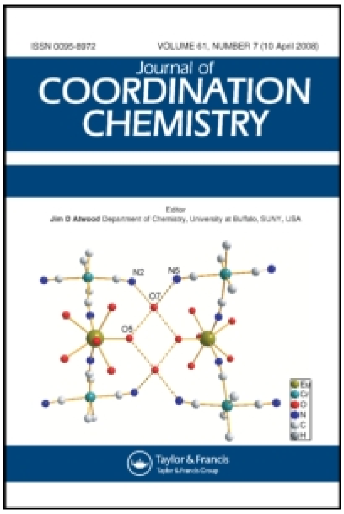

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A new inorganic-organic hybrid polyoxometalate constructed by $[PMo_8V_6O_{42}]$ clusters and transition metal complexes

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A new inorganic–organic hybrid polyoxometalate constructed by [$PMo_8V_6O_{42}$] clusters and transition metal complexes

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A new compound $[Zn(phen)_2]_2[PMo_8^{VI}V_4^{V}V_2^{IV}O_{42}][Zn(phen)_2(H_2O)]_2[PMo_8^{VI}V_2^{V}V_4^{IV}O_{42}]\cdot 7H_2O$ (phen = phenanthroline) has been synthesized under hydrothermal conditions and characterized by IR, TG analysis and single-crystal X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group $P2_1/C$, $a = 21.609(4)$ Å, $b = 16.537(3)$ Å, $c = 21.279(4)$ Å, $\alpha = 90^\circ$, $\beta = 100.25(3)^\circ$, $\gamma = 90^\circ$, $V = 7483(3)$ Å^3, $Z = 2$. The basic building unit in **1** is the [$PMo_8V_6O_{42}$] cluster. The most remarkable structural feature of **1** is that there exist two distinct [$PMo_8V_6O_{42}$] clusters. One is covalently linked by [$Zn(phen)_2$] complexes to form a 2D covalent layer, the other supports two [$Zn(phen)_2(H_2O)$] complexes forming a discrete bisupporting structure. It is interesting that discrete bisupporting clusters locate in the space of two adjacent covalently layers to form a 3D supramolecular framework.

Keywords: Inorganic–organic hybrid; Polyoxometalates; Hydrothermal synthesis; Transition metal complexes; Vanadium-containing molybdophosphate

1. Introduction

Polyoxometalates (POMs) attract interest in materials chemistry owing to their interesting structural features and various potential applications in catalysis, sorption, electrical conductivity, magnetism and photochemistry [1, 2]. Modification of metal-oxo clusters with various organic and/or transition metal complexes *via* self-assembly proved a reasonable strategy to construct hybrid materials based on POMs [3, 4]. Such modified polyoxometalate derivatives possess combined or enhanced functionalities of both organic and inorganic subunits and, therefore, can be designed to have special optical, electronic or magnetic properties by exploiting appropriate transition metal fragments [5, 6]. To date, many modified polyoxometalate derivatives based

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on vanadium-containing molybdophosphate anions have been reported. One kind are capped/supporting structures such as $[PMo_8V_6O_{42}Cu(en)(1,10\text{-}phen)]^{5-}$ [7], $[PMo_8V_6O_{42}]$ [8] and $[PMo_8V_8O_{44}\{Co(2,2'\text{-}bipy)_2(H_2O)\}_4]$ $[PMo_8V_8O_{44}\{Co(2,2'\text{-}bipy)_2(H_2O)\}_2]\cdot 4H_2O$ [9]. Besides discrete capped/supporting structures, Liu's group synthesized extended frameworks such as $[Co(en)_2][Co(bpy)_2]_2[PMo_8V_8O_{44}]\cdot 4.5H_2O$ (en = ethylenediamine, bipy = 2,2-bipyridine) [10], $\{Mo_6^{VI}Mo_2^{V}V_8^{IV}O_{40}\ (PO_4)[Co(phen)_2\ (H_2O)]_2\}[Co_2(phen)_2\ (OH)_2(H_2O)_4]_{1/2}$ [11] and $\{Ni(phen)_2(H_2O)[Ni(phen)_2][V_8Mo_8O_{40}(PO_4)]\}\{[Ni\ (phen)_2(H_2O)]_2[V_8Mo_8O_{40}(PO_4)_2]\}\cdot 5H_2O\cdot 2EtOH$ [12]. In addition, Hill *et al.*, reported $Ag_5PV_2Mo_{12}O_{40}$, which involves two $[PV_2Mo_{12}O_{40}]^{5-}$ units bridged by two Ag(I) ions bonded to both bridging and terminal oxygen atoms of the POM units [13]. However, compounds which contain both capped/supporting structures and extended structures based on mixed molybdenum-vanadium polyoxometalates, have rarely been reported. Our group synthesized one such compound $[PMo_8^{VI}Mo_4^{V}O_{40}(V^{IV}O)_2\{Co(Phen)_2\}_2](H_3O)_2[PMo_4^{VI}Mo_8^{V}O_{40}(V^{IV}O)_2\{Co(Phen)_2(H_2O)\}_2]$ [14].

