

Hydrothermal synthesis and characterization of the tri-capped and mono-supported pseudo-Keggin-type tungstovanadophosphate: $\{\text{PW}_4^{\text{VI}}\text{W}_5^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_3[\text{Cu}(\text{en})_2]\}^{6-}$

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Abstract

A novel polyoxometalate $[\text{Cu}(\text{phen})_2]_3\{\text{PW}_4^{\text{VI}}\text{W}_5^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_3[\text{Cu}(\text{en})_2]\} \cdot 4\text{H}_2\text{O}$ **1** (en = ethylenediamine, phen = 1,10-phenanthroline) has been synthesized hydrothermally and characterized by elemental analysis, IR, XPS, TG, EPR and single-crystal X-ray diffraction analysis. The crystal structure analysis shows that compound **1** contains a novel highly reduced tri-capped and mono-supported pseudo-Keggin-type heteropolyanion, $\{\text{PW}_4^{\text{VI}}\text{W}_5^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_3[\text{Cu}(\text{en})_2]\}^{6-}$, three $[\text{Cu}(\text{phen})_2]^{2+}$ cations and four lattice water molecules. They are further linked to form three-dimensional supramolecular networks through extensive hydrogen bonding and π - π stacking interactions. Interestingly, the water dimer and terminal oxygen of the cluster polyanion constitute a beautiful supramolecular helix chain. The heteropolyanion is the first example of tri-capped and mono-supported pseudo-Keggin-type tungstovanadophosphate and the pH value is crucial for obtaining compound **1** in synthetic procedure.

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Keywords: POMs; Hydrothermal synthesis; Tri-capped Keggin structure; Tungstovanadophosphate; Crystal structure

1. Introduction

Polyoxometalates (POMs) have attracted extensive attention for many years owing to their interesting structural diversity and various potential applications in different areas such as catalysis, sorption, electrical conductivity, magnetism, photochemistry, medicine and material science [1–3]. In recent years, more and more researchers and groups focus their attentions on decorating and fine-tuning POMs at molecular level by capping and supporting them in order to explore their performances and various potential applications [4–11]. Up to now, some of bi- [5,12–15], tetra- [4,16] and hexa- [17] capped Keggin polyanions have been reported, but unsymmetrical odd-capped Keggin polyanion is rather rare. To date, tri- and penta-capped Keggin polyanion has not been observed

except mono-capped [18,19] ones. Among reported capped Keggin POMs, we found that many kinds of the elements can be cap atoms such as Mo [20], V [4,5,7–11], Sb [21], As [6,22], Ni [8,23,24], Cu [25], Zn [26], and La [27] etc., in which V was the common one. Meanwhile, many mono- [9,28], bi- [7,11], and tetra- [8,10,16] supporting Keggin polyanions have also been observed. In supporting Keggin and capping Keggin clusters, linking point of supported complex with cluster can be divided into three situations: (I) terminal-oxygen atom of cluster [7–9,11,14,29,30], (II) bridge-oxygen atom of cluster [25,28] and (III) both terminal- and bridge-oxygen atoms for multi-supporting cluster [10,16,31]. For the heteropolyanion class, the Mo/V/O system has been extensively studied [4–8,12,14,16,32–34], in contrast, the W/V/O system has remained relatively unexplored [13,15,35–37]. In this paper, we report a new POM $\{\text{PW}_4^{\text{VI}}\text{W}_5^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_3[\text{Cu}(\text{en})_2]\} [\text{Cu}(\text{phen})_2]_3 \cdot 4\text{H}_2\text{O}$ **1** being the first tri-capped and mono-supported highly reduced tungstovanadophosphate

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containing a novel tri-capped pseudo-Keggin polyanion, three $[\text{Cu}(\text{phen})_2]^{2+}$ cations and four lattice water molecules. The heteropolyanions are linked through the hydrogen bonds to form an extended three-dimensional (3D) supramolecular network.

2. Experimental

2.1. Materials and methods

All reagents used are of analytical grade and obtained from commercial sources without further purification. Elemental analysis (C, H, and N) was 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. Determination of electron paramagnetic resonance (EPR) was carried out on Bruker ER 200D-SRC spectrometer. XPS analysis was performed on Thermo ESCALAB 250 spectrometer with an Mg- $K\alpha$ (1253.6 eV) achromatic X-ray source. Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer TAG-7000 instrument from room temperature to 800 °C with a heating rate of 20 °C/min.

