min under a nitrogen atmosphere.

2.2. Preparations

2.2.1. Preparation of $[Fe(phen)_3]_2[W_{10.5}V_{4.5}O_{42}] \cdot 3H_2O$ (1)

Compound **1** was hydrothermally synthesized in 72% yield (based on W). A mixture of $Na_2WO_4 \cdot 2H_2O$ (1.6 g, 4.8 mmol), V_2O_5 (0.45 g, 2.4 mmol), $H_2C_2O_4 \cdot 2H_2O$ (0.56 g, 4.8 mmol), $FeCl_3 \cdot 6H_2O$ (0.32 g, 1.2 mmol), phen (0.12 g, 3.6 mmol) and distilled water (24 mL) in a molar ratio of 4:2:4:1:1.5:1110 were stirred for 60 min and then transferred to a Teflon-lined reactor with 70% filling and heated at 170 °C for 3 days. $H_2C_2O_4 \cdot 2H_2O$ was used as a reducing agent and was necessary to maintain the pH = 5. After cooling to room temperature, the crystalline product was filtered, washed with distilled water and dried at ambient temperature to give 1.36 g solids. Anal. calc. for $C_{72}H_{54}Fe_2N_{12}O_{45}V_{4.5}W_{10.5}$: C, 21.21%; H, 1.35%; N, 4.09%. Found: C, 21.18%; H, 1.32%; N, 4.12%.

2.2.2. Preparation of $[Fe(phen)_3]_2[W_{11}V_5O_{42}] \cdot 6H_2O$ (2)

Compound **2** was hydrothermally synthesized in 78% yield (based on W). A mixture of WO_3 (0.56 g, 2.4 mmol), V_2O_5 (0.45 g, 2.4 mmol), NaOH (0.05 g, 1.2 mmol), $H_2C_2O_4 \cdot 2H_2O$ (0.56 g, 4.8 mmol), $K_3Fe(CN)_6$ (0.4 g, 1.2 mmol), phen (0.09 g, 0.24 mmol) and distilled water (24 mL) in a molar ratio of 2:2:1:4:1:0.1:1111 were stirred for 60 min and then transferred to a Teflon-lined reactor with 70% filling and heated at 170 °C for 3 days. $H_2C_2O_4 \cdot 2H_2O$ was used as a reducing agent and was necessary to maintain the pH = 5. After cooling to room temperature, the crystalline product was filtered, washed with distilled water and dried at ambient temperature to give 0.77 g solids. Anal. calc. for $C_{72}H_{60}Fe_2N_{12}O_{48}V_5W_{11}$: C, 21.31%; H, 1.38%; N, 4.09%. Found: C, 21.25%; H, 1.48%; N, 4.13%.

2.3. X-ray crystallgrapphy

The structures of compounds **1** and **2** were determined by single-crystal X-ray diffraction. A red block single crystal of **1** with dimensions $0.34 \times 0.19 \times 0.12\,mm^3$ was mounted on a glass fiber. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K in the range of $1.65 < \theta < 28.55°$. An empirical absorption correction was applied. A total of 30814 (11608 unique, $R_{int} = 0.0539$) reflections were measured ($-40 \leqslant h \leqslant 22$, $-17 \leqslant k \leqslant 15$, $-21 \leqslant l \leqslant 33$). Structure solution and refinement based on 11608 independent reflections and 7950 parameters gave $R_1(wR_2) = 0.0799(0.2099)$.

A red block single crystal of **2** with dimensions $0.27 \times 0.22 \times 0.14\,mm^3$ was mounted on a glass fiber. The data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å) at 293 K in the range of $1.75 < \theta < 27.48°$. An empirical absorption correction was applied. A total of 11321 (11321 unique, $R_{sigma} = 0.1162$) reflections were measured ($0 \leqslant h \leqslant 39$, $0 \leqslant k \leqslant 18$, $-32 \leqslant l \leqslant 32$). Structure solution and refinement based on 11321 independent reflections and 5286 parameters gave $R_1(wR_2) = 0.0846(0.2178)$.

The structures of **1** and **2** were solved by direct methods and refined by the full-matrix least squares on F^2 SHELXL-97 software [10]. All of the non-hydrogen atoms were refined anisotropically in compound **1**. All atoms except six lattice water molecules were refined anisotropically in compound **2**. The positions of the hydrogen atoms attached to carbon and nitrogen atoms were fixed at their ideal positions, and those attached to oxygen atoms were not located. A summary of crystal data and structure refinement for compounds **1** and **2** is provided in Table 1. Selected bond lengths and angles of **1** and **2** are listed in Tables 2 and 3.

