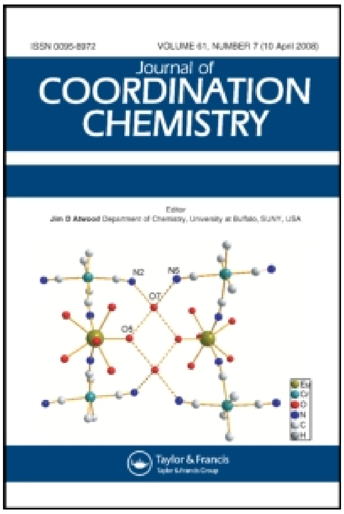

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A polymeric chain formed by bicapped pseudo-Keggin polyoxometalate and $[Ni(en)_2]^{2+}$ complexes: synthesis, structure and catalytic properties of $\{[H_3PMo_8V_6O_{46}][Ni(en)_2]\} \cdot 2[Ni(en)_2] \cdot 5H_2O$

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A polymeric chain formed by bicapped pseudo-Keggin polyoxometalate and $[Ni(en)_2]^{2+}$ complexes: synthesis, structure and catalytic properties of $\{[H_3PMo_8V_6O_{46}][Ni(en)_2]\} \cdot 2[Ni(en)_2] \cdot 5H_2O$

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A new compound $\{[H_3PMo_8V_6O_{46}][Ni(en)_2]\} \cdot 2[Ni(en)_2] \cdot 5H_2O$ with a polymeric chain structure was hydrothermally synthesized and characterized by single crystal X-ray diffraction, IR and TG. The molybdovanadophosphate cluster anion is a bicapped 'pseudo-Keggin' structure, in which two vanadium atoms are located at two 'capping' metal atom positions, another four vanadium atoms and eight molybdenum atoms are arranged as phosphorus-centered alternate layers of molybdenum and vanadium oxides. The title compound exhibits high catalytic activity for selective oxidation of benzyl alcohol to benzaldehyde. The influence of catalyst amount, the ratio, $H_2O_2/C_6H_5CH_2OH$, reaction time and catalyst lifetime on the catalytic activity was studied.

Keywords: Polyoxometalate; Molybdovanadophosphate; Inorganic-organic hybrid compound; Hydrothermal synthesis; Catalysis

1. Introduction

Polyoxometalate-based composite solids assembled by polyoxometalates and transition metal–organic coordination complexes have unlimited structural versatility and rich electrical, optical and catalytic properties. A number of such materials constructed from polyoxometalate clusters and transition metal complexes have been hydrothermally synthesized [1–11], but only a few compounds are formed by bi-capped or tetra-capped Keggin vanadium-containing molybdophosphates and transition metal–organic complexes have been reported. Two-dimensional extended layered complexes $[Co(en)_2][Co(bpy)_2]_2[PMo_5^{VI}Mo_3^{V}V_8^{IV}O_{44}] \cdot 4.5H_2O$ [9] composed of tetra-capped Keggin $[PMo_5^{VI}Mo_3^{V}V_8^{IV}O_{44}]^{6-}$ polyoxoanion clusters and $Co(en)_2$ and $Co(bpy)_2$ fragments as bridges, a two-dimensional network $[Cu(en)_2(H_2O)]\{[PMo_8^{VI}V_6^{IV}O_{42}Cu(en)_2][Cu_{0.5}(en)]_3\} \cdot 5.5H_2O$ [10] formed by a reduced bicapped Keggin heteropolyanion $[PMo_8^{VI}V_6^{IV}O_{42}]^{7-}$, $[Cu(en)_2(H_2O)]$ cations and some

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water molecules and a discrete bicapped-Keggin structure polyoxoanion supported copper complex $[Cu(en)_2(H_2O)]_2[Cu(en)_2]_{0.5}[Mo_8V_7O_{42}\{Cu(en)_2\}]$ [11] provide examples.

In this article, we report the synthesis, crystal structure and catalytic properties of a new complex $\{[H_3PMo_8V_6O_{46}][Ni(en)_2]\} \cdot 2[Ni(en)_2] \cdot 5H_2O$. The most remarkable structural feature of the compound is that the mixed molybdenum-vanadium tetradecametal polyoxoanion clusters $[PMo_8V_6O_{46}]^{9-}$ with higher negative charges are linked to each other *via* $[Ni(en)_2]^{2+}$ cations. This kind of organic-inorganic hybrid material with a one-dimensional chain structure constructed from bi-capped Keggin anions and mixed transition metal complexes is rare.

2. Experimental

2.1. *General procedures*

All reagents were purchased commercially and used without any further purification. The hydrothermal reaction was carried out in a 30 mL Teflon-lined stainless steel autoclave under an autogenous pressure with a filling capacity of 50%.