2.2. Synthesis of Compound 1

The starting materials Na_2WO_4 (0.50 g, 1.5 mmol), $\text{VOSO}_4 \cdot 2\text{H}_2\text{O}$ (0.30 g, 1.5 mmol), KH_2PO_4 (0.20 g, 1.5 mmol), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.30 g, 1.8 mmol), adipic acid (0.20 g, 1.4 mmol), 1,10-phen (0.20 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 6.0 using ethylenediamine. The mixture was sealed in a Teflon-lined reactor, and heated at 160 °C for 72 h. Then the autoclave was cooled to room temperature slowly. The dark blue hexagonal prisms were obtained in a 80.4% yield (based on W). Anal. Calc. for $\text{C}_{76}\text{H}_{72}\text{N}_{16}\text{Cu}_4\text{W}_9\text{O}_{47}$: C, 21.70; H, 1.73; N, 5.33. Found: C, 22.13; H, 1.90; N, 5.57. IR (cm^{-1}): 3434(s), 1623(m), 1583(w), 1423(m), 1048(m), 947(s), 874(m), 840(s), 801(s), 723(s).

2.3. X-ray crystallography

The data were collected on a Rigaku R-AXIS RAPID IP diffractometer with Mo- $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) at 293 K in the range $6.00 < 2\theta < 54.96^\circ$. Empirical absorption correction was applied. Crystal data: $\text{C}_{76}\text{H}_{72}\text{Cu}_4\text{W}_9\text{N}_{16}\text{O}_{47}\text{PV}_6$, orthorhombic, $Pna2_1$, $M_r = 4206.92 \text{ g mol}^{-1}$, $a = 33.039(7)$, $b = 22.611(5)$, $c = 13.955(3) \text{ \AA}$, $V = 10,425(4) \text{ \AA}^3$, $T = 293 \text{ K}$, $Z = 4$, $D_c = 2.680 \text{ g cm}^{-3}$, $F(000) = 7804$. A total of 92,440 (23,642 unique, $R_{\text{int}} = 0.0990$) reflections were measured ($-42 \leq h \leq 42$, $-25 \leq k \leq 29$, $-18 \leq l \leq 18$). Structure solution and refinement based on 1402 parameters gave R_1 (wR_2) = 0.0691 (0.1696). The structure for compound 1 was solved by the direct methods and refined by the full-matrix least squares on F^2 SHELXL-97 software. The metal

Table 1
Crystal data and structure refinement information for 1

Empirical formula	$\text{C}_{76}\text{H}_{72}\text{Cu}_4\text{N}_{16}\text{O}_{47}\text{PV}_6\text{W}_9$
Formula weight	4206.92
Temperature	293(2) K
Wavelength	0.71073 \AA
Crystal system	Orthorhombic
Space group	$Pna2_1$
Unit cell dimensions	$a = 33.039(7) \text{ \AA}$ $b = 22.611(5) \text{ \AA}$ $c = 13.955(3) \text{ \AA}$
Volume (\AA^3)	10,425(4)
Z	4
Calculated density (g/cm^3)	2.680
Absorption coefficient	11.299 mm^{-1}
Reflections collected /unique	92,440/23642
Data/ restraints/parameters	23,642/3/1402
Goodness-of-fit on F^2	0.988
Final R indices [$I > 2\theta$ (I)]	$R1 = 0.0691$, $wR2 = 0.1696$
R indices (all data)	$R1 = 0.1261$, $wR2 = 0.1963$
Largest diff. peak and hole	1.600 and $-1.726 \text{ e \AA}^{-3}$

positions for M(1), M(3), M(4), M(5), M(6), M(7), M(8), M(11) and M(12) of the Keggin unit are crystallographically disordered with occupancy factors of 0.67 for W and 0.33 for V. All the other non-hydrogen atoms were refined anisotropically except for C5, C12, C17, C36, C53, O3, O9 and four lattice water molecules. A summary of crystal data and structure refinement for compounds 1 is provided in Table 1. Selected bond lengths of 1 are listed in Table 2. Bond lengths and angles for 1 are listed in Table S1.

3. Results and discussion

3.1. Synthesis

Compound 1 was synthesized under hydrothermal condition at 160 °C and pH = 6, no title compound was obtained when $\text{pH} < 5.0$ or $\text{pH} > 7.0$. This shows that preparation of 1 needs strictly control pH value of the reaction system. The original aim of adding adipic acid to the reaction mixture was synthesizing metal-oxo cluster polymer with adipic acid as linkage, but compound 1 without adipic acid ligand was obtained. Despite all this, adipic acid still plays an important role in preparing compound 1, when it was removed from the reaction mixture or substituted by oxalic acid, only dark blue slurry was obtained. Ethylenediamine plays ligand and reductant double roles in preparation of compound 1.