3. Results and discussion

3.1. Synthesis

Compound **1** was prepared from the hydrothermal reactions of $Na_2WO_4 \cdot 2H_2O$, V_2O_5, $H_2C_2O_4 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$, phen and distilled water at 170 °C for 3 days, respectively, while compound **2** was prepared by the hydrothermal reaction of WO_3, V_2O_5, NaOH, $H_2C_2O_4 \cdot 2H_2O$, $K_3Fe(CN)_6$, phen and distilled water in similar conditions to compound **1**. In the synthesis reactions, it seemed as if $H_2C_2O_4 \cdot 2H_2O$ would not play any part in assembly of compounds **1** and **2**. To investigate the role of the $H_2C_2O_4 \cdot 2H_2O$, we tried to synthesize **1** and **2** under the same conditions without $H_2C_2O_4 \cdot 2H_2O$, no desired crystal was found. It shows that $H_2C_2O_4 \cdot 2H_2O$ not only influences pH values of the system, but also act as a reducing agent. Fe^{III}, W^{VI} and V^V in reagent were reduced in the presence of $H_2C_2O_4 \cdot 2H_2O$.

Table 1
Crystal data and structure refinement information for **1**–**2**

Empirical formula	$C_{72} H_{54} Fe_2 N_{12} O_{45} V_{4.5} W_{10.5}$	$C_{72} H_{60} Fe_2 N_{12} O_{48} V_5 W_{10}$
Formula weight	4078.58	4066.22
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
a (Å)	30.244(9)	30.246(6)
b (Å)	13.586(3)	13.909(3)
c (Å)	24.707(6)	25.329(5)
β (deg.)	99.882(8)	100.34(3)
V (Å^3)	10002(5)	10483(4)
Z	4	4
D_C (Mg/m^3)	2.705	2.576
M (mm^{-1})	12.787	11.701
Goodness-of-fit on F^2	1.044	0.938
Final R indices [$I > 2\theta(I)$]	$R_1 = 0.0799$ w$R_2 = 0.2099$	$R_1 = 0.0846$, w$R_2 = 0.2178$

Table 2
Selected lengths (Å) and angle (deg.) for compound **1**

W(1)–O(11)	1.676(13)	W(1)–O(15)	2.014(11)
W(1)–O(20)#1	1.775(13)	W(1)–O(23)	2.052(11)
W(1)–O(9)	1.817(11)	W(1)–O(3)#1	2.307(16)
W(2)–O(18)	1.651(11)	W(2)–O(22)	1.978(14)
W(2)–O(17)	1.775(15)	W(2)–O(10)	2.056(15)
W(2)–O(6)	1.830(18)	W(2)–O(2)#1	2.441(17)
M(3)–O(8)	1.613(12)	*M*(3)–O(13)#1	1.935(13)
M(3)–O(17)	1.901(14)	*M*(3)–O(7)	1.961(16)
M(3)–O(9)#1	1.923(14)	*M*(3)–O(4)	2.400(15)
M(4)–O(19)	1.603(14)	*M*(4)–O(20)	1.938(14)
M(4)–O(6)	1.930(15)	*M*(4)–O(5)	1.988(19)
M(4)–O(12)#1	1.937(13)	*M*(4)–O(2)#1	2.352(16)
W(5)–O(14)	1.685(11)	W(5)–O(15)	2.005(12)
W(5)–O(7)	1.802(14)	W(5)–O(22)	2.059(11)
W(5)–O(12)	1.805(12)	W(5)–O(4)	2.347(15)
W(6)–O(16)	1.630(12)	W(6)–O(23)	2.014(13)
W(6)–O(5)	1.794(19)	W(6)–O(10)	2.023(13)
W(6)–O(13)	1.824(15)	W(6)–O(2)#1	2.370(18)
M(7)–O(21)	1.614(10)	*M*(7)–O(10)	1.962(15)
M(7)–O(22)	1.944(13)	*M*(7)–O(15)	1.981(12)
M(7)–O(23)	1.948(11)		
V(1)–O(1)	1.643(9)	V(1)–O(3)	1.667(9)
V(1)–O(2)	1.706(9)	V(1)–O(4)	1.665(9)
Fe(1)–N(1)	1.961(14)	Fe(1)–N(2)	1.967(13)
Fe(1)–N(3)	1.965(13)	Fe(1)–N(4)	1.961(12)
Fe(1)–N(5)	1.965(13)	Fe(1)–N(6)	1.959(13)
O(9)–W(1)–O(15)	155.0(7)	O(11)–W(1)–O(9)	103.6(8)
O(11)–W(1)–O(15)	99.4(6)	O(9)–W(1)–O(23)	89.8(5)
O(15)–W(1)–O(23)	76.8(4)	O(15)–W(1)–O(1)	61.1(5)
O(6)–W(2)–O(22)	156.0(8)	O(18)–W(2)–O(17)	106.0(7)
O(17)–W(2)–O(6)	93.1(9)	O(22)–W(2)–O(4)	61.2(5)
O(8)–*M*(3)–O(4)	158.0(6)	O(7)–*M*(3)–O(4)	61.0(7)
O(20)–*M*(4)–O(5)	161.1(10)	O(20)–*M*(4)–O(1)#1	61.9(5)
O(14)–W(5)–O(1)	156.1(6)	O(22)–W(5)–O(4)	63.4(6)
O(5)–W(6)–O(23)	158.3(9)	O(10)–W(6)–O(2)#1	63.1(7)
O(22)–*M*(7)–O(23)	130.0(6)	O(21)–*M*(7)–O(22)	115.3(6)
O(22)–*M*(7)–O(10)	80.1(6)	O(23)–*M*(7)–O(10)	79.6(6)
O(1)#1–V(1)–O(4)	111.7(9)	O(1)–V(1)–O(2)#1	107.5(9)
O(4)–V(1)–O(2)	103.7(9)	O(1)–V(1)–O(3)	118.2(9)
N(4)–Fe(1)–N(1)	175.2(6)	N(5)–Fe(1)–N(3)	82.9(5)
N(6)–Fe(1)–N(3)	172.7(5)	N(1)–Fe(1)–N(2)	83.1(6)
N(5)–Fe(1)–N(2)	174.2(6)	N(6)–Fe(1)–N(4)	83.0(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x$; $-y+1$; $-z$.