IR spectra were measured on a Nicolet AVATAR 360 FT-IR spectrometer as KBr pellets in the 4000–400 cm^{-1} region. TG measurement was carried out on a Perkin–Elmer TG-7 thermal analysis system in flowing N_2 atmosphere with a heating rate of 10°C min^{-1}.

2.2. *Hydrothermal synthesis*

A mixture of $NiCl_2 \cdot 6H_2O$ (1.67 g), $Na_2MoO_4 \cdot 2H_2O$ (1.60 g), NH_4VO_3 (0.81 g), en (0.6 mL), H_3PO_4 (1.00 mL) and distilled water (12.00 mL) was heated at 170°C at pH 7.0 for three days in a Teflon-lined reactor. Black prism crystals were isolated after cooling to room temperature.

2.3. *X-ray crystallography*

Crystal structure determination by X-ray diffraction was performed on a Bruker SMART 1000 CCD diffractometer with a graphite-monochromator using Mo-Kα radiation ($\lambda = 0.71073$ Å). An empirical absorption correction was applied using the SADABS program. The crystal structure was solved by the Bruker SHELXTL program. The crystallographic data are presented in table 1 and selected bond lengths and angles are listed in tables 2 and 3.

2.4. *Catalytic activity evaluation*

The title compound, benzyl alcohol and 30% hydrogen peroxide were added to a 100 mL three-necked quartz flask and the mixture was refluxed 4 h at 120°C. The catalyst was separated out after reaction completion. Product analysis was performed by a CP3380 (VARIAN) gas chromatography instrument with column temperature at 200°C, detector temperature 220°C, and post temperature 260°C. The byproducts are

Table 1. Crystallographic data for $\{[H_3PMo_8V_6O_{46}][Ni(en)_2]\} \cdot 2[Ni(en)_2] \cdot 5H_2O$.

Formula	$C_{12}Mo_8N_{12}Ni_3O_{51}PV_6$
Molecular weight	2476.04
Temperature (K)	293(2)
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions (Å, °)	
a	25.907(1)
b	13.3355(3)
c	19.9193(6)
α	90
β	106.529(1)
γ	90
V (Å^3)	6597.3(4)
Z	4
D_{Calcd} (g cm^{-3})	2.493
Limiting indices (mm^3)	$-24 \le h \le 30$, $-12 \le k \le 15$, $-23 \le l \le 23$
μ(Mo-Kα) (mm^{-1})	3.237
F(000)	4816
θ Range (°)	2.13–25.14
Reflections collected	16921
Independent reflection	5862 (R(int) = 0.0469)
Goodness-of-fit on F^2	1.127
R_1, ωR_2 ($I > 2\sigma(I)$)	0.0650, 0.1933
R_1, ωR_2 (all data)	0.0774, 0.2053
Largest difference peak and hole (e Å^{-3})	1.865 and −1.200

Table 2. Bond lengths (Å) for title compound.

Mo(1)–O(6)	1.658(8)	Mo(1)–O(2)	1.786(8)	Mo(1)–O(4)	1.796(8)
Mo(1)–O(3)	2.053(8)	Mo(1)–O(5)	2.058(7)	Mo(2)–O(11)	1.674(7)
Mo(2)–O(8)	1.762(10)	Mo(2)–O(9)	1.777(10)	Mo(2)–O(10)	2.055(8)
Mo(2)–O(3)	2.059(8)	Mo(3)–O(15)	1.688(7)	Mo(3)–O(18)#1	1.778(9)
Mo(3)–O(13)	1.785(8)	Mo(3)–O(5)	2.052(7)	Mo(3)–O(14)	2.055(7)
Mo(4)–O(16)	1.670(8)	Mo(4)–O(22)	1.770(10)	Mo(4)–O(19)	1.794(10)
Mo(4)–O(10)	2.047(8)	Mo(4)–O(14)	2.052(8)	V(1)–O(17)	1.638(7)
V(1)–O(14)	1.918(8)	V(1)–O(10)	1.920(8)	V(1)–O(3)	1.930(8)
V(1)–O(5)	1.935(7)	V(2)–O(20)	1.583(8)	V(2)–O(9)	1.914(9)
V(2)–O(18)	1.916(10)	V(2)–O(19)#1	1.923(10)	V(2)–O(2)	1.940(10)
V(3)–O(21)	1.590(8)	V(3)–O(13)#1	1.902(9)	V(3)–O(8)	1.922(9)
V(3)–O(22)	1.924(9)	V(3)–O(4)#1	1.941(8)	P(1)–O(12)	1.481(13)
P(1)–O(23)	1.518(13)	P(1)–O(7)	1.550(13)	P(1)–O(1)	1.575(14)
O(1)–Mo(1)#1	2.397(14)	O(4)–V(3)#1	1.941(8)	O(13)–V(3)#1	1.902(9)
O(17)–Ni(1)	2.123(7)	O(18)–Mo(3)#1	1.778(9)	O(19)–V(2)#1	1.923(10)
O(23)–Mo(3)#1	2.462(12)	O(23)–Mo(4)#1	2.511(13)	Ni(1)–N(1)	2.092(10)
Ni(1)–N(1)#2	2.092(10)	Ni(1)–N(2)	2.096(10)	Ni(1)–N(2)#2	2.096(10)
Ni(1)–O(17)#2	2.123(7)	Ni(2)–N(6)	1.836(16)	Ni(2)–N(5)	1.872(15)
Ni(2)–N(3)	1.897(19)	Ni(2)–N(4)	1.907(13)		

Symmetry codes: #1 $-x+1/2$, $-y+3/2$, $-z+1$; #2 $-x$, $-y+1$, $-z+1$.