3.2. Crystal structure of compound 1

Single-crystal X-ray diffraction study reveals that compound 1 consists of a highly reduced tri-capped and mono-supported $\{\text{PW}_4^{\text{VI}}\text{W}_5^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_3\}[\text{Cu}(\text{en})_2]^{6-}$ heteropolyoxoanion (Fig. 1), three $[\text{Cu}(\text{phen})_2]^{2+}$ cations and four lattice water molecules. The $[\text{PW}_4^{\text{VI}}\text{W}_5^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_3]^{8-}$

Table 2
Selected bondlengths (Å) of 1

V(1)–O(12)	1.627(17)	M(5)–O(21)	2.09(2)
V(1)–O(35)	1.918(15)	M(6)–O(46)	1.618(13)
V(1)–O(23)	1.922(16)	M(6)–O(30)	1.913(15)
V(1)–O(45)	1.932(18)	M(6)–O(20)	1.923(17)
V(1)–O(38)	1.967(15)	M(6)–O(27)	1.925(16)
V(2)–O(9)	1.64(2)	M(6)–O(39)	1.927(13)
V(2)–O(40)	1.984(14)	M(6)–O(8)	2.48(2)
V(2)–O(14)	1.990(18)	M(7)–O(36)	1.677(15)
V(2)–O(42)	2.01(2)	M(7)–O(24)	1.865(15)
V(2)–O(11)	2.06(2)	M(7)–O(31)	1.88(2)
V(3)–O(47)	1.69(3)	M(7)–O(18)	1.897(16)
V(3)–O(10)	1.94(2)	M(7)–O(17)	1.906(14)
V(3)–O(17)	1.955(19)	M(7)–O(4)	2.48(3)
V(3)–O(41)	1.98(2)	M(8)–O(32)	1.695(14)
V(3)–O(31)	2.06(2)	M(8)–O(13)	1.849(17)
M(1)–O(44)	1.681(13)	M(8)–O(28)	1.876(16)
M(1)–O(27)	1.75(2)	M(8)–O(10)	1.898(17)
M(1)–O(37)	1.815(15)	M(8)–O(41)	1.974(16)
M(1)–O(38)	1.967(17)	M(8)–O(1)	2.51(2)
M(1)–O(45)	2.058(15)	W(9)–O(16)	1.666(16)
M(1)–O(8)	2.46(2)	W(9)–O(39)	1.874(12)
W(2)–O(15)	1.645(16)	W(9)–O(22)	1.889(17)
W(2)–O(21)	1.737(15)	W(9)–O(14)	1.925(16)
W(2)–O(24)	1.783(14)	W(9)–O(40)	1.935(13)
W(2)–O(35)	2.000(12)	W(9)–O(6)	2.44(2)
W(2)–O(38)	2.057(16)	W(10)–O(25)	1.687(11)
W(2)–O(5)	2.39(2)	W(10)–O(19)	1.819(16)
M(3)–O(43)	1.663(12)	W(10)–O(18)	1.833(18)
M(3)–O(13)	1.835(16)	W(10)–O(42)	1.958(15)
M(3)–O(20)	1.898(19)	W(10)–O(14)	1.996(18)
M(3)–O(45)	1.949(15)	W(10)–O(4)	2.48(2)
M(3)–O(23)	2.025(16)	M(11)–O(26)	1.641(15)
M(3)–O(8)	2.51(2)	M(11)–O(30)	1.806(17)
M(4)–O(34)	1.639(16)	M(11)–O(28)	1.836(17)
M(4)–O(10)	1.862(19)	M(11)–O(11)	1.954(17)
M(4)–O(17)	1.900(16)	M(11)–O(40)	1.969(14)
M(4)–O(23)	1.963(15)	M(11)–O(2)	2.43(2)
M(4)–O(35)	1.974(15)	M(12)–O(29)	1.641(16)
M(4)–O(1)	2.39(2)	M(12)–O(41)	1.864(17)
M(5)–O(33)	1.656(12)	M(12)–O(11)	1.946(16)
M(5)–O(22)	1.85(2)	M(12)–O(31)	1.95(2)
M(5)–O(37)	1.871(15)	M(12)–O(42)	2.000(16)
M(5)–O(19)	1.923(16)	M(12)–O(4)	2.45(2)