The aim of our work is to synthesize compounds based on mixed molybdenum-vanadium polyoxometalates. In this article, we report the hydrothermal synthesis and crystal structure of a new compound $[Zn(phen)_2]_2[PMo_8^{VI}V_4^{V}V_2^{IV}O_{42}][Zn(phen)_2(H_2O)]_2[PMo_8^{VI}V_2^{V}V_4^{IV}O_{42}]\cdot 7H_2O$ **1**. In **1**, there exist two distinct $[PMo_8V_6O_{42}]$ clusters. One is covalently linked by $[Zn(phen)_2]$ complexes to form a 2D covalent layer, the other supports two $[Zn(phen)_2(H_2O)]$ complexes forming a 2D discrete bicapped bisupporting structure. Discrete bicapped bisupporting clusters locate in the space of two adjacent covalently layers to form a 3D supramolecular framework.

2. Experimental

2.1. *Materials and methods*

All reagents were purchased commercially and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. IR spectrum was recorded in the range $4000–400\,cm^{-1}$ on an Alpha Centaurt FT/IR spectrometer with a pressed KBr pellet. TG analysis was carried out on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$.

2.2. *Hydrothermal synthesis*

A mixture of $NH_4VO_3\cdot 2H_2O$ (0.225g), $Na_2MoO_4\cdot 2H_2O$ (0.565 g), $Zn(OAc)_2\cdot 2H_2O$ (0.200 g), phen (0.051 g) and distilled water (10 mL) neutralized to pH = 5.5 with H_3PO_4 was stirred for 20 min. The mixture was then added to a 23 mL Teflon-lined reactor and heated at 150°C for 6 days. After slowly cooling to room temperature, the black, block crystals of **1** were isolated, washed with deionized water, filtered off and dried in air (60% yield based on Mo). The crystals were manually selected for structural determination and further characterization. The ICP analysis showed that **1** contains Mo, 30.30%; Zn, 4.81%; P, 1.24% V, 11.39% (Calcd: Mo, 28.38%; Zn, 4.84%; P, 1.15% V, 11.30%). The elemental analysis found: C, 21.79%; H, 1.43%; N, 3.98% (Calcd: C, 21.32%; H, 1.36%; N, 4.14%).

2.3. *X-ray crystallography*

Crystal data for **1** was collected on a Rigaku R-AXIS RAPID IP diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293K. The structure for **1** was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 program package [15, 16]. All of the non-hydrogen atoms were refined anisotropically. Positions of the hydrogen atoms attached to carbon atoms were fixed at their ideal positions, and those attached to oxygen atoms were not located. A summary of the crystallographic data and structural determination for **1** is provided in table 1. Selected bond lengths and bond angles for **1** are listed in tables 2 and 3, respectively.

CCDC reference number is 649281 for compound **1**.