Table 3. Bond angles (°) for title compound.

O(6)–Mo(1)–O(2)	103.9(6)	O(6)–Mo(1)–O(4)	103.6(5)	O(2)–Mo(1)–O(4)	95.9(4)
O(6)–Mo(1)–O(3)	97.5(5)	O(2)–Mo(1)–O(3)	90.5(4)	O(4)–Mo(1)–O(3)	155.7(4)
O(6)–Mo(1)–O(5)	97.7(4)	O(2)–Mo(1)–O(5)	155.7(5)	O(4)–Mo(1)–O(5)	89.7(3)
O(3)–Mo(1)–O(5)	75.5(3)	O(6)–Mo(1)–V(1)	99.2(3)	O(2)–Mo(1)–V(1)	125.7(3)
O(4)–Mo(1)–V(1)	125.2(3)	O(1)#1–Mo(1)–V(1)	73.8(3)	O(11)–Mo(2)–O(8)	104.6(6)
O(11)–Mo(2)–O(9)	103.9(6)	O(8)–Mo(2)–O(9)	96.8(6)	O(11)–Mo(2)–O(10)	99.2(4)
O(8)–Mo(2)–O(10)	89.7(4)	O(9)–Mo(2)–O(10)	153.4(4)	O(11)–Mo(2)–O(3)	98.2(4)
O(8)–Mo(2)–O(3)	154.1(5)	O(9)–Mo(2)–O(3)	89.2(4)	O(10)–Mo(2)–O(3)	74.5(3)
O(11)–Mo(2)–O(7)	158.3(5)	O(8)–Mo(2)–O(7)	64.2(5)	O(9)–Mo(2)–O(7)	96.1(5)
O(10)–Mo(2)–O(7)	63.7(4)	O(3)–Mo(2)–O(7)	90.1(4)	O(11)–Mo(2)–V(1)	100.6(3)
O(8)–Mo(2)–V(1)	124.2(3)	O(9)–Mo(2)–V(1)	123.9(3)	O(7)–Mo(2)–V(1)	74.2(3)
O(15)–Mo(3)–O(18)#1	104.5(6)	O(15)–Mo(3)–O(13)	102.4(5)	O(18)#1–Mo(3)–O(13)	97.9(5)
O(15)–Mo(3)–O(5)	97.6(4)	O(18)#1–Mo(3)–O(5)	154.9(4)	O(13)–Mo(3)–O(5)	88.9(3)
O(15)–Mo(3)–O(14)	99.8(4)	O(18)#1–Mo(3)–O(14)	89.5(4)	O(13)–Mo(3)–O(14)	153.9(4)
O(5)–Mo(3)–O(14)	74.7(3)	O(15)–Mo(3)–O(12)	157.4(5)	O(18)#1–Mo(3)–O(12)	96.8(6)
O(13)–Mo(3)–O(12)	66.5(5)	O(5)–Mo(3)–O(12)	63.7(4)	O(14)–Mo(3)–O(12)	87.8(4)
O(15)–Mo(3)–V(1)	100.5(3)	O(18)#1–Mo(3)–V(1)	124.3(3)	O(13)–Mo(3)–V(1)	123.9(3)
O(12)–Mo(3)–V(1)	72.9(3)	O(16)–Mo(4)–O(22)	105.5(6)	O(16)–Mo(4)–O(19)	104.1(5)
O(22)–Mo(4)–O(19)	94.2(6)	O(16)–Mo(4)–O(10)	97.2(4)	O(22)–Mo(4)–O(10)	91.2(4)
O(19)–Mo(4)–O(10)	155.8(4)	O(16)–Mo(4)–O(14)	97.8(4)	O(22)–Mo(4)–O(14)	154.2(5)
O(19)–Mo(4)–O(14)	90.8(4)	O(10)–Mo(4)–O(14)	74.7(3)	O(16)–Mo(4)–O(7)	157.0(5)