*The M positions are crystallographically disordered with occupancy factors of 0.67 for W and 0.33 for V.

cluster anion is essentially built on the well-known α -Keggin structure with three additional five coordinating terminal $\{\text{VO}\}^{2+}$ units as caps. This novel unsymmetrical tri-capped structure containing 12 coordination octahedra including three $\{\text{WO}_6\}$ and nine $\{\text{MO}_6\}$ octahedra can be described as the common tetra-capped Keggin POMs missing one cap, and this kind of structural type of POMs has not been observed before. V(1), V(2) and V(3) at the cap positions shows a distorted $\{\text{VO}_5\}$ square pyramidal environment with V–O distances in the range of 1.64(2)–2.06(2) Å and O–V–O angles varying from 77.5(9)–131.4(9)° (Table S1). The disordered $\{\text{PO}_4\}$ tetrahedron possessing eight central O atoms with occupancy factor being 0.5 is located in the centre of the host cage. The four central oxygen atoms are shared by four $\{\text{W}_3\text{O}_{13}\}$

trials, respectively, each of which is made up of three edge-sharing $\{\text{WO}_6\}$ octahedra. The P–O distances are between 1.49(3) and 1.58(2) Å. All tungsten atoms exhibit a $\{\text{WO}_6\}$ octahedral environment with the terminal W–O distances which range from 1.645(16) to 1.687(11) Å, and other W–O distances which range from 1.737(15) to 2.50(3) Å. In the $\{\text{MO}_6\}$ octahedra, M site is crystallographically disorderly occupied with occupancy factor of 2/3 for W and 1/3 for V, respectively. The M–O distances can be divided into three groups: M–O_t 1.618(13)–1.695(14) Å, M–O_b 1.75(2)–2.09(2) Å and M–O_c 2.39(2)–2.520(19) Å. To the best of our knowledge, such a heteropolytungstovanadophosphate possessing unsymmetrical tri-capped Keggin structure is reported for the first time. In fact, compound **1** is also an unprecedented structure type in all reported and decorated Keggin clusters. The $[\text{PW}_4^{\text{VI}}\text{W}_5^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_3]^{8-}$ unit acting as a ligand is bonded to $[\text{Cu}(\text{en})_2]^{2+}$ via the terminal oxygen atom of M(1) being not at cap site with Cu(1)–O(44) distances of 2.455 Å to form a new mono-supporting Keggin cluster. In known capped Keggin clusters, complex fragment is generally supported at coordination polyhedron of skeleton metal atom being at cap site [7,8,14,30], while it is rare that complex fragment is supported at coordination polyhedron of framework metal atom not being at cap position. Besides O(44), Cu(1) is coordinated by four nitrogen atoms from two en ligands with Cu–N distances of 1.93(4)–2.19(4) Å and N–Cu–N angles of 71.3(17)–172.7(12)°. In three compensating cations, $[\text{Cu}(\text{phen})_2]^{2+}$, every Cu atom is coordinated by four N atoms from two 1,10-phen ligands with the Cu–N distances of 1.972(17)–2.123(16) Å, and N–Cu–N angles of 80.3(6)–149.7(7)°.

There exist many kinds of hydrogen bonds and π – π stacking interactions in compound **1** (Fig. 2). Firstly, the tri-capped and mono-supported POMs cluster joins neighboring ones through hydrogen bonding interactions between terminal O(46) of the cluster and N(3) from en coordinating to Cu(1) with the O(46)···N(3) distance of 2.943 Å, resulting in an interesting zigzag supramolecular chain along *c*-axis. Secondly, the supramolecular chains are connected by water dimer via hydrogen bonding to form a 2D supramolecular layer. It is interesting that the water dimer and terminal oxygen O (29) of the polyanion cluster constitute a beautiful supramolecular helix chain with helical pitch of 13.96 Å along the *c*-axis through hydrogen bonding interactions (O29···OW2 = 2.935 Å, O29···OW3 = 3.26 Å, OW2···OW3' = 3.012 Å) as shown in Fig. 3 (Fig S1). The $\{\text{PW}_4^{\text{VI}}\text{W}_5^{\text{V}}\text{V}_3^{\text{IV}}\text{O}_{40}(\text{V}^{\text{IV}}\text{O})_3[\text{Cu}(\text{en})_2]\}^{6-}$ cluster units are linked with the supramolecular chains and regularly arranged on both its sides, just like watermelons link the vine (Fig. 2). It can be also said that the zigzag supramolecular chains of the polyanion clusters are connected by the supramolecular helix chains into a 2D layer structure along the *bc* plane. Thirdly, the hydrogen-bonding contacts are also observed between the polyanions

