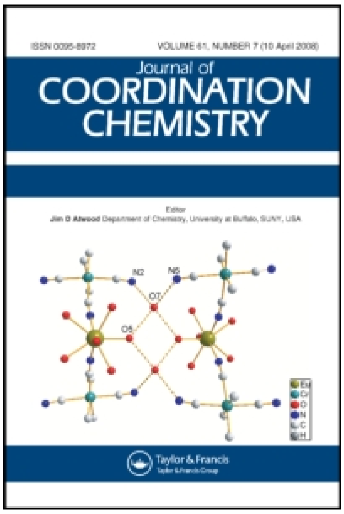


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A new mixed molybdenum-vanadium polyoxometalate double-supporting transition metal complex: {[Co(phen)$_2$]$_2$-C$_2$O$_4$} {H$_2$P O$_{44}$[Co(phen)$_2$(H$_2$O)]$_2$}·7H$_2$O

Ying-Hua Sun[ab]; Xiao-Bing Cui[a]; Guang-Hua Li[a]; Ji-Qing Xu[a]; Tie-Gang Wang[a]; Wei Xu[a]; Ling-Yun Pan[c]; Qing-Xin Yang[c]
[a] College of Chemistry and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, China [b] Department of Chemistry, Baicheng Teachers College, Baicheng Jilin 137000, China [c] College of Physics, Jilin University, Changchun 130023, China

To cite this Article Sun, Ying-Hua , Cui, Xiao-Bing , Li, Guang-Hua , Xu, Ji-Qing , Wang, Tie-Gang , Xu, Wei , Pan, Ling-Yun and Yang, Qing-Xin(2005) 'A new mixed molybdenum-vanadium polyoxometalate double-supporting transition metal complex: {[Co(phen)$_2$]$_2$-C$_2$O$_4$} {H$_2$P O$_{44}$[Co(phen)$_2$(H$_2$O)]$_2$}·7H$_2$O', Journal of Coordination Chemistry, 58: 17, 1561 — 1571

To link to this Article: DOI: 10.1080/00958970500244039
URL: http://dx.doi.org/10.1080/00958970500244039

Journal of Coordination Chemistry
Vol. 58, No. 17, November 2005, 1561–1571

Taylor & Francis
Taylor & Francis Group

A new mixed molybdenum–vanadium polyoxometalate double-supporting transition metal complex: $\{[Co(phen)_2]_2\text{-}C_2O_4\}\{H_2PMo^{VI}_3Mo^{V}_5V^{IV}_8O_{44}[Co(phen)_2(H_2O)]_2\} \cdot 7H_2O$

YING-HUA SUN†‡, XIAO-BING CUI†, GUANG-HUA LI†,
JI-QING XU*†, TIE-GANG WANG†, WEI XU†, LING-YUN PAN§
and QING-XIN YANG§

†College of Chemistry and State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130023, China
‡Department of Chemistry, Baicheng Teachers College, Baicheng Jilin 137000, China
§College of Physics, Jilin University, Changchun 130023, China

(*Received 13 October 2004; in final form 17 June 2005*)

The new polyoxometalate double-supporting transition metal complexes, $\{[Co(phen)_2]_2C_2O_4\}\{H_2PMo^{VI}_3Mo^{V}_5V^{IV}_8O_{44}[Co(phen)_2H_2O]_2\} \cdot 7H_2O$ (**1**) (phen = 1,10-phenanthroline) have been hydrothermally synthesized and characterized by single crystal X-ray analysis, IR, XPS, ESR and elemental analysis. Compound **1** is composed of a highly reduced tetra-capped pseudo-Keggin polyoxoanion supporting two transition metal complexes, a binuclear cobalt complex cation and lattice water. The magnetism and third-order non-linear optical properties of **1** have also been studied.