O(22)–Mo(4)–O(7)	63.6(5)	O(19)–Mo(4)–O(7)	97.2(5)	O(10)–Mo(4)–O(7)	64.4(4)
O(14)–Mo(4)–O(7)	90.7(4)	O(16)–Mo(4)–V(1)	99.2(3)	O(22)–Mo(4)–V(1)	125.5(3)
O(19)–Mo(4)–V(1)	125.7(3)	O(7)–Mo(4)–V(1)	74.8(3)	O(17)–V(1)–O(14)	111.6(4)
O(17)–V(1)–O(10)	112.6(4)	O(14)–V(1)–O(10)	80.8(3)	O(17)–V(1)–O(3)	115.5(4)
O(14)–V(1)–O(3)	132.8(4)	O(10)–V(1)–O(3)	80.7(4)	O(17)–V(1)–O(5)	114.2(4)
O(14)–V(1)–O(5)	80.6(3)	O(10)–V(1)–O(5)	133.2(4)	O(3)–V(1)–O(5)	81.3(3)
O(17)–V(1)–Mo(4)	119.4(3)	O(3)–V(1)–Mo(4)	110.0(3)	O(5)–V(1)–Mo(4)	110.2(2)
O(17)–V(1)–Mo(1)	123.1(3)	O(14)–V(1)–Mo(1)	110.4(2)	O(10)–V(1)–Mo(1)	110.4(3)
Mo(4)–V(1)–Mo(1)	117.47(5)	O(17)–V(1)–Mo(3)	120.2(3)	O(10)–V(1)–Mo(3)	110.5(3)
O(3)–V(1)–Mo(3)	110.7(3)	Mo(4)–V(1)–Mo(3)	74.43(5)	Mo(1)–V(1)–Mo(3)	74.68(4)
O(17)–V(1)–Mo(2)	121.9(3)	O(14)–V(1)–Mo(2)	110.2(3)	O(5)–V(1)–Mo(2)	110.8(2)
Mo(4)–V(1)–Mo(2)	74.11(5)	Mo(1)–V(1)–Mo(2)	74.65(4)	Mo(3)–V(1)–Mo(2)	117.87(5)
O(20)–V(2)–O(9)	101.1(6)	O(20)–V(2)–O(18)	99.9(5)	O(9)–V(2)–O(18)	89.2(5)
O(20)–V(2)–O(19)#1	102.3(5)	O(9)–V(2)–O(19)#1	156.6(6)	O(18)–V(2)–O(19)#1	87.6(4)
O(20)–V(2)–O(2)	101.9(5)	O(9)–V(2)–O(2)	87.5(4)	O(18)–V(2)–O(2)	158.1(5)
O(19)#1–V(2)–O(2)	86.9(5)	O(21)–V(3)–O(13)#1	101.8(5)	O(21)–V(3)–O(8)	102.4(6)
O(13)#1–V(3)–O(8)	89.9(5)	O(21)–V(3)–O(22)	103.4(6)	O(13)#1–V(3)–O(22)	154.8(5)
O(8)–V(3)–O(22)	86.6(4)	O(21)–V(3)–O(4)#1	100.7(5)	O(13)#1–V(3)–O(4)#1	87.2(4)
O(8)–V(3)–O(4)#1	156.7(6)	O(22)–V(3)–O(4)#1	86.3(4)	O(21)–V(3)–O(7)	160.0(5)
O(13)#1–V(3)–O(7)	93.3(5)	O(8)–V(3)–O(7)	64.1(5)	O(22)–V(3)–O(7)	62.8(5)
O(4)#1–V(3)–O(7)	93.1(4)	O(12)–P(1)–O(23)	111.3(7)	O(12)–P(1)–O(7)	112.5(7)
O(23)–P(1)–O(7)	106.9(7)	O(12)–P(1)–O(1)	111.4(7)	O(23)–P(1)–O(1)	109.2(6)
O(7)–P(1)–O(1)	105.2(7)				