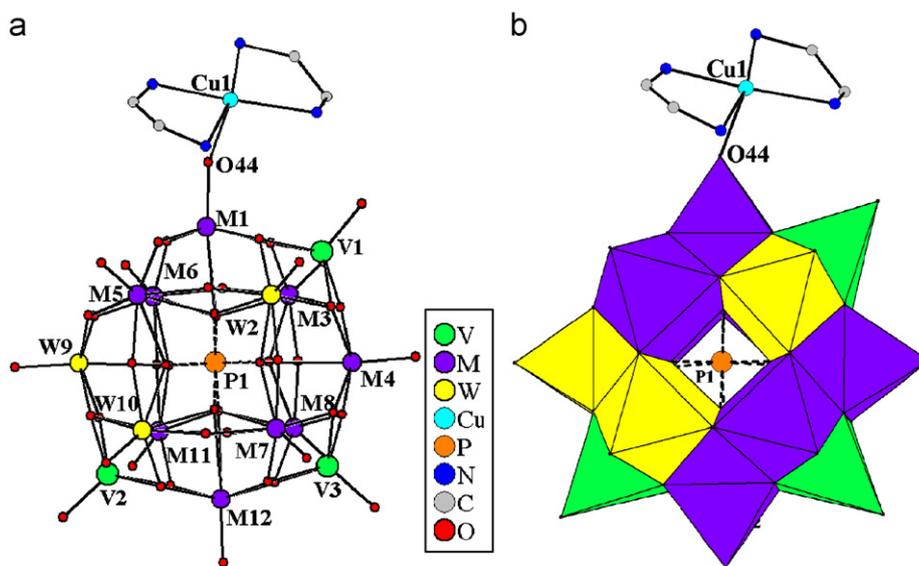


Fig. 1. (a) View of crystal structure of $\{[PW_4^Y W_5^Y V_3^{IV} O_{40}(V^{IV}O)_3] \cdot [Cu(en)_2]\}^{6-}$ and (b) polyhedral representation of the polyanion.

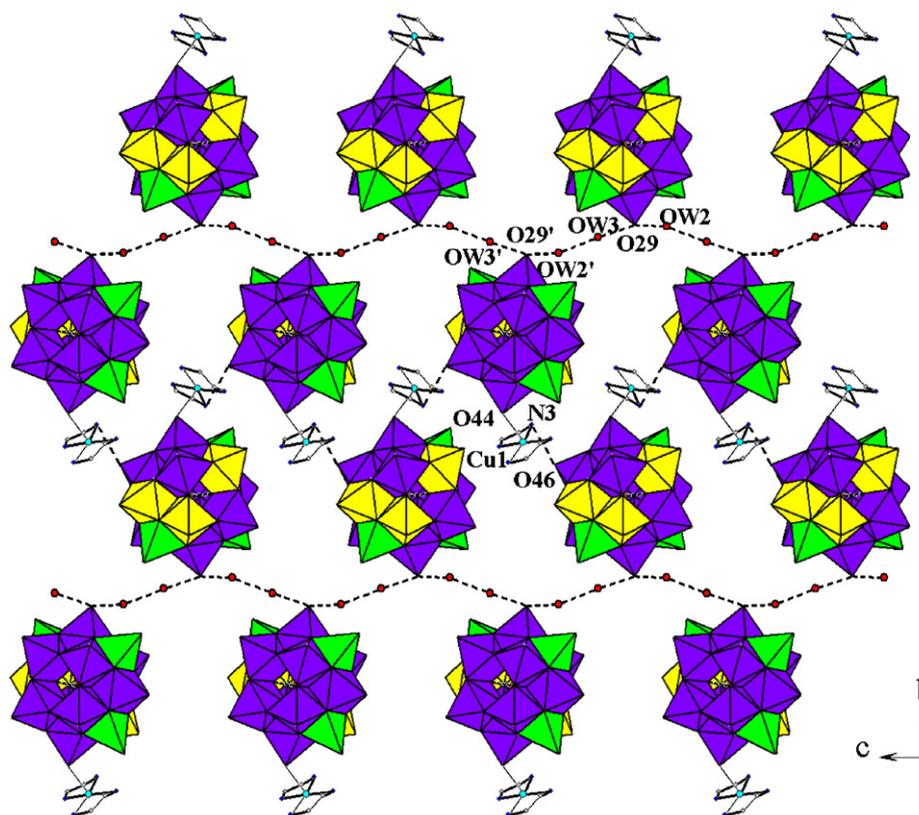


Fig. 2. A supramolecular layer consisting of $\{[PW_4^Y W_5^Y V_3^{IV} O_{40}(V^{IV}O)_3][Cu(en)_2]\}^{6-}$ through the hydrogen bonding, phen molecules were omitted for clarity.