3. Results and discussion

3.1. *Structure description*

The X-ray diffraction analysis reveals that the structure of **1** consists of $[PMo_8V_6O_{42}]$ clusters, $[\{Zn(phen)_2(H_2O)]$ and $[Zn(phen)_2]_2]$ complex fragments, as well as lattice water molecules. The basic building unit $[PMo_8V_6O_{42}]$ is essentially the well-known α-Keggin structure with two additional five-coordinating terminal {VO} units. Six vanadium atoms show a distorted $\{VO_5\}$ square pyramidal environment with

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	$C_{96}H_{73}\,Mo_{16}\,N_{16}\,O_{93}\,P_2\,V_{12}\,Zn_4$
Formula weight	5408.44
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions (Å, °)	
a	21.609(4)
b	16.537 (3)
c	21.279(4)
α	90
β	100.25(3)
γ	90
Volume (Å^3)	7483(3)
Z	2
Calculated density (mg m^{-3})	2.400
Absorption coefficient (mm^{-1})	2.757
F (000)	5206
Crystal size (mm^3)	0.341 × 0.286 × 0.275
Theta range for data collection (°)	3.12–25.00
Limiting indices	$-25 \le h \le 25$, $-19 \le k \le 17$, $-24 \le l \le 25$
Reflections collected/unique	53368/12703 [R(int) = 0.1226]
Completeness to $\theta = 25.00$	96.3%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	12703/92/957
Goodness-of-fit on F^2	1.046
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0778$, $wR_2 = 0.1823$
R indices (all data)	$R_1 = 0.1389$, $wR_2 = 0.2178$
Largest diff. peak and hole (e Å^{-3})	1.671 and −0.919