Symmetry codes: #1 $-x+1/2$, $-y+3/2$, $-z+1$; #2 $-x$, $-y+1$, $-z+1$.

benzoic acid in a neglible amount and unreacted benzyl alcohol under the detection conditions.

3. Results and discussion

3.1. *IR spectrum*

In the 1100–700 cm^{-1} region, four major bands characteristic for a Keggin type structure, were observed (as shown in figure 1). These bands at 1039, 929, 826 and

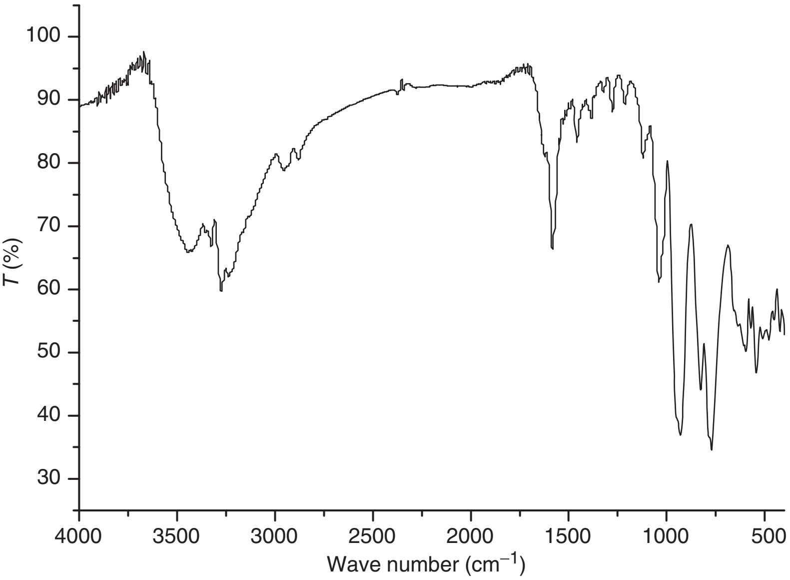

Figure 1. IR spectrum of the title compound.

770 cm^{-1} were assigned to ν_{as} (P–Oa), ν_{as} (Mo–Od, V–Od), ν_{as} (Mo–Ob–Mo, V–Ob–V) and ν_{as} (Mo–Oc–Mo, V–Oc–V), respectively. The bands at 1583, 1460, 1385, 1278 and 1213 cm^{-1} are characteristic of ethylenediamine [10].

3.2. *TG analysis*

The TG analysis (figure 2) showed three steps with weight losses in the ranges of 50–250°C, 250–414°C and 414–830°C of 5.85%, 10.01% and 15.93%, respectively. These weight losses are assigned to removal of water, the ethylenediamine ligands and decomposition of the title compound, respectively [12]. This indicates that the thermal stability of the title compound is good enough for catalytic reaction.

3.3. *Crystal structure*

The crystal structure of the title compound is composed of one dimensional $\{(H_3PMo_8V_6O_{46})\cdot[Ni(en)_2]\}_n^{4n-}$ anions, discrete $[Ni(en)_2]^{2+}$ complex cations and H_2O molecules of crystallization. The cluster anion $[PMo_8V_6O_{46}]^{9-}$ (figure 3) is of a bicapped Keggin structure which contains eight MoO_5, four VO_5 square pyramids and additional five-coordinate terminal $\{VO\}^{2+}$ units. The central P atom is surrounded by a cube of eight oxygen atoms with each site half-occupied. The P–O distances are 1.481(14)–1.575(14) Å, and the O–P–O angles vary from 106.9(7)° to 112.5(7)°. The Mo–O and V–O distances can be grouped into three sets: Mo–O$_t$ (terminal oxygen), 1.658(8)–1.688(7) Å; V–O$_t$ 1.583(8)–1.590(8) Å Mo–O$_b$ (bridged oxygen), 1.762(10)–1.796(8) Å V–O$_b$, 1.902(9)–1.941(8) Å and Mo–O$_c$, 2.047(8)–2.059(12) Å and V–O$_c$, 1.918(8)–1.935(7) Å. Weak coordination exists between Mo, V and O linked to the central P atom because of a distorted and disordered PO_4 tetrahedron with Mo–O(–P) distances

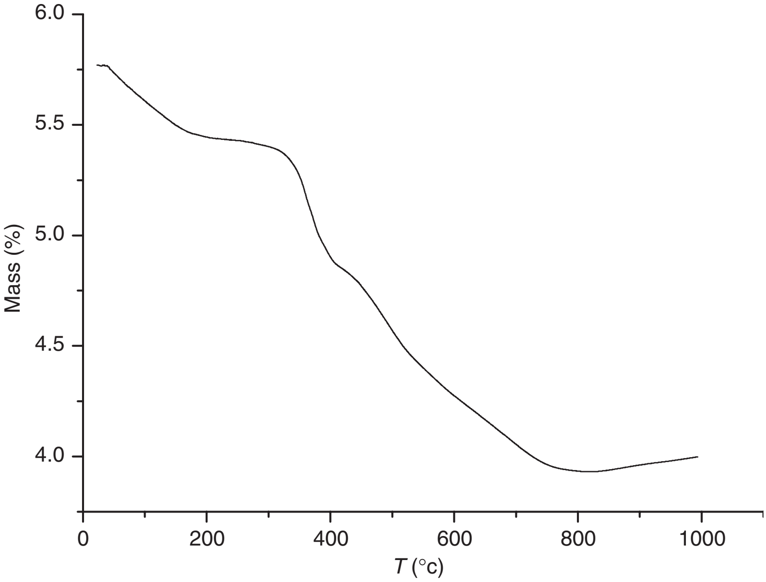

Figure 2. TG curve of the title compound.