Keywords: Hydrothermal synthesis; Transition metal; Polyoxometalate; Magnetic property

1. Introduction

Heteropolyoxometalate (POMs) clusters are of current interest due mainly to their diverse properties with applications to sorption clathration, catalysis, electrical conductivity, magnetism and photochemistry [1–11]. It is therefore vital to design and prepare novel organic–inorganic hybrids with different structural characteristics in order to explore their potential properties. Recently an important advance in transition metal oxide cluster chemistry is the "decoration" of polyoxoanion with various organic and/or transition metal complex moieties [12–17]. These decorated polyoxometalate derivatives can be regarded as an atomic-level structure model for the determination of the mechanisms of oxide-supported catalysts [8]. Furthermore, such compounds

---

*Corresponding author. Fax: +86-431-516-8624. Email: xjq@mail.jlu.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500244039

can be molecularly tuned to provide potentially new types of catalyst systems as well as interesting functional materials with optical, electronic and magnetic properties [3, 5, 18], Some non-classical metal oxygen clusters such as Keggin- and Dawson-type polyoxoanions supporting transition metal complexes, correspond to this kind of compound. Examples include Keggin molecular clusters supporting one transition metal complex: $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni\text{-}(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$ [14] and $(Bu_4N)_5[(C_5Me_5)Rh(SiW_9Nb_3O_{40})]$ [15], bi-capped pseudo-Keggin clusters supporting one transition metal complex: $[Cu(en)_2(H_2O)]_4\text{-}[Cu(en)_2]_{3.5}[PMo_8V_6O_{42}\text{-}Cu(en)(1,10\text{-phen})]_3\cdot 14H_2O$ [19], tetra-capped pseudo-Keggin clusters supporting two transition metal complex: $\{Mo^{VI}_6Mo^{V}_2V^{IV}_8O_{40}(PO_4)[Co(phen)_2\text{-}(H_2O)]_2\}[Co_2(phen)_2(OH)_2(H_2O)_4]_{1/2}$ [20] and $\{Mo^{VI}_5Mo^{V}_3V^{IV}_8O_{40}(PO_4)[Co(phen)(en)\text{-}(H_2O)]_2\}[Co(phen)_3]\cdot 1.5H_2O$ [20], Keggin clusters supporting four transition metal complexes, $\{PW_9V_3O_{40}[Ag(2,2'\text{-bipy})]_2[Ag_2(2,2'\text{-bipy})_3]_2\}$ [21] and Dawson-type polyoxoanions supporting one organometallic complex, $Na[(n\text{-}C_4H_9)_4N][(C_5H_5)Rh(P_2\text{-}W_{15}Nb_3O_{62})]\cdot 10MeCN\cdot 10MeCO$ [16].

As a part of our work aimed at rational design and preparation of functional supramolecular compounds, we carried out a study of polyoxometalate derivatives. Several such compounds have been studied by crystal structure analyses, but their magnetism and third-order non-linear optical properties have been less well noted [13, 25]. In this article, we report the hydrothermal synthesis, crystal structure, magnetism and third-order non-linear optical properties of a new polyoxometalate, $\{[Co(phen)_2]C_2O_4\}\{H_2PMo^{VI}_3Mo^{V}_5V^{IV}_8O_{44}\ [Co(phen)_2H_2O]_2\}\cdot 7H_2O$.

2. Experimental

2.1. *Materials and methods*

All reagents were purchased commercially and used without further purification. Infrared spectra of the compound were recorded with a Perkin–Elmer Spectrum One spectrophotometer in the 225–4000 cm^{-1} region using a powdered sample on a KBr plate. The elemental analyses were determined using a Perkin–Elmer 2400 Series II CHNS/O elemental analyzer. Inductively coupled plasma (ICP) analysis was conducted on a Perkin–Elmer Optima 3300DV spectrometer. Electron spin resonance (ESR) was carried out on Bruker ER 200D-SRC spectrometer. XPS analyses were performed on a VG ESCALAB MK II spectrometer with a Mg–Kα (1253.6 eV) monochromatic X-ray source. Variable temperature magnetic susceptibility measurements were performed on a Quantum Design MPMS XL-5 SQUID magnetometer in 2–300 K.

2.2. *Synthesis of the compound*

$\{[Co(phen)_2]_2C_2O_4\}\{H_2PMo^{VI}_3Mo^{V}_5V^{IV}_8O_{44}[Co(phen)_2H_2O]_2\}\cdot 7H_2O$ (**1**). Compound **1** was synthesized as big black block crystals in 80% yield based on Mo using the hydrothermal method. A mixture of $CoCl_2\cdot 6H_2O$ (0.4 g), NH_4VO_3 (0.38 g), $Na_2MoO_4\cdot 2H_2O$ (0.8 g), $H_2C_2O_4\cdot 2H_2O$ (0.4 g), H_3PO_4 (0.1 mL), phen (0.66 g) and H_2O (18 mL) was adjusted to pH = 9 with aqueous ammonia and sealed in a 30 mL Teflon-lined reactor, which was heated at 160°C for three days; after cooling to room temperature, big black block crystals were isolated. Elemental analysis: Calc.