Table 3
Selected lengths (Å) and angle (deg.) for compound **2**

W(1)–O(16)	1.682(16)	W(1)–O(12)	2.009(13)
W(1)–O(17)	1.753(15)	W(1)–O(20)	2.036(12)
W(1)–O(15)#1	1.849(13)	W(1)–O(4)#1	2.320(17)
W(2)–O(14)	1.657(13)	W(2)–O(12)	1.964(14)
W(2)–O(9)	1.820(17)	W(2)–O(5)	2.035(15)
W(2)–O(10)	1.823(13)	W(2)–O(2)	2.355(17)
M(3)–O(23)	1.611(13)	*M*(3)–O(7)#1	1.97(2)
M(3)–O(10)	1.897(14)	*M*(3)–O(17)	2.002(19)
M(3)–O(6)	1.912(16)	*M*(3)–O(1)	2.40(3)
M(4)–O(13)	1.572(14)	*M*(4)–O(21)#1	1.901(13)
M(4)–O(15)	1.882(15)	*M*(4)–O(11)	1.910(17)
M(4)–O(9)	1.892(17)	*M*(4)–O(2)	2.391(19)
W(5)–O(19)	1.614(13)	W(5)–O(8)	2.000(19)
W(5)–O(6)#1	1.798(19)	W(5)–O(5)	2.05(2)
W(5)–O(11)	1.84(2)	W(5)–O(1)#1	2.48(2)
W(6)–O(18)	1.655(15)	W(6)–O(20)	1.998(13)
W(6)–O(7)	1.780(19)	W(6)–O(8)	2.051(15)
W(6)–O(21)	1.795(15)	W(6)–O(1)#1	2.39(3)
V(1)–O(1)	1.624(10)	V(1)–O(2)	1.618(9)
V(1)–O(3)	1.581(9)	V(1)–O(4)	1.584(9)
V(2)–O(22)	1.631(14)	V(2)–O(5)	2.036(18)
V(2)–O(20)	1.944(12)	V(2)–O(12)	2.088(15)
V(2)–O(8)	1.973(18)		
Fe(1)–N(1)	2.068(15)	Fe(1)–N(2)	2.090(15)
Fe(1)–N(3)	2.069(14)	Fe(1)–N(4)	2.079(14)
Fe(1)–N(5)	2.059(13)	Fe(1)–N(6)	2.107(16)
O(16)–W(1)–O(3)	156.5(7)	O(16)–W(1)–O(20)	101.8(8)
O(16)–W(1)–O(15)#1	104.7(8)	O(16)–W(1)–O(17)	97.4(10)
O(20)–W(1)–O(3)	86.9(6)	O(17)–W(1)–O(3)	71.9(7)
O(14)–W(2)–O(2)	159.8(9)	O(14)–W(2)–O(10)	105.2(10)
O(10)–W(2)–O(12)	89.0(6)	O(5)–W(2)–O(2)	65.8(8)
O(10)–*M*(3)–O(6)	158.6(10)	O(6)–*M*(3)–O(1)	65.9(10)
O(15)–*M*(4)–O(9)	158.1(10)	O(11)–*M*(4)–O(2)	68.5(8)
O(11)–W(5)–O(8)	158.2(9)	O(8)–W(5)–O(1)#1	63.0(8)
O(7)–W(6)–O(20)	157.9(9)	O(7)–W(6)–O(1)#1	67.9(11)
O(3)–V(1)–O(4)	118.6(10)	O(3)–V(1)–O(2)#1	113.5(10)
O(4)–V(1)–O(2)#1	111.7(11)	O(2)–V(1)–O(1)	101.1(11)
O(20)–V(2)–O(5)	129.9(7)	O(22)–V(2)–O(20)	117.8(7)
O(22)–V(2)–O(8)	111.7(9)	O(5)–V(2)–O(12)	75.2(6)
N(5)–Fe(1)–N(3)	174.1(7)	N(1)–Fe(1)–N(2)	79.1(6)
N(2)–Fe(1)–N(6)	169.6(6)	N(3)–Fe(1)–N(4)	80.6(7)
N(1)–Fe(1)–N(4)	170.4(7)	N(5)–Fe(1)–N(6)	79.3(6)