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

N(1)–Zn(1)	2.099(8)	Mo(1)–O(39)	1.788(12)
N(2)–Zn(1)	2.119(7)	Mo(1)–O(24)	1.810(10)
N(3)–Zn(1)	2.137(8)	Mo(1)–O(2)	2.009(10)
N(4)–Zn(1)	2.121(8)	Mo(1)–O(5)	2.055(11)
N(6)–Zn(2)	2.086(8)	Mo(1)–O(43)#1	2.452(16)
N(5)–Zn(2)	2.085(7)	Mo(1)–O(46)	2.474(16)
N(8)–Zn(2)	2.068(10)	Mo(1)–V(1)	3.081(3)
N(7)–Zn(2)	2.080(9)	Mo(2)–O(12)	1.663(10)
Mo(1)–O(4)	1.640(11)	Mo(2)–O(11)	1.779(11)
Mo(2)–O(43)#1	2.479(16)	Mo(2)–O(20)	1.798(13)
Mo(2)–O(42)#1	2.483(16)	Mo(2)–O(5)	2.040(11)
Mo(2)–V(1)	3.062(3)	Mo(2)–O(1)	2.054(10)
Mo(3)–O(25)	1.639(10)	Mo(3)–O(30)	1.793(11)
Mo(3)–O(23)	1.781(10)	Mo(3)–O(17)	2.020(10)
Mo(4)–O(7)	2.048(9)	Mo(3)–O(6)	2.061(9)
Mo(4)–O(45)	2.408(19)	Mo(3)–O(44)	2.436(19)
Mo(4)–O(28)	2.453(15)	Mo(3)–V(2)	3.083(3)
Mo(4)–V(2)	3.088(3)	Mo(4)–O(13)	1.619(10)
Mo(5)–O(16)	1.647(9)	Mo(4)–O(10)	1.798(11)
Mo(5)–O(36)	1.765(12)	Mo(4)–O(29)	1.800(13)
Mo(5)–O(27)	1.774(12)	Mo(4)–O(17)	2.046(11)
Mo(5)–O(18)	2.027(12)	Mo(5)–O(46)	2.501(15)
Mo(5)–O(2)	2.048(11)	Mo(5)–V(1)	3.093(3)
Mo(5)–O(41)	2.382(16)	Mo(6)–O(8)	1.653(10)
Mo(7)–O(26)	1.668(10)	Mo(6)–O(32)	1.792(13)
Mo(7)–O(40)	1.795(11)	Mo(6)–O(9)	1.810(11)
Mo(7)–O(37)	1.798(14)	Mo(6)–O(6)	2.028(10)
Mo(7)–O(1)	2.028(10)	Mo(6)–O(21)	2.028(11)
Mo(7)–O(18)	2.039(12)	Mo(6)–O(33)#2	2.467(18)
Mo(7)–O(41)	2.459(18)	Mo(6)–V(2)	3.115(3)
Mo(7)–V(1)	3.077(3)	Mo(8)–O(31)	1.790(12)
Mo(8)–O(34)	1.675(10)	Mo(8)–O(19)	1.795(13)
Mo(8)–V(2)	3.070(3)	Mo(8)–O(21)	2.027(12)
V(4)–O(22)	1.602(11)	Mo(8)–O(7)	2.031(10)
V(4)–O(29)#2	1.878(12)	Mo(8)–O(33)#2	2.431(16)
V(4)–O(19)#2	1.901(12)	V(5)–O(31)#2	1.892(11)
V(4)–O(9)	1.902(11)	V(5)–O(10)	1.896(11)
V(4)–O(30)	1.908(12)	V(5)–O(32)#2	1.897(14)
V(5)–O(3)	1.610(9)	V(5)–O(23)	1.939(12)
V(5)–O(33)	2.398(15)	V(3)–O(24)	1.912(12)
V(3)–O(38)	1.603(9)	V(3)–O(36)#1	1.923(12)
V(3)–O(20)	1.895(13)	V(6)–O(47)	1.613(11)
V(3)–O(37)#1	1.902(14)	V(6)–O(40)	1.908(10)
V(6)–O(27)#1	1.911(10)	O(14)–Zn(2)	2.128(10)
V(6)–O(11)	1.925(11)	O(15)–Zn(1)	2.121(10)
V(6)–O(39)#1	1.924(11)	O(35)–Zn(1)	2.172(12)
O(1)–V(1)	1.920(10)	Zn(2)–O(3)#4	2.489(10)
O(2)–V(1)	1.939(11)	O(3)–Zn(2)#3	2.489(10)
O(14)–Zn(2)	2.128(10)	O(5)–V(1)	1.904(10)
O(15)–Zn(1)	2.121(10)	O(6)–V(2)	1.918(11)
O(3)–Zn(2)#3	2.489(10)	O(7)–V(2)	1.932(12)
O(15)–V(1)	1.624(10)	O(14)–V(2)	1.612(10)
O(17)–V(2)	1.935(10)	O(31)–V(5)#2	1.892(11)
O(18)–V(1)	1.956(11)	O(32)–V(5)#2	1.897(14)
O(19)–V(4)#2	1.901(12)	O(5)–V(1)	1.904(10)
O(21)–V(2)	1.946(11)	O(6)–V(2)	1.918(11)
O(27)–V(6)#1	1.911(10)	O(7)–V(2)	1.932(12)
O(29)–V(4)#2	1.878(12)	O(14)–V(2)	1.612(10)
O(18)–V(1)	1.956(11)	O(15)–V(1)	1.624(10)
O(19)–V(4)#2	1.901(12)	O(17)–V(2)	1.935(10)

(*Continued*)

Table 2. Continued.

O(21)–V(2)	1.946(11)	O(32)–V(5)#2	1.897(14)
O(27)–V(6)#1	1.911(10)	O(33)–Mo(8)#2	2.431(16)
O(29)–V(4)#2	1.878(12)	O(33)–Mo(6)#2	2.467(18)
O(31)–V(5)#2	1.892(11)	O(36)–V(3)#1	1.923(12)
O(39)–V(6)#1	1.924(11)	O(37)–V(3)#1	1.902(14)
O(42)–Mo(2)#1	2.483(16)	O(43)–Mo(2)#1	2.479(16)
O(43)–Mo(1)#1	2.452(16)	P(1)–O(42)#1	1.498(16)
P(1)–O(46)	1.507(15)	P(1)–O(46)#1	1.507(15)
P(1)–O(43)#1	1.523(15)	P(1)–O(41)#1	1.594(16)
P(2)–O(28)#2	1.458(16)	P(2)–O(44)#2	1.50(2)
P(2)–O(45)#2	1.532(19)	P(2)–O(33)#2	1.620(14)
O(41)–P(1)	1.594(16)	O(44)–P(2)	1.50(2)
O(42)–P(1)	1.498(16)	O(45)–P(2)	1.532(19)
O(43)–P(1)	1.523(15)	O(33)–P(2)	1.620(14)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y, -z+1$; #2 $-x+1, -y, -z$; #3 $-x+1, y-1/2, -z+1/2$; #4 $-x+1, y+1/2, -z+1/2$.