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

Empirical formula	$C_{98}H_{80}Co_4Mo_8N_{16}O_{57}PV_8$
Formula weight	3835.52
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, *P*-1
Unit cell dimensions	$a = 13.1098(2)$ Å
	$b = 14.2845(3)$ Å
	$c = 17.0576(4)$ Å
	$\alpha = 90.7550(10)^\circ$
	$\beta = 104.6340(10)^\circ$
	$\gamma = 100.8690(10)^\circ$
Volume	3029.03(11) $Å^3$
Z, $\rho_{\text{Calc.}}$ (mg m^{-3})	1, 2.103
Absorption coefficient	2.027 mm^{-1}
$F(000)$	1879
Crystal size	$0.28 \times 0.25 \times 0.22\ \text{mm}^3$
θ range for data collection	2.14° to 23.28°
Limiting indices	$-14 \le h \le 14$, $-15 \le k \le 15$, $-18 \le l \le 16$
Reflections collected/unique	14358/8605 [$R(\text{int}) = 0.0265$]
Completeness to $\theta = 23.28$	98.6%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8605/0/886
Goodness-of-fit on F^2	1.122
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0389$, $wR_2 = 0.1030$
R indices (all data)	$R_1 = 0.0434$, $wR_2 = 0.1071$
Largest diff. peak and hole	1.583 and −0.540 e. $Å^{-3}$

for $C_{98}H_{80}Co_4Mo_8N_{16}O_{57}PV_8$: C: 30.64, H: 2.18, N: 5.8%, Co: 6.1%, Mo: 20.01%, P: 0.81%, V: 10.62%; Found C: 30.51, H: 2.16, N: 5.62%, Co: 5.95%, Mo: 19.8%, P: 0.78%, V: 10.15%. IR (KBr, cm^{-1}) for **1** 3428s, 2918s, 1643w, 1491m, 1423w, 1340m, 1304m, 1222m, 1144m, 1103m, 1044m, 949w, 868s, 847m, 723w, 706w, 641m.

2.3. *X-ray crystallography*

The molecular structure determination of **1** was performed with a Siemens SMART CCD diffractometer employing Mo–Kα radiation at 293 K. The structure solution and refinement were carried out using SHELXL 97. The structure was solved using direct methods and all of the non-hydrogen atoms were located from the initial solution or from subsequent electron density difference maps during the initial stages of the refinement. All of the non-hydrogen atoms in the structure were refined using anisotropic thermal displacement parameters. Hydrogen atoms were treated as idealized contributions. Selected crystallographic data and structure determination parameters are given in table 1.

3. Results and discussion

3.1. *Crystal structure*

The single crystal structure analysis of $\{[Co(phen)_2]_2C_2O_4\}\{H_2PMo_3^{VI}Mo_5^{V}V_8^{IV}O_{44}[Co(phen)_2H_2O]_2\} \cdot 7H_2O$ revealed that **1** consists of a discrete polyoxoanion $\{H_2PMo_3^{VI}Mo_5^{V}V_8^{IV}O_{44}[Co(phen)_2H_2O]_2\}^{2-}$ (figure 1), in which two complex fragments

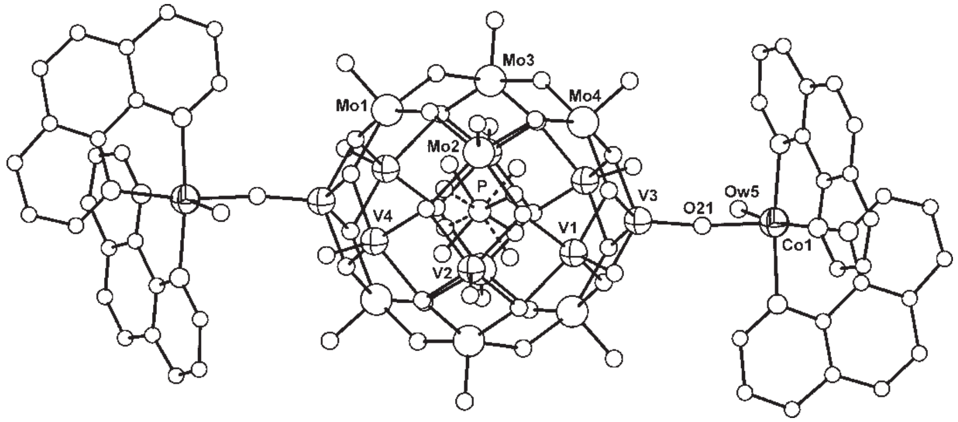


Figure 1. The structure of the tetra-capped Keggin polyoxoanion of **1** supporting two transition metal complexes.