Symmetry transformations used to generate equivalent atoms: #1 $-x$; $-y+1$; $-z$.

The organonitrogen ligand is significant. For compound **1**, if phen was substituted by 2,2′-bipy, oxalate-bridged transition-metal supramolecular polymer [Fe(2,2′-bipy)₂(C₂O₄)] would be synthesized; if phen was substituted by 4,4′-bipy, we only got some homogenized red slurry.

We also failed to synthesize compound **1** and **2** under the same conditions when pH values are 4 or lower and 7 or higher. It indicates that pH values are also a key factor to hydrothermally synthesize **1** and **2**.

3.2. Structure description

3.2.1. Crystal structure of compound 1

The single crystal X-ray structure analysis revealed that compound **1** consists of one discrete anion $[W_{10.5}V_{4.5}O_{42}]^{4-}$, two $[Fe(phen)_3]^{2+}$ cations and three crystallization water molecules (see Fig. 1). The polyoxoanion is based on the bicapped Keggin structure, which contains twelve coordination octahedra including eight {WO_6} and four {MO_6} octahedra, and one {VO_4} disordered tetrahedron at the center as well as two additional five coordinated {MO_5} units at capping position. In the disordered polyoxoanion, the central V(1) atom is located at the inversion center (0, 1/2, 0), two {VO_4} tetrahedron with each oxygen site half-occupied form an almost regular cube. The V(1)–O distances are in the range of 1.638(9)–1.711(9) Å and the O–V(1)–O angles vary from 103.8(8) to 110.1(8)°. All tungsten centers exhibit a {WO_6} octahedral environment with the terminal W–O distances range from 1.631(11) to 1.688(10) Å, and other W–O distances range from 1.755(12) to 2.455(16) Å, the bond angles at W atoms range from 60.6(6) to 157.2(6)°.
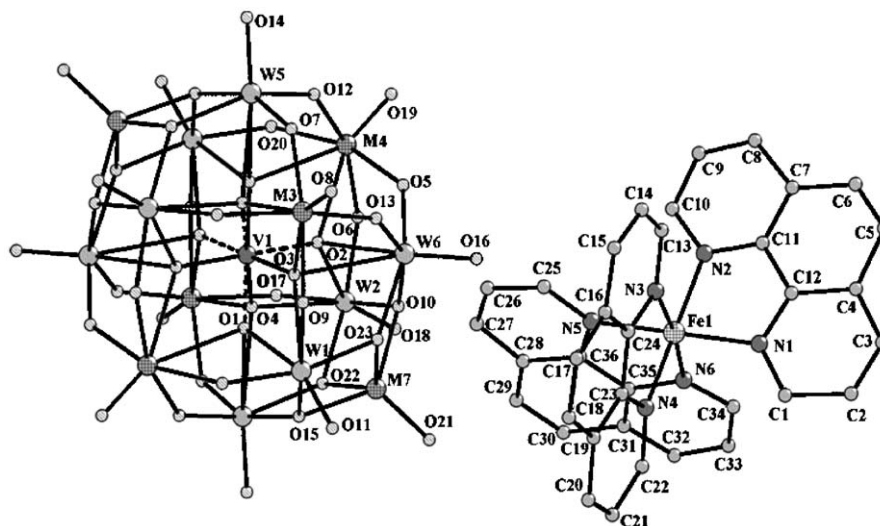
Fig. 1. View of crystal structure of $[Fe(phen)_3]_2[W_{10.5}V_{4.5}O_{42}] \cdot 3H_2O$. Only parts of atoms are labelled, all water molecule and H atoms are omitted for clarity.