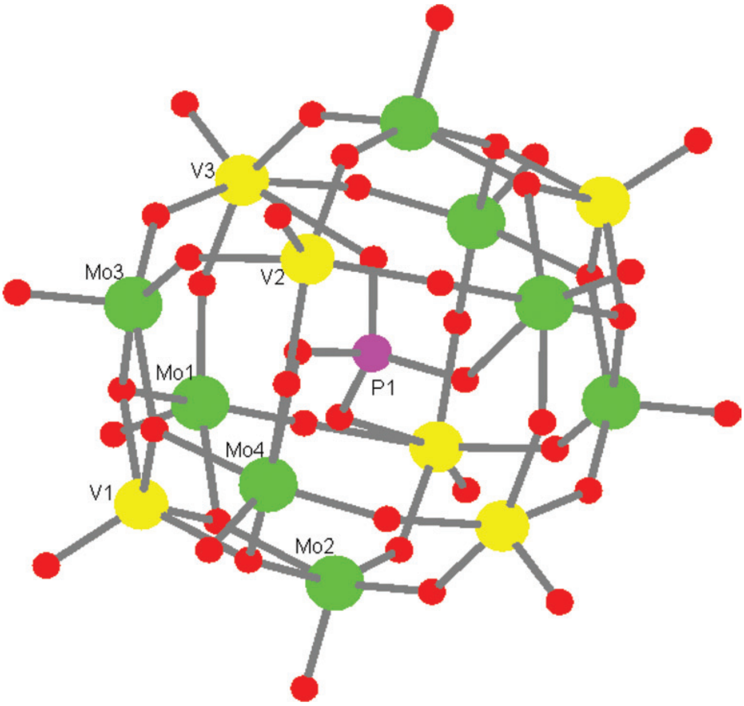

Figure 3. Structure of the building block unit $[PMo_8V_6O_{46}]^{9-}$ in compound **1**.

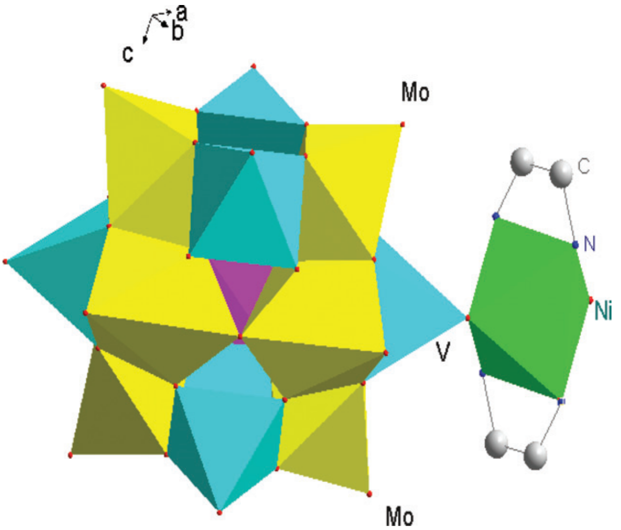

Figure 4. Structure of molecular segment $\{(PMo_8V_6O_{46})\cdot[Ni(en)2]\}$ in compound **1**.

of 2.397(14)–2.509(13) Å and V–O(–P) distances of 2.443(13) Å. The assignments of oxidation state for the vanadium and molybdenum are consistent with their coordination geometries and are confirmed by valence sum calculation [13]. The valence sums for four Mo atoms are 6.036, 6.111, 5.958, and 6.064, with average value of 6.042. For three V atoms the values are 4.433, 4.704 and 4.678, the average value being 4.605. For P atom the valence value is 5.070.

In the polymeric anion chain, the bicapped Keggin cluster $[PMo_8V_6O_{46}]^{9-}$ anions coordinate to nickel(II) through the terminal oxygen atoms (figures 4 and 5) with Ni–O distance 2.122(8)Å. The one-dimensional wave-like chain structure of this compound is the first example of a new topology in bi-capped Keggin molybdovanadophosphate. The only reported example of bi-capped Keggin polyoxometalate clusters is $[Cu(en)_2(H_2O)]\{[PMo_8^{VI}V_6^{IV}O_{42}\ Cu(en)_2][Cu_{0.5}(en)]_3\}\cdot 5.5H_2O$ [10], in which the polyoxoanion cluster $[PMo_8^{VI}V_6^{IV}O_{42}]^{7-}$ acts as a ligand supported $[Cu(en)_2]^{2+}$ unit forming a two-dimensional framework and its net valence is −7 rather than −9.

3.4. *Catalytic properties*

To evaluate the catalytic activity of the title compound, the oxidation of $C_6H_5CH_2OH$ to C_6H_5CHO was carried out at ambient pressure and reflux temperature (120°C). In a control experiment without catalyst, oxidation of $C_6H_5CH_2OH$ was negligible. The title compound greatly enhanced the conversion of $C_6H_5CH_2OH$ to C_6H_5CHO. The effect of catalyst amount, $H_2O_2/C_6H_5CH_2OH$ (volume ratio), reaction time and times of re-use of the catalyst on catalytic activity were investigated.

Increased quantity of catalyst improved the conversion of $C_6H_5CH_2OH$ to C_6H_5CHO (illustrated in figure 6). However, the conversion and selectivity increased much more slowly with catalyst quantity greater than $10\,mg\,mL^{-1}$, so the optimum quantity was $10\,mg\,mL^{-1}$.