Table 3. Selected bond angles (°) for **1**.

N(1)–Zn(1)–N(2)	78.7(4)	N(1)–Zn(1)–O(15)	91.3(4)
N(2)–Zn(1)–O(15)	165.3(4)	N(1)–Zn(1)–N(4)	177.5(4)
N(2)–Zn(1)–N(4)	103.6(4)	O(15)–Zn(1)–N(4)	86.6(4)
N(1)–Zn(1)–N(3)	100.2(4)	N(2)–Zn(1)–N(3)	96.6(4)
O(15)–Zn(1)–N(3)	95.8(4)	N(4)–Zn(1)–N(3)	78.6(4)
N(1)–Zn(1)–O(35)	87.4(5)	N(2)–Zn(1)–O(35)	80.7(4)
O(15)–Zn(1)–O(35)	88.2(4)	N(4)–Zn(1)–O(35)	94.0(5)
N(3)–Zn(1)–O(35)	171.4(5)	N(8)–Zn(2)–N(7)	80.3(5)
N(8)–Zn(2)–N(5)	171.8(4)	N(7)–Zn(2)–N(5)	96.8(5)
N(8)–Zn(2)–N(6)	108.6(4)	N(7)–Zn(2)–N(6)	96.3(4)
N(5)–Zn(2)–N(6)	79.3(4)	N(8)–Zn(2)–O(14)	88.8(5)
N(7)–Zn(2)–O(14)	168.5(5)	N(5)–Zn(2)–O(14)	93.5(4)
N(6)–Zn(2)–O(14)	90.7(4)	N(8)–Zn(2)–O(3)#4	79.8(4)
N(7)–Zn(2)–O(3)#4	82.7(4)	N(5)–Zn(2)–O(3)#4	92.3(3)
N(6)–Zn(2)–O(3)#4	171.3(4)	O(14)–Zn(2)–O(3)#4	91.8(4)

Symmetry transformations used to generate equivalent atoms: #4 $-x+1, y+1/2, -z+1/2$.

V–O distances in the range 1.602(11)–1.956(11) Å and bond angles 63.9(6)–163.7(6)°. All molybdenum atoms have a distorted $\{MoO_6\}$ octahedral environment with Mo–O distances 1.6194(10)–2.501(20) Å and bond angles 37.5(4)–160.6(3)°. The central P atom is surrounded by a cube of eight oxygen atoms with each site half-occupied. The P–O distances are in the range 1.458(16)–1.620(14) Å, and O–P–O angles 65.9(9)–112.5(8)°. Each trimetallic group $\{Mo_3O_{13}\}$ is made up of three edge-sharing $\{MoO_6\}$ octahedra. The $\{Mo_3O_{13}\}$ subunits are joined to each other by corner-sharing. Thus, a closed spherical structure with two half-occupied $\{PO_4\}$ tetrahedra encapsulated is formed. Each $[PMo_8V_6O_{42}]$ unit is a multidentate ligand covalently bonded to $[Zn(phen)_2(H_2O)]$ or $[Zn(phen)_2]$ subunits, respectively. The assignments of oxidation state for the molybdenum and vanadium are consistent with their coordination geometries and confirmed by valence sum calculations [17]. The valence sum calculations (see table S6 in the supplementary material) show that three vanadium atoms V_1,V_2 and V_6 are in the +4 oxidation states (calculated average value 4.29); The other three vanadium atoms V_3,V_4 and V_5 are in the +5 oxidation states (calculated average value 4.82), while all molybdenum atoms of polyoxoanion are in the +6 oxidation states (calculated average value 6.02).