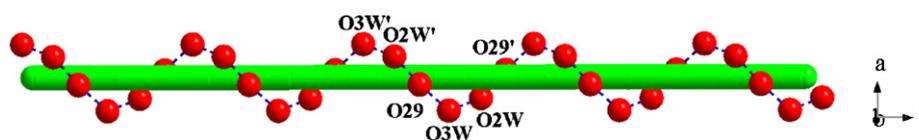


Fig. 3. A helix chain consisting of the water dimer and terminal O (29) of Keggin cluster.

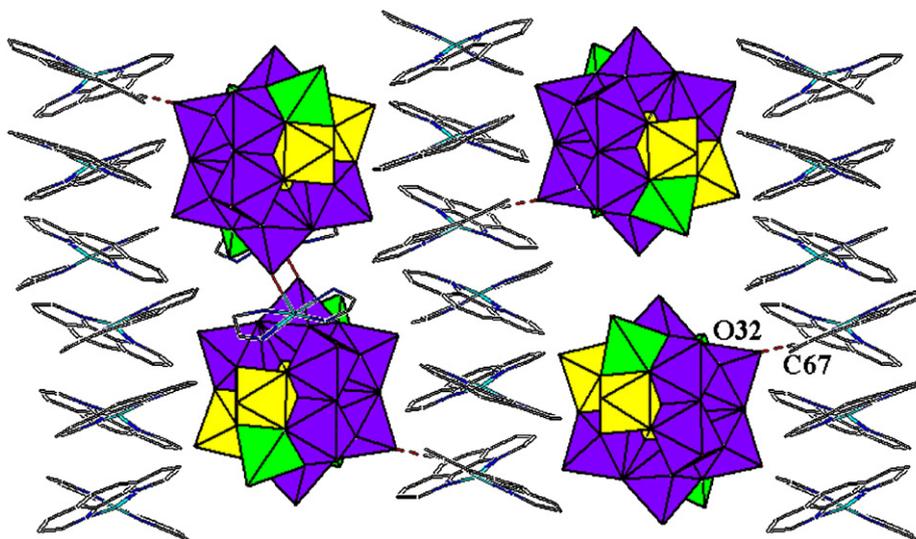


Fig. 4. A supramolecular structure of compound **1** along *ab* plane; the lattice water molecules were omitted for clarity.