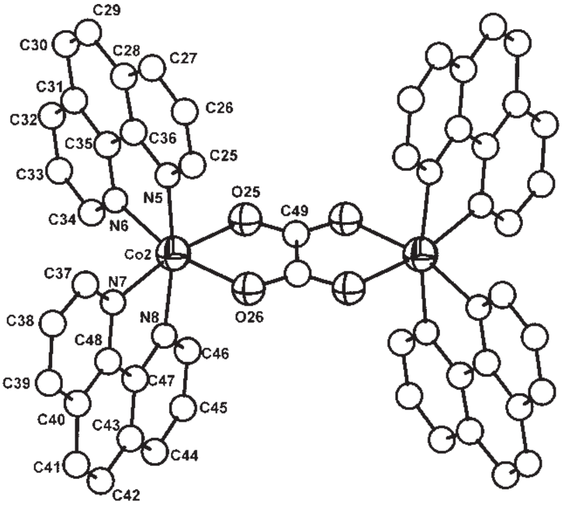


Figure 2. The structure of the binuclear counter cation of compound **1**.

$[\mathrm{Co(phen)_2H_2O}]^{2+}$ are oppositely supported on the tetra-capped Keggin polyoxoanion $[\mathrm{PMo_3^{VI}Mo_5^{V}V_8^{IV}O_{44}}]^{8-}$, and binuclear counter cation $\{[\mathrm{Co(phen)_2}]_2\mathrm{C_2O_4}\}^{2+}$ (figure 2). Select bond lengths are given in table 2. Capped Keggin metal-oxygen clusters with double-supporting metal complex fragments are unusual although some mixed Mo/V polyoxoanions have been reported [20, 22, 23].

The polyoxoanion $[\mathrm{PMo_3^{VI}Mo_5^{V}V_8^{IV}O_{44}}]^{8-}$ is based on the well-known α-Keggin structure with four additional five-coordinate terminal VO^{2-} units to form a hexadecametal shell $[\mathrm{Mo_3^{VI}Mo_5^{V}V_8^{IV}O_{40}}]^{5-}$. A distorted and disordered tetrahedral $\mathrm{PO_4^{3-}}$ anion lies inside the host shell. The $\mathrm{PO_4}$ tetrahedron has P–O distances of 1.518–1.551 Å and bond angles in the range of $108.7(4) \sim 110.5(4)^{\circ}$. The host shell $[\mathrm{Mo_3^{VI}Mo_5^{V}V_8^{IV}O_{40}}]^{5-}$ is constructed from eight $\mathrm{VO_5}$ square pyramids by sharing square edges to form a central belt and two $\mathrm{Mo_4}$ rings lie above and below this $\mathrm{V_8}$ belt. Each $\mathrm{MoO_5}$ also exhibits