The coordination environments of the $M(3)$ and $M(4)$ are distorted octahedra and that of $M(7)$ is square pyramids. In the $\{MO_6\}$ octahedra $M(3)$ position is crystallographically disordered with occupancies of 0.49 and 0.51 for W and V, and $M(4)$, 0.45 and 0.55 for W and V, respectively. The terminal M–O distances range from 1.608(13) to 1.621(11) Å, and other M–O distances range from 1.908(13) to 2.407(14) Å. In the $\{MO_5\}$ square pyramids, $M(7)$ sites are disorderly occupied by W and V with occupancies 0.32 and 0.68, respectively, and is bonded with one terminal oxygen and four triply bridging oxygen. The M–O distances range from 1.608(10) to 1.976(11) Å, and the bond angles at M atoms range from 61.1(7) to 159.7(10)°. These W–O/M–O distances and O–W–O/ O–M–O bond angles are comparable to those reported for other heteropoly tungstovanadates [9]. Four $\{WO_6\}$ octahedra form a $\{W_4O_{18}\}$ ring vis the corner- and or edge-sharing mode. Two $\{W_4O_{18}\}$ rings formed are connected with four $\{MO_6\}$ octahedra and two $\{MO_5\}$ tetragonal pyramids at capping sites through the edge-sharing mode. Thus, a closed spherical structure with disordered tetrahedral $\{VO_4\}$ locating at the center is formed. To our knowledge, such a heteropoly tungstovanadate is reported for the first time.

Each Fe^{2+} site in compound **1** is defined by six nitrogen atoms from three 1,10′-phenanthroline molecules and form a distorted FeN_6 octahedron with Fe–N bond distances ranging from 1.959(13) to 1.965(13) Å. Concerning number of reference, neither bicapped Mo/V Keggin type or W/V Keggin type is decorated by the $[Fe(phen)_3]^{2+}$.

Supramolecular interactions are the striking feature of the crystal structure of compound **1**. Water molecules link adjacent polyoxoanions $[W_{10.5}V_{4.5}O_{42}]^{4-}$ together through hydrogen bonding interactions along the c-axis although the polyoxoanions are discrete from the view point of the covalent bond. The typical hydrogen bond is Ow(1)$\cdots$O(5)
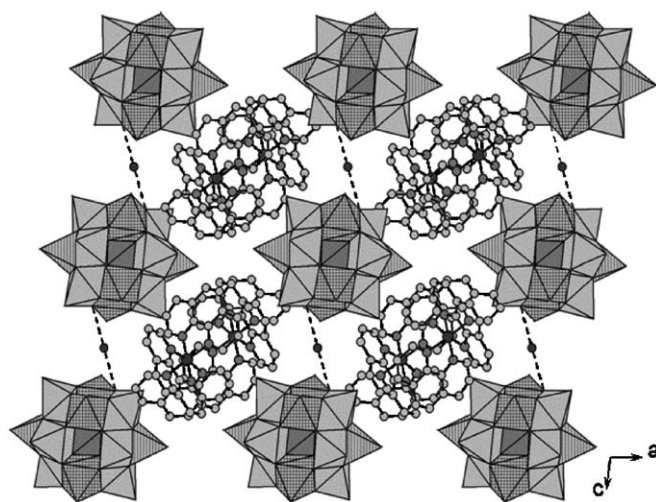

Fig. 2. View of the 2D supramolecular layer of compound **1** down the b-axis.

3.026 Å .Thus a 1D supramolecular chain is formed via hydrogen bonding interactions. Meanwhile, the adjacent polyoxoanions and $[Fe(phen)_3]^{2+}$ are further connected together via hydrogen bonding interactions with the shortest C(18)$\cdots$O(18) distance of 3.195(6) Å in the supramolecular network as shown in Fig. 2.