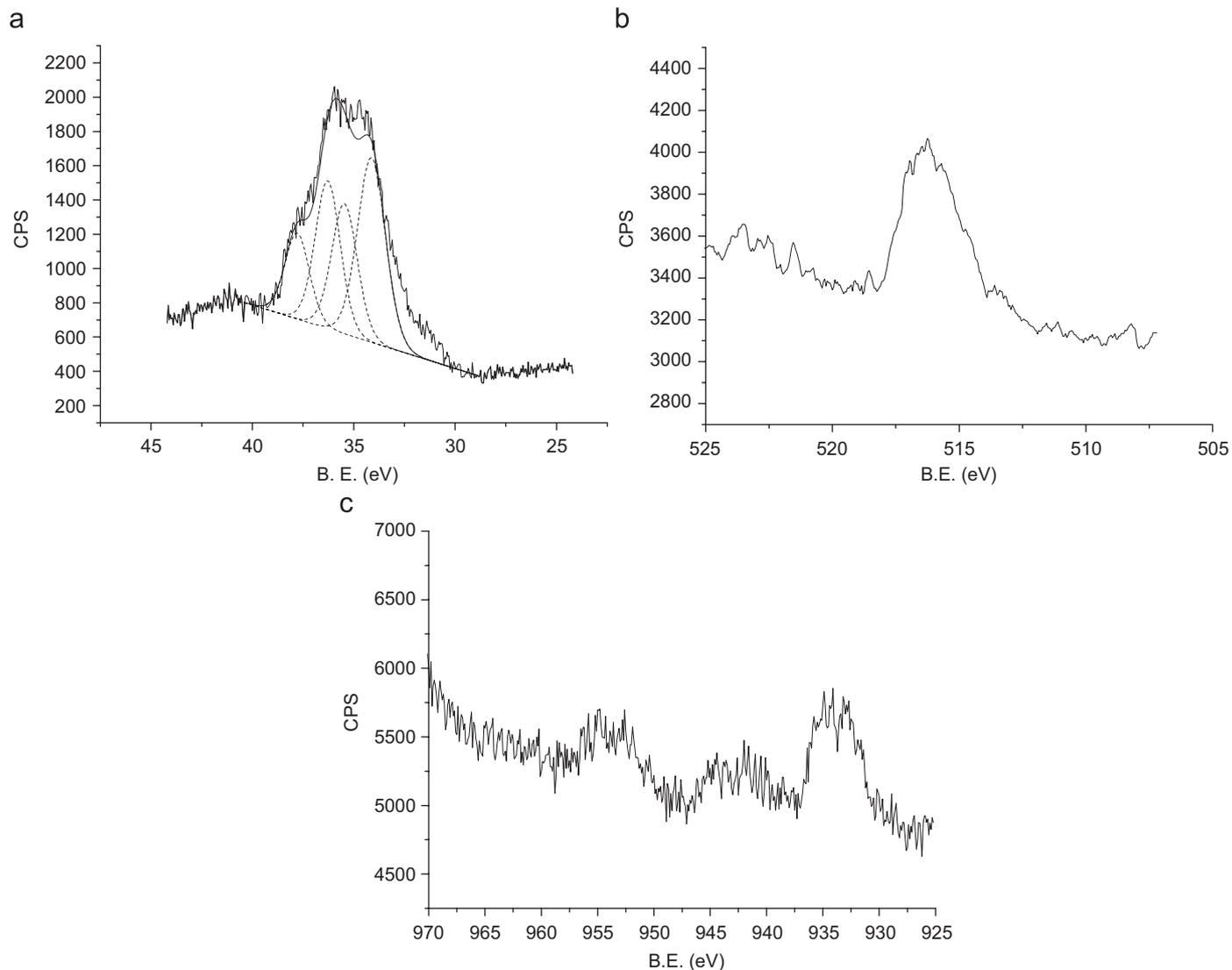


Fig. 5. (a) The XPS spectrum with peaks at 34.1, 35.4, 36.3 and 37.8 eV, which are attributed to $W_{4f7/2}^V$, $W_{4f7/2}^{VI}$, $W_{4f7/2}^V$ and $W_{4f7/2}^{VI}$ in compound **1**. (b) The XPS spectrum with peak at 516.2 eV, which is attributed to $V^{IV}2p_{3/2}$ in compound **1**. (c) The XPS spectrum with peak at 933.7 eV, which is attributed to $Cu^{II}2p_{3/2}$ in compound **1**.

and coordinated 1,10-phen with the shortest distance of $O(32)\cdots C(67)$ being 3.095 Å (Fig. 4), this kind of hydrogen bonding adding π - π stacking interaction between phen rings make the 2D supramolecular layers form a 3D supramolecular network.

3.3. Bond valence sum (BVS) and spectroscopic characterizations

According to elements analyses, BVS calculation, coordination geometry and charge balance, compound **1** is formulated as $\{PW_4^{VI}W_5^V V_3^{IV}O_{40}(V^{IV}O)_3[Cu(en)_2]\}[Cu(phen)_2]_3 \cdot 4H_2O$. Using the empirical formula of bond valence $S = \exp[-(R-R_0)/B]$ (S = bond valence, R = bond length, R_0 and B are fitted constants) [38]. We can obtain the valence states of V(1), V(2) and V(3) being 4.29, 3.94 and 3.93, respectively, with an average value of 4.05. This shows that oxidation state of all V atoms in compound **1** is +4. It has been proved by XPS measurements of compound **1**. The XPS spectra of **1** (Fig. 5) give two overlapped peaks at 34.1 and 35.4 eV attributed to $W_{4f_{7/2}}^V$ and $W_{4f_{7/2}}^{VI}$, respectively, and one peak at 516.2 eV attributed to $V^{IV} 2p_{3/2}$ [13]. These results further confirm the valences of V and W atoms. The XPS of **1** gives a peak at 933.7 eV attributed to $Cu_{2p_{3/2}}^{II}$ [25], and the EPR spectrum (Fig. 6) for **1** also exhibits the Cu^{II} signal at 293 K with $g = 2.028$ [28,29].