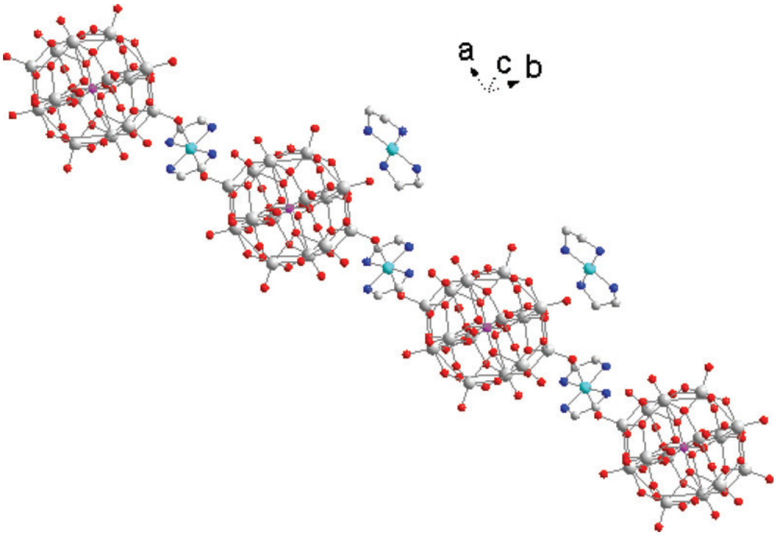

Figure 5. One-dimensional chain structure in title compound **1**.

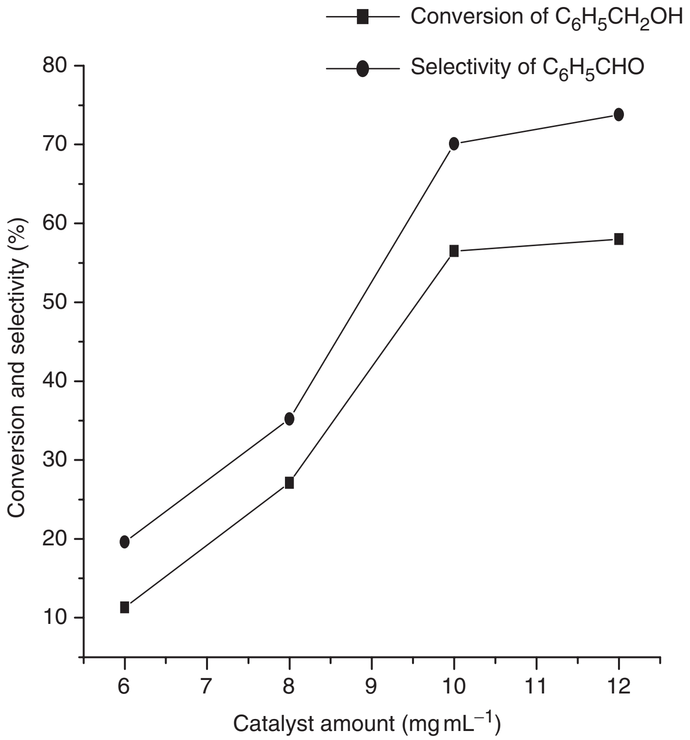

Figure 6. Influence of catalyst amount $V(H_2O_2)/V(C_6H_5CH_2OH) = 1.25$; Time: 4 h.

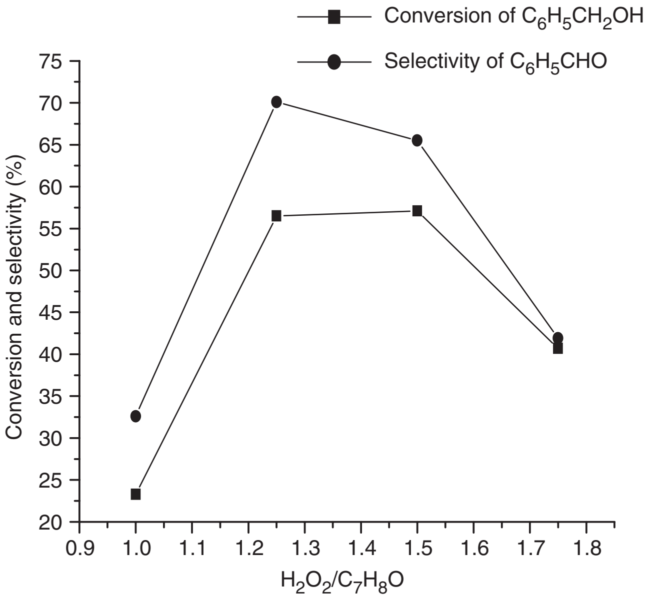

Figure 7. Influence of $H_2O_2/C_6H_5CH_2OH(V/V)$ $V(H_2O_2)/V(C_6H_5CH_2OH) = 1.25$; Time: 4 h; Catalyst amount: 10 mg mL^{-1}.