According to elemental analysis, bond valence sum (BVS) calculations, coordination geometries, and charge balance, compound **1** is formulated as $[Fe(phen)_3]_2$ $[(V^VO_4)W_{8.5}^{VI}W_2^VV_{3.5}^{IV}O_{30}] \cdot 3H_2O$. Using an empirical formula of bond valence, $S = \exp[-(R - R_o)/B]$ (S = bond valence, R = bond length) [11], we can obtain the S values of 3.88–4.24 for V (except 5.37 for the central V(1)) and 5.76–6.48 for W, respectively, indicating the oxidation state of the V atoms is +4 and the central V(1) in the +5 oxidation state. The BVS values of the W atoms, however,

do not clearly 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 [12] and hexatangstates [13].

3.2.2. Crystal structure of compound 2

Structure determination showed that compound **2** consists of three kinds of subunits: $[W_{10}V_5O_{42}]^{4-}$ anion, $[Fe(phen)_3]^{2+}$ cation, and uncoordinated water molecules. The $[W_{10}^{VI}V_4^{IV}O_{38}(V^{IV}O_4)]^{4-}$ (Fig. 3) unit is based on the Keggin structure $[W_{10}^{VI}V_2^{IV}O_{36}(V^{IV}O_4)]^{8-}$ with two capping five coordinated terminal {VO} units. All tungsten centers exhibit a {WO$_6$} octahedral environment with the terminal W–O distances range from 1.614(13) to 1.682(16) Å, other W–O distances range from 1.753(15) to 2.48(2) Å, and the bond angles at W atoms range from 60.8(9) to 159.8(9)°. The coordination environments of the M sites of the polyoxoanion are distorted octahedra. In the {MO$_6$} octahedra, M sites are disorderly occupied by W and V with the same occupancy of 50%, the M–O distances range from 1.572(14) to 2.40(3) Å, and the bond angles at M atoms range from 60.8(9) to 163.3(10)°. Compared to the bicapped Keggin structure $[W_{10.5}V_{4.5}O_{42}]^{4-}$ of compound **1**, the $[W_{10}V_5O_{42}]^{4-}$ unit contains a central $[V^{IV}O_4]$ tetrahedron with disordered oxygen atoms. In the $[V^{IV}O_4]$, the O–V–O bond angles vary from 101.1(11) to 118.6(10)°, and the average V–O bond distance (1.601 Å) is almost equal to the corresponding that in the $[Mo_6^{VI}V_{10}^{IV}O_{40}(V^{IV}O_4)]^{6-}$ [14] and $[VW_{12}O_{40}]^{7-}$ [9(b)], indicating a reduced vanadium (V^{4+}) in **2**. The assignment of oxidation states for the tungsten and vanadium atoms is consistent with their coordination geometries and is confirmed by valence sum calculations which gives an average value for W and V of 6.48 and 3.68, respectively. To the best of our knowledge, the presence of the reduced $[V^{IV}O_4]$ group at the center of such a Keggin anion is seldom seen.
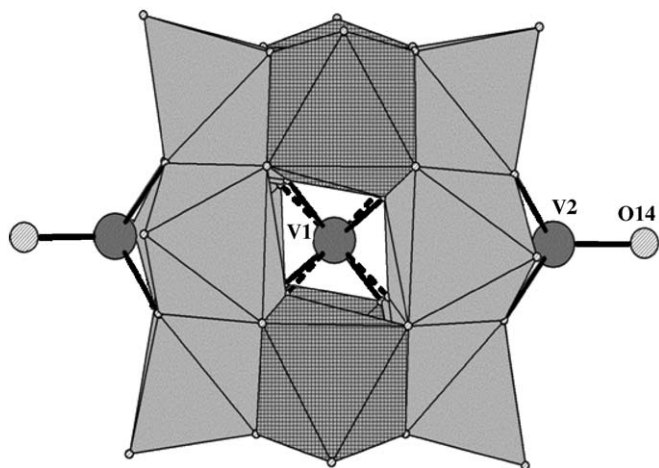