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

Mo(1)–O(10)	1.664(4)	V(2)–O(19)	1.935(4)
Mo(1)–O(5)	1.862(5)	V(2)–O(22)	1.944(4)
Mo(1)–O(8)	1.869(5)	V(2)–O(20)	1.947(4)
Mo(1)–O(24)#1	1.986(4)	V(3)–O(21)	1.646(4)
Mo(1)–O(16)#1	1.995(4)	V(3)–O(18)	1.920(4)
Mo(1)–O(4)	2.505(7)	V(3)–O(16)	1.926(4)
Mo(2)–O(11)	1.664(4)	V(3)–O(24)	1.934(4)
Mo(2)–O(5)	1.872(5)	V(3)–O(23)	1.936(4)
Mo(2)–O(9)	1.875(5)	V(4)–O(15)	1.613(4)
Mo(2)–O(13)#1	1.967(4)	V(4)–O(19)	1.959(4)
Mo(2)–O(20)#1	1.985(4)	V(4)–O(20)	1.972(4)
Mo(3)–O(14)	1.661(4)	V(4)–O(16)	1.984(4)
Mo(3)–O(8)	1.867(4)	V(4)–O(18)	1.991(4)
Mo(3)–O(7)	1.876(4)	Co(1)–O(21)	2.049(4)
Mo(3)–O(19)	1.981(4)	Co(1)–N(1)	2.106(6)
Mo(3)–O(22)	1.994(4)	Co(1)–OW5	2.119(5)
Mo(3)–O(3)	2.508(7)	Co(1)–N(4)	2.120(5)
Mo(4)–O(12)	1.670(4)	Co(1)–N(3)	2.158(5)
Mo(4)–O(7)	1.862(5)	Co(1)–N(2)	2.185(5)
Mo(4)–O(9)	1.864(5)	Co(2)–N(5)	2.104(5)
Mo(4)–O(23)	1.979(4)	Co(2)–O(26)	2.110(4)
Mo(4)–O(18)	2.001(4)	Co(2)–N(6)	2.112(6)
V(1)–O(17)	1.598(4)	Co(2)–O(25)	2.120(4)
V(1)–O(13)	1.977(4)	Co(2)–N(8)	2.122(5)
V(1)–O(23)#1	1.983(4)	Co(2)–N(7)	2.140(5)
V(1)–O(22)	1.990(4)	P–O(2)	1.518(7)
V(1)–O(24)#1	1.997(4)	P–O(3)	1.529(7)
V(2)–O(6)	1.616(4)	P–O(1)	1.546(7)
V(2)–O(13)	1.932(4)	P–O(4)	1.551(7)

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

square pyramidal configuration. In each Mo_4 ring, four MoO_5 square pyramids are linked through four μ_2-O atoms, whereas the other non-terminal oxygen atoms are shared with neighboring VO_5 square pyramids in the V_8 central belt. The Mo–O and V–O bond lengths are in the range Mo–O_t 1.661(4)–1.670(4) Å, Mo–O_b 1.862(5)–2.001(4) Å, V–O_t 1.598(4)–1.613(4) Å, V–O_b 1.920(4)–1.997(4) Å, respectively. Each cobalt in the polyoxoanion $\{H_2PMo_3^{VI}Mo_5^{V}V_8^{IV}O_{44}[Co(phen)_2H_2O]_2\}^{2-}$ is octahedrally coordinated by four N atoms from two 1,10-phenantholine ligands, one terminal oxygen atom linked to V(3) at a cap site of tetracapped Keggin anion $[PMo_3^{VI}Mo_5^{V}V_8^{IV}O_{44}]^{8-}$ and one water molecule, with Co(1)–N bond distances of 2.106(5) – 2.158(5) Å, Co(1)–O_{21}, 2.049(4) Å, Co–Ow5, 2.119(5) Å and V(3)–O(21), 1.646(4) Å.

In the binuclear cation $\{[Co(phen)_2]_2C_2O_4\}^{2+}$, each cobalt center is coordinated by two bidentate 1,10-phenantholine ligands and two oxygen [O(25), O(26)] atoms of the oxalate group to form a distorted octahedron with Co–N bond lengths of 2.104(5)–2.140(5) Å and Co–O bond lengths of 2.110(4) and 2.120(4) Å. Two $[Co(phen)_2]^{2+}$ complexes are bridged by an oxalate group forming a binuclear counter cation.

The polyoxometalate derivative exhibits an interesting 3-D supramolecular framework. The four phenanthroline groups of each polyoxoanion extend along different

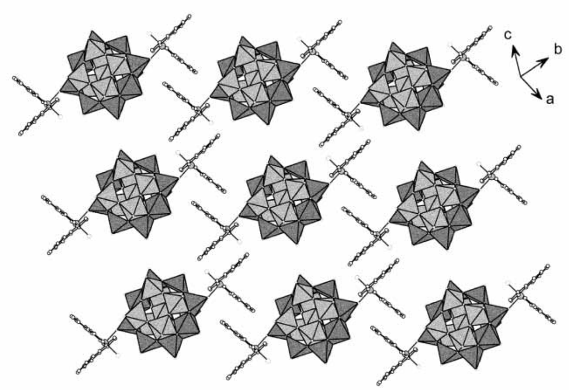


Figure 3. The π–π stacking interactions of compound **1**.

Table 3. Length of C–H $\cdots$ O hydrogen bond (Å) and angles (°) for the compound **1**.