There are two distinct zinc coordination environments in **1**. The first (figure 1A), Zn(1) is six-coordinate, defined by four nitrogen atoms from two phen molecules (Zn(1)–N = 2.099(8)–2.137(8) Å), one oxygen atom of the $\{VO_5\}$ square pyramidal from the $[PMo_8V_6O_{42}]$ cluster unit (Zn(1)–O(15) = 2.121(10) Å) and a water molecule (Zn(1)–O(35) = 2.172(12) Å). The second (figure 1B), Zn(2) is also six-coordinate, but coordinated by four nitrogen atoms from two phen molecules (Zn(2)–N = 2.068(10)–2.086(8) Å), two oxygen atoms from $\{VO_5\}$ square pyramid (Zn(2)–O(14) = 2.128(10) Å) and $\{MoO_6\}$ octahedra (Zn(2)–O(3) = 2.489(10) Å) of two different $[PMo_8V_6O_{42}]$ cluster units, respectively. Thus, the cationic 2D sheet $\{[Zn(phen)_2]_2[PMo_8^{VI}V_4^{V}V_2^{IV}O_{42}]\}^+$ is formed, which is built from $[PMo_8^{VI}V_2^{V}V_4^{IV}O_{42}]$ cluster units linked from $[Zn(2)(phen)_2]$ coordination complexes, as shown in figure 2. Meanwhile, the bicapped bisupporting heterpolyoxoanion cluster $\{[Zn(phen)_2(H_2O)]_2\ [PMo_8^{VI}V_2^{V}V_4^{IV}O_{42}]\}^-$ is formed *via* coordination of $[\{Zn(phen)_2(H_2O)_2]$ with $[PMo_8^{VI}V_2^{V}V_4^{IV}O_{42}]$ cluster units (see figure 1B). As far as we know, both the $\{[Zn(phen)_2]_2[PMo_8^{VI}V_4^{V}V_2^{IV}O_{42}]\}^+$ cationic 2D sheet and $\{[Zn(phen)_2(H_2O)]_2\ [PMo_8^{VI}V_2^{V}V_4^{IV}O_{42}]\}^-$ polyoxoanion in one compound have not been observed before in materials chemistry. The most remarkable structural feature of **1** is that a unique three-dimensional supramolecular framework is constructed from two-dimensional covalent layers pillared by bisupporting herepolyanion clusters, as shown in figure 3.

According to bond valence sum calculations, charge balance, elemental analyses and IR spectrum, compound **1** is formulated as $[Zn(phen)_2]_2[PMo_8^{VI}V_4^{V}V_2^{IV}O_{42}]$ $[Zn(phen)_2(H_2O)]_2\ [PMo_8^{VI}V_2^{V}V_4^{IV}O_{42}]\cdot 7H_2O$.

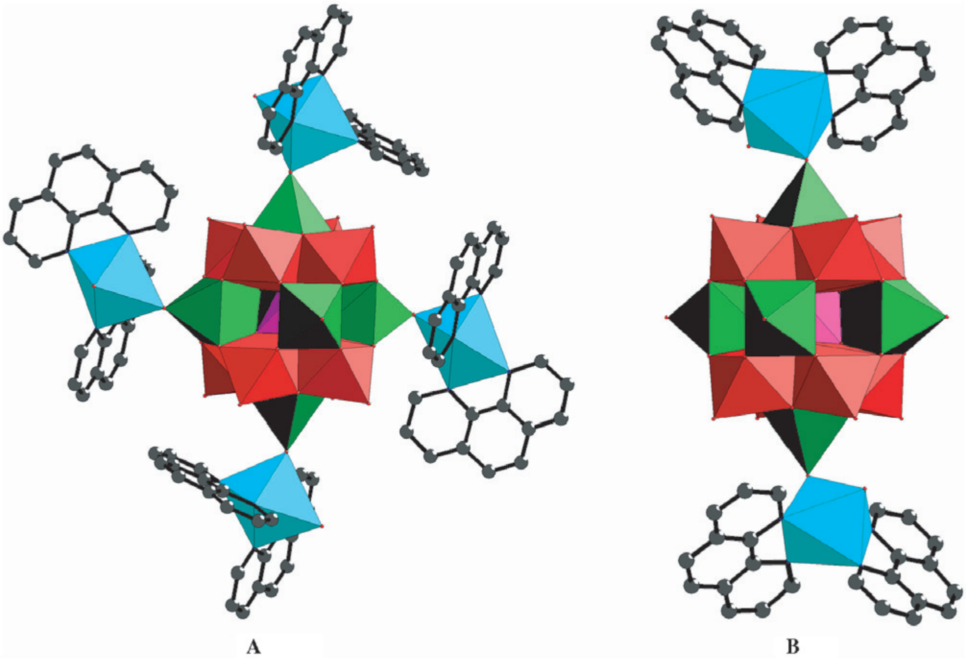

Figure 1. View of the two compositional units in **1** (color code online: Mo, red; V, green; P, purple; Zn, blue).