As shown in figure 7, conversion of $C_6H_5CH_2OH$ and selectivity to C_6H_5CHO increase with increasing [H_2O_2]; beyond a ratio of 1.25 : 1, the conversion of C_6H_5CHO continues to increase while selectivity is falling. The reason for this decrease is probably further oxidation of C_6H_5CHO with excessive H_2O_2. Therefore, the ratio H_2O_2/$C_6H_5CH_2OH$ (v/v) = 1.25 : 1 is chosen for the reaction.

As reported in figure 8, the conversion of $C_6H_5CH_2OH$ and selectivity for C_6H_5CHO are enhanced with increasing reaction time to a maximum at 4 h. A further increase in reaction time leads to a decline in catalyst activity. Reaction times longer than 4 h may result in oxidation of $C_6H_5CH_2OH$ to C_6H_5COOH.

Figure 9 shows that the catalyst can be reused but the conversion of $C_6H_5CH_2OH$ and the selectivity to C_6H_5CHO decrease with reuse. A large drop of catalyst activity for the third use may indicate decomposition of the catalyst.

4. Conclusion

A new one-dimensional chain compound constructed from molybdenum-vanadium bi-capped Keggin polyoxometalate and [Ni(en)$_2$]$^{2+}$ has been prepared and characterized by X-ray crystallography. The title compound was used as a catalyst for selective oxidation of benzyl alcohol to benzaldehyde, the conversion of $C_6H_5CH_2OH$ reaches 56.5% and selectivity to C_6H_5CHO reaches 70.1% at the optimal conditions of catalyst concentration, 10 mg mL^{-1}, $H_2O_2/C_6H_5CH_2OH$, 1.25 : 1(v/v), reaction time, 4 h at 120°C.

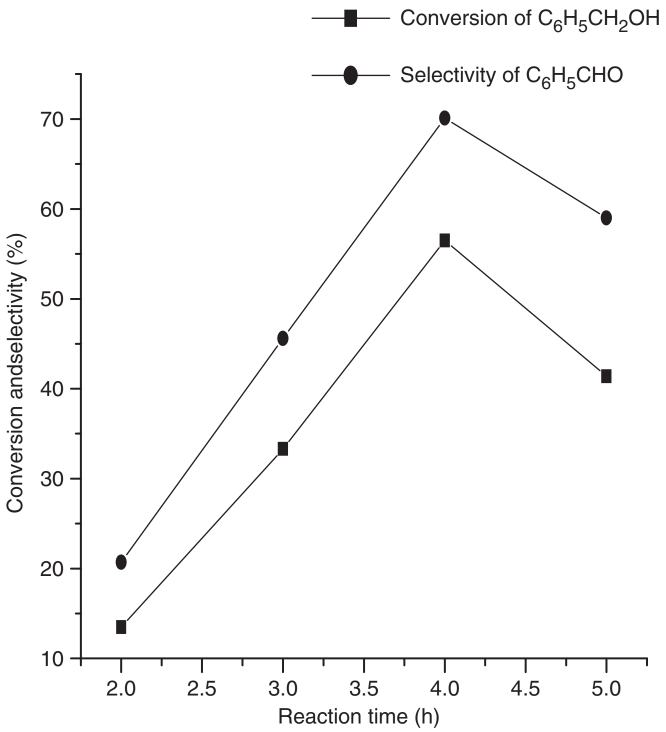

Figure 8. Influence of reaction time $V(H_2O_2)/V(C_6H_5CH_2OH) = 1.25$; Catalyst amount t: $10\,mg\,mL^{-1}$.

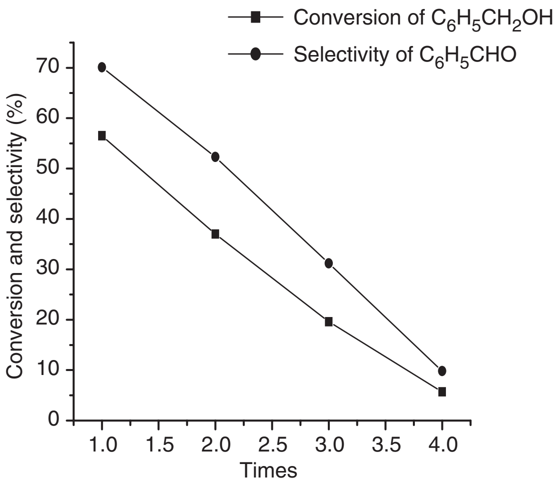

Figure 9. Influence of reusable times $V(H_2O_2)/V(C_6H_5CH_2OH) = 1.25$; Catalyst amount: $10\,mg\,mL^{-1}$; Time: 4 h.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center with the deposited numbers CCDC Number 299101. Copies of this information may be obtained free from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax:+44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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