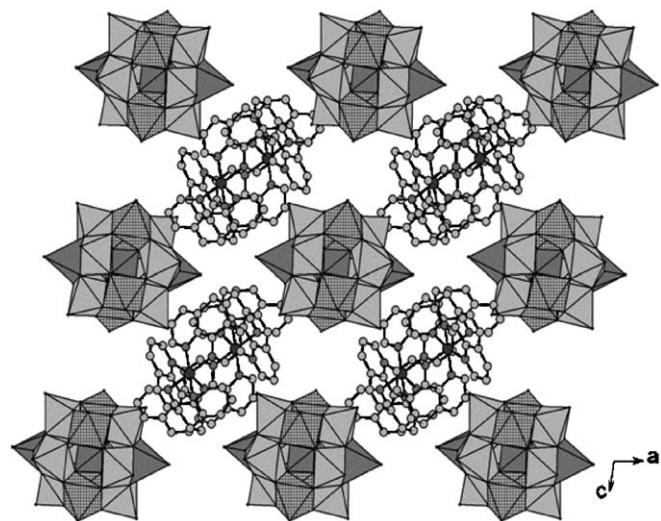Fig. 3. Polyhedral representation of the cluster anion of compound **2**.

Fig. 4. View of the 2D supramolecular layer of compound **2** down the b-axis.

The iron site in **2** possesses the distorted octahedral geometry coordinated with six nitrogen donors from the 1,10′-phenanthroline ligands with the Fe–N bond lengths of 2.059(13)–2.107(16) Å. The cations link the polyoxoanions through hydrogen bondings between the carbon atoms of 1,10′—phenanthroline and oxygen atoms of polyoxoanion, forming a 2D supramolecular layer as shown in Fig. 4. Some of data for hydrogen bondings (C–H···O) are listed in Table 4.

3.3. IR spectra

In the IR spectrum of **1**, the strong absorptions at 948, 846 and 783 cm^{-1} are due to v (M = O$_t$), $v(M$–O$_b)$ and $v(M$–O$_c)$ (M = W or V) [15], respectively. Features at 1630, 1512 and 1425 cm^{-1} are attributed to stretching vibrations of C=N and C–N bonds. Features at 1208 and 1144 cm^{-1} are ascribed to ring stretching of 1,10′-phenanthroline [16].

The IR spectrum of **2** is similar to that of **1**, in which there are absorption peaks at 945, 874 and 787 cm^{-1} assigning to $v(M$ = O$_t)$, $v(M$–O$_b)$ and $v(M$–O$_c)$ (M = W or V) [15], respectively, that at 1631, 1507 and 1409 cm^{-1} attributing to stretching vibrations of C=N and C–N bonds, and that at 1179 cm^{-1} ascribing to ring stretching of 1,10′—phenanthroline [16].

3.4. XPS spectra and EPR spectra

The EPR spectra for both compounds **1** and **2** recorded at room temperature (298 K) on a crystalline samples show the V^{4+} signal with $g_{II} = 1.926$, $g_\perp = 1.985$, $A_{II} = 184.7 \times 10^{-4}$ cm^{-1}, and $A_\perp = 63.4 \times 10^{-4}$ cm^{-1} for compound **1** (S, Fig. 1), and $g = 1.926$ for compound **2** (S, Fig. 2), being consistent with the results of valence sum calculations of compounds **1** and **2**.

Table 4
Lengths of C–H···O hydrogen bondings (Å) and angles (deg.) for compound **2**

D···A	Distance (Å)	D–H···A	Angle (deg.)
C9–O17	3.372(46)	C9–H9···O17	150.86(2) [x, $-1+y$, z]
C8–O23	3.349(46)	C8–H8···O23	122.05(2) [x, $-1+y$, z]
C29–O22	3.333(22)	C29–H29···O22	139.57(2) [x, $1-y$, $0.5+z$]
C1–O22	3.245(39)	C1–H1···O22	130.44(2) [$0.5-x$, $0.5+y$, $0.5-z$]
C15–O18	3.038(29)	C15–H15···O18	139.57(2) [$0.5+x$, $-0.5-y$, $-z$]
C21–O9	3.387(18)	C21–H21···O9	170.84(2) [x, y, z]
C33–O12	3.234(42)	C33–H33···O12	107.11(2) [x, $-1+y$, z]
C13–O14	3.273(50)	C13–H13···O14	116.18(2) [x, $-1+y$, z]

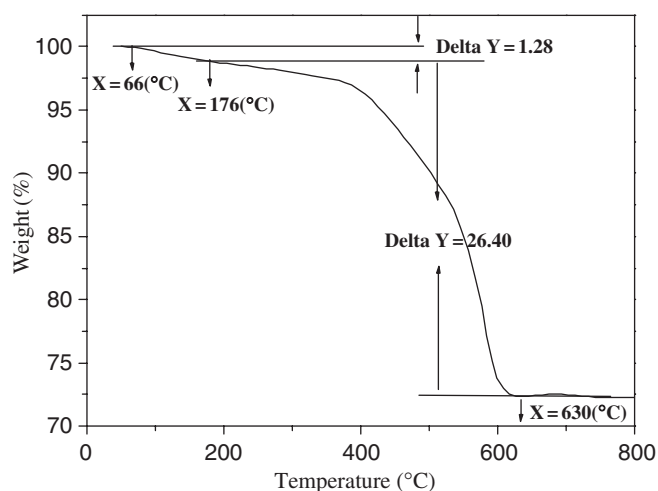Fig. 5. Thermogravimetric analysis of Compound **1**.