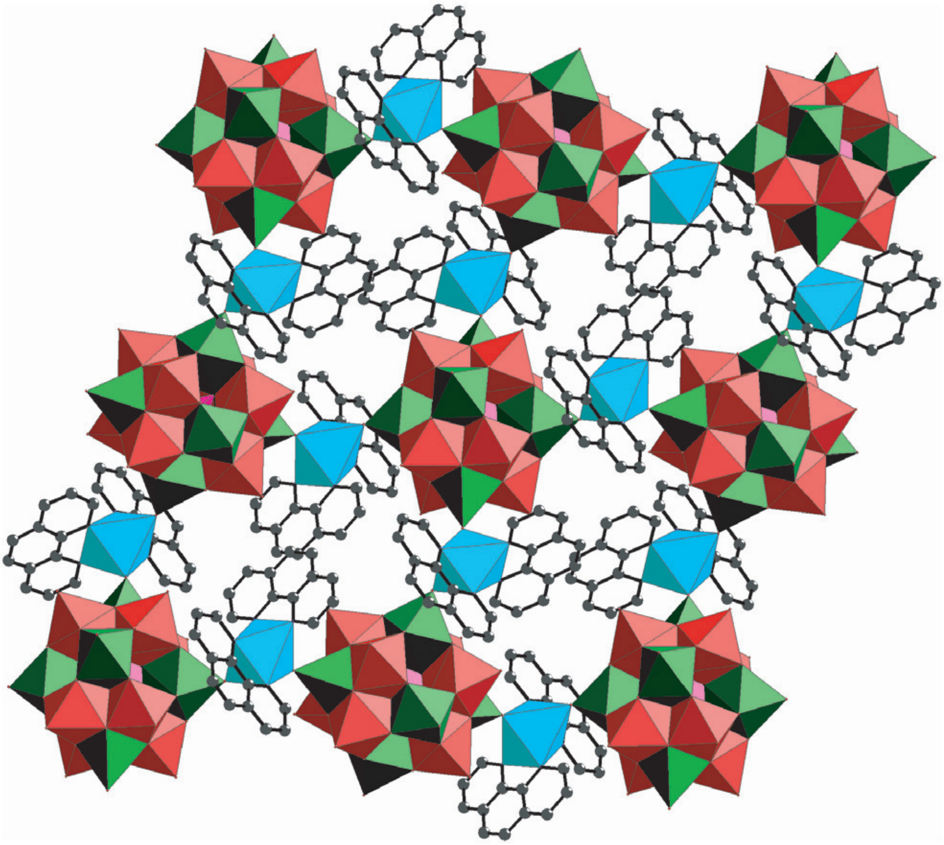

Figure 2. Polyhedral representation of the two-dimensional sheet in **1** (color code online: Mo, red; V, green; P, purple; Zn, blue).