C34 $\cdots$ O11	3.341(3)	C34–H34 $\cdots$ O11	137.05(0)
C27 $\cdots$ O17A	3.255(0)	C27–H27 $\cdots$ O17A	127.6(0)
C26 $\cdots$ O14B	3.248(3)	C26–H26 $\cdots$ O14B	129.93(0)
C37 $\cdots$ O6A	3.151(1)	C37–H37 $\cdots$ O6A	133.46(0)
C3 $\cdots$ O15C	3.312(2)	C3–H3 $\cdots$ O15C	145.63(0)
C3 $\cdots$ O19C	2.932(1)	C3–H3 $\cdots$ O19C	105.27(0)
C21 $\cdots$ O26D	3.152(1)	C21–H21 $\cdots$ O26D	137.86(0)
C17 $\cdots$ O1wE	3.377(3)	C17–H17 $\cdots$ O1wE	173.87(0)

Symmetry code: A: x, y, $1+z$; B: $-x$, $-y$, $2-z$; C: $-x$, $-1-y$, $1-z$; D: $1+x$, y, $1+z$; E: $-1-x$, $-1-y$, $-z$.

directions, and through π–π stacking interaction between phenanthroline groups with contact distances of 3.290(2) and 3.374(1) Å, respectively, form 2-D supramolecular layers (figure 3). The counter cations $\{[Co(phen)_2]_2C_2O_4\}^{2+}$ are arranged between the polyoxoanion layers, and the 3-D supramolecular framework is produced through π–π stacking interaction between phenanthroline groups of polyoxoanions and counter cation with contact distance of 3.418(1) Å. In fact, several types of hydrogen bonds (table 3) play important roles in constructing the 3-D supramolecular framework of compound **1**.

The assignment of oxidation states for the vanadium and molybdenum atoms are consistent with their coordination geometries and are confirmed by valence sum calculations which gives the values 5.42, 5.43, 5.41 and 5.39 for Mo(1), Mo(2), Mo(3) and Mo(4), respectively, while the calculated valence sums for V(1), V(2), V(3) and V(4) are 3.9, 4.2, 4.15 and 3.97, respectively [24]. The average value for calculated oxidation state of Mo and V are 5.41 and 4.06, respectively.

3.2. *ESR spectrum and X-ray photoelectron spectrum (XPS)*

The ESR spectrum of **1** at room temperature (figure 4) shows the weak signal of V^{4+} with $g = 1.957$, in accord with the results of valence sum calculations. The lack of the Mo^{5+} signal suggests the Mo^{5+} centers are delocalized. This is also proved by XPS measurements of compounds **1** and **2**. The XPS for **1** (figure 5), shows four overlapped

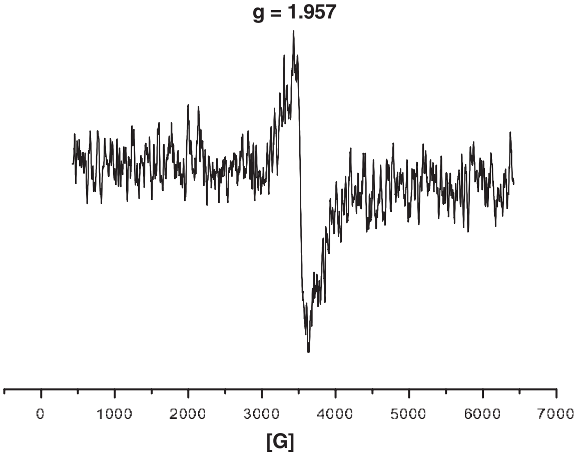
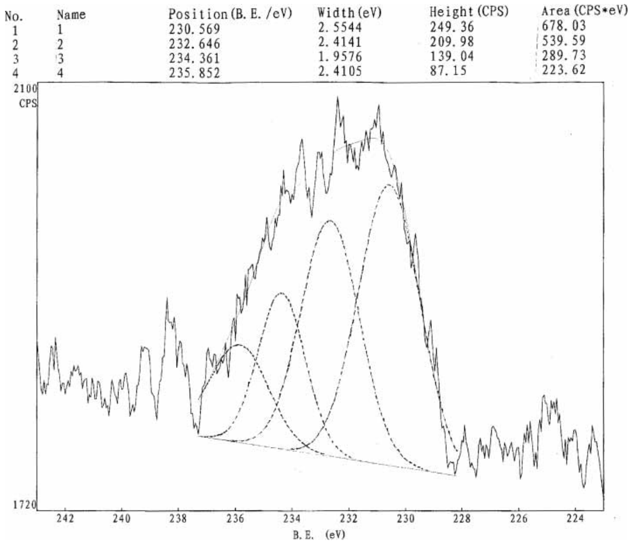


Figure 4. ESR spectrum for compound **1**, showing the signal of V^{4+}.