In the IR spectrum of compound **1** (Fig S2), absorption peaks at 1048, 947, 874, 840, 801 and 723 cm^{-1} can be attributed to $\nu(P-O_a)$, $\nu(M-O_t)$, $\nu(M-O_b-M)$, and $\nu(M-O_c-M)$ ($M = W$ or V) [8,10,39], respectively, while the bands at 1623, 1583, 1423 cm^{-1} are characteristic absorption of 1,10-phen ligand [8,13]. The strong broad band around 3434 cm^{-1} could be due to absorption of coordinated water molecules.

Thermogravimetric analysis indicates two steps of weight loss (Fig. 7). The first stage of weight loss of 1.75% (calculated, 1.81%) occur in the temperature range 75–275 °C, corresponding to the release of the lattice water

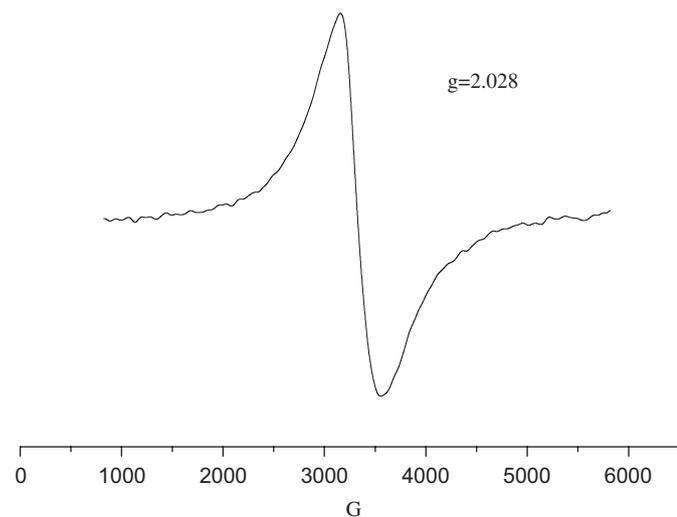


Fig. 6. EPR spectrum of **1**.

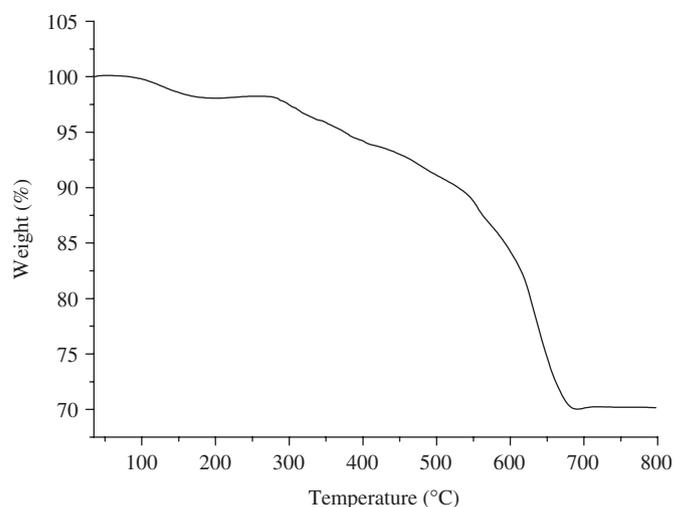


Fig. 7. Thermogravimetric analysis of **1**.

molecules. The second weight loss of 28.1% (calculated, 28.4%) from 275 to 690 °C is ascribed to the vanishing of the ethylenediamine and phenanthroline.

4. Conclusion

In this paper, we report synthesis and characterizations of a novel polyoxometalate, $\{PW_4^{VI}W_5^V V_3^{IV}O_{40}(V^{IV}O)_3[Cu(en)_2]\}[Cu(phen)_2]_3 \cdot 4H_2O$ **1**, which has three unusual interesting structural features: (1) a tri-capped pseudo-Keggin structure cluster which has not been reported before; (2) the first example of mono-supported Keggin type tungstovanadate in the rare tungstovanadate derivatives; (3) the existence of interesting supramolecular helical chains consisting of water dimers and terminal oxygen atoms of polyanions, which link the supramolecular chains composed of cluster anions into 2D supramolecular layers.

The successful synthesis of compound **1** provides an example of new structure type for decorated Keggin clusters. Strictly controlling pH value of reaction system being about 6 is one of the essential conditions for successful preparation of compound **1**.

Acknowledgments

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Appendix A. Supplementary materials

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC_634041. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2007.09.018](https://doi.org/10.1016/j.jssc.2007.09.018).

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