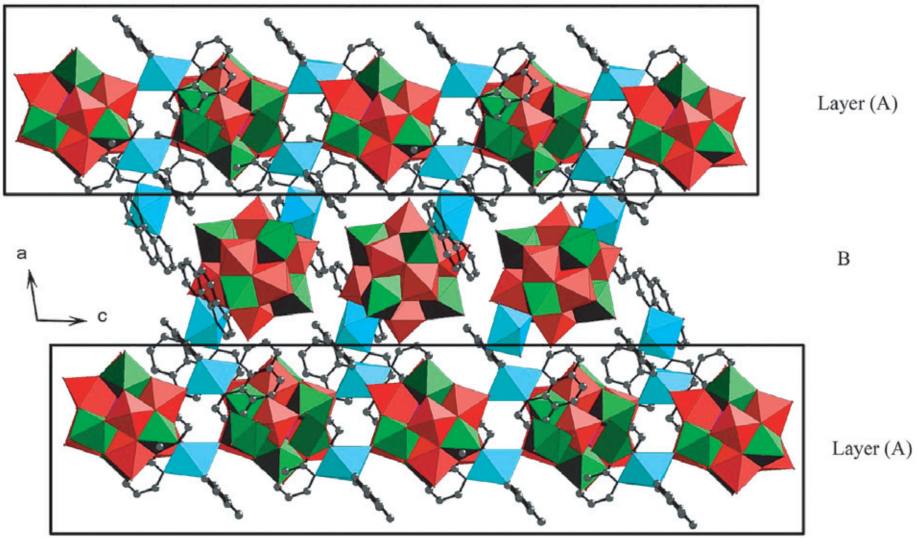

Figure 3. Polyhedral representation of the three-dimensional supramolecular structure in **1** (color code online: Mo, red; V, green; P, purple; Zn, blue).

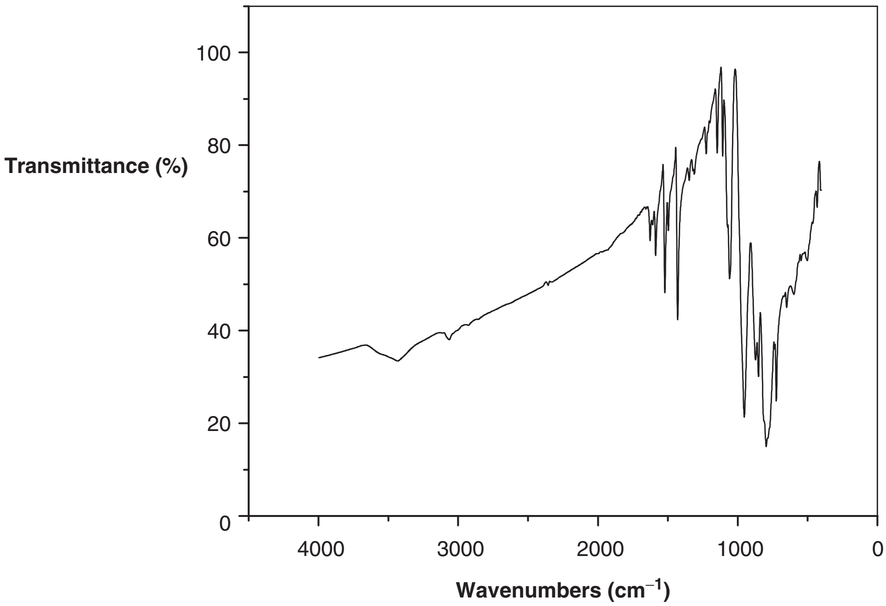

Figure 4. The IR spectrum of 1.

3.2. *IR spectrum*

The IR spectrum of **1** (figure 4) exhibits a broad absorption at 3433 cm^{-1} associated with water and a series of bands in the 1345–1585 cm^{-1} region associated with the phen groups. The bands at 1056, 950, 870, 849 and 722 cm^{-1} are due to ν(P–O$_a$), ν(M = O$_d$), ν(M–O$_b$–M) and ν(M–O$_c$–M) (M = V or Mo), respectively.

3.3. *Thermal analysis*

TG curve of **1** supports its chemical composition with two steps of weight loss. The first weight loss of 3.26% in the temperature range 55–220°C corresponds to release of lattice and ligand water molecules (Calcd 3.00%); the second weight loss of 29.08% at 260–740°C is ascribed to decomposition of phen ligands (Calcd 29.32%). The total weight loss (32.67%) is in agreement with the calculated value (32.32%).

4. Conclusion

In this work, a new inorganic-organic hybrid polyoxometalate has been hydrothermally synthesized and structurally characterized. Preparation of the compound confirms that modification of polyoxometalate clusters with transition metal complexes is a way to construct hybrid materials based on modified polyoxometalate subunits with distinctive structural features.

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