Fig. 6. Thermogravimetric analysis of Compound **2**.

The XPS spectrum of compound **1** (S, Fig. 3) gives two overlapped peaks at 517.1 and 515.6 eV, attributable to V^{5+} $2p_{3/2}$ and V^{4+} $2p_{3/2}$, respectively, and two overlapped peaks at 35.5 and 33.5 eV assigning to W^{6+} $4f_{7/2}$ and W^{5+} $4f_{7/2}$, respectively. The XPS spectrum (S, Fig. 4) for compound **2** shows one peak at 516.7 eV, attributed to V^{4+} $2p_{3/2}$, and that at 35.9 eV ascribed to W^{6+} $4f_{7/2}$. These results further confirm the valences of V and W atoms in compound **1** and **2**.

3.5. Thermal analysis

As shown in Fig. 5, the TG curve of compound **1** (S, Fig. 5) is divided into two stages. The first weight loss is 1.28% in the temperature range 66–176 °C, corresponding to the release of crystal water. The second weight loss of 26.40% from 176–630 °C is ascribed to the vanishing of the phenanthroline. The whole weight loss (27.68%) is in good agreement with the calculated value (27.85%). The compound **1** does not lose weight at temperatures higher than 630 °C.

As shown in Fig. 6, the TG curve of compound **2** (S, Fig. 6) is also divided into two stages. The first weight loss is 2.44% in the temperature range 76–200 °C, corresponding
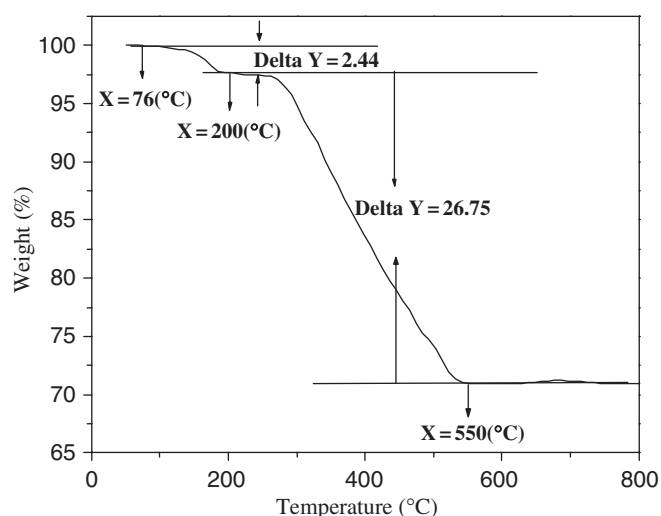
to the release of crystal water. The second weight loss of 26.75% from 240–550 °C is attributed to the disappearing of the phenanthroline. The total weight loss (29.19%) is in good agreement with the calculated value (29.52%). Compound **2** does not lose weight at temperatures higher than 550 °C.

4. Conclusion

Two new bicapping Keggin tungstovanadate, [Fe (phen)$_3$]$_2$[W$_{10.5}$V$_{4.5}$O$_{42}$]·3H$_2$O (**1**) and [Fe(phen)$_3$]$_2$[W$_{10}$V$_5$O$_{42}$]·6H$_2$O (**2**) (phen = 1,10′-phenanthroline), have been hydrothermal synthesized for the first time, and characterized by single-crystal X-ray analysis and many kinds of spectroscopies. Although anions of both the compounds possess discrete structures from the viewpoint of covalent bond, they are linked vis hydrogen bondings to form 2D supramolecular layers, respectively. It is found that existence of suitable reductant, such as oxalic acid, during preparation of these two compounds is necessary, and that pH value of reaction system is also an important factor effecting results of synthesis.

Supplementary data

Supplementary data have been deposited with the Cambridge crystallographic center, CCDC Nos. 278078 and 278079. Copy of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambrdge, CB2 IEZ, UK (fax: +44123336033; e-mail: deposit@ccdc.cam.ac.uk.

Acknowledgments

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2005.10.005.

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