No.	Name	Position (B. E. /eV)	Width (eV)	Height (CPS)	Area (CPS*eV)
1	1	230. 569	2. 5544	249. 36	678. 03
2	2	232. 646	2. 4141	209. 98	539. 59
3	3	234. 361	1. 9576	139. 04	289. 73
4	4	235. 852	2. 4105	87. 15	223. 62

Figure 5. XPS for Mo in compound **1**.

peaks at 230.6, 232.6, 234.4 and 235.9 eV, ascribed to Mo^{5+} $3d_{5/2}$, Mo^{6+} $3d_{5/2}$, Mo^{5+} $3d_{3/2}$ and Mo^{6+} $3d_{3/2}$, respectively. These results further confirm Mo atoms are in mixed valences state.

3.3. *Magnetic property of 1*

The variable temperature magnetic susceptibility of **1** was measured from 2 to 299 K at 5000 Oe. The thermal variations of μ_{eff} and $1/\chi_{\text{m}}$ are displayed in figure 6. The plot of μ_{eff} versus T shows a μ_{eff} value of $9.37\mu_{\text{B}}\,\text{mol}^{-1}$ at 299 K and exhibits a continuous decrease on cooling to a value of $6.48\mu_{\text{B}}$ at 2 K. This behavior for μ_{eff} indicates an

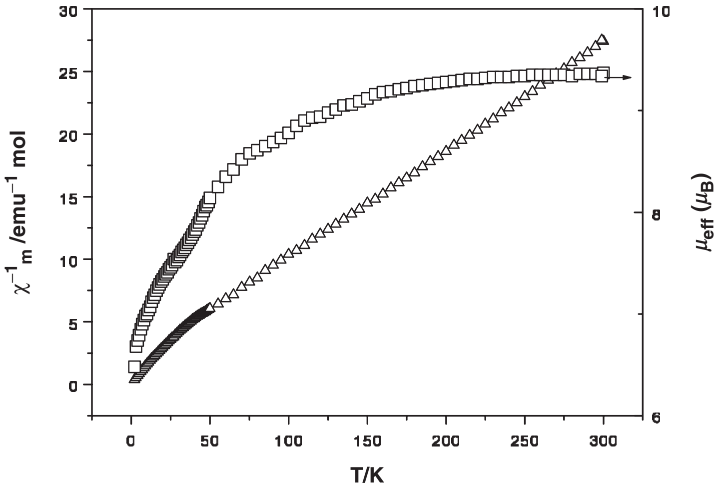


Figure 6. The effective magnetic movement μ_{eff} and inverse molar susceptibility *vs.* temperature for compound **1**.

antiferromagnetic interaction in **1**. The effective magnetic moment μ_{eff} value ($\mu_{\mathrm{eff}} = 9.37\mu_{\mathrm{B}}$) at room temperature is smaller than that expected for the total value of four uncoupled, $S = 3/2$ spin, Co^{2+} atoms and five uncoupled, $S = 1/2$ spin, Mo^{5+} atoms and eight uncoupled, $S = 1/2$ spin, V^{4+} atoms ($\mu_{\mathrm{eff}} = 12.11\mu_{\mathrm{B}}$ assuming $g = 2.0$ for Mo^{5+} and V^{4+} and $g = 2.68$ for Co^{2+}) [25], indicating antiferromagnetic coupling. Similar trends have also been observed in other high-nuclearity spin polyoxometalate clusters [25–27]. Unfortunately, it is too difficult to fit the experimental magnetic data of this heterometallic high nuclearity spin system by using a suitable theoretical model. However, the magnetic data of sample **1** obeys the Curie–Weiss law in the high-temperature region and fitting in the range 50–300 K gives value of $C = 11.65\,\mathrm{emu\,K\,mol^{-1}}$ and $\theta = -18.29\,\mathrm{K}$, characteristic of an overall antiferromagnetic interaction.

3.4. *The third-order non-linear optical (NLO) property of 1*

The third-order non-linear optical property of compound **1** was investigated at 532 nm with a 8 ns pulse width produced by a frequency-doubled Q-switched Nd: YAG laser in $1.95 \times 10^{-4}\,\mathrm{mol\,mL^{-3}}$ DMF solution, and revealed by using a Z-scan technique with a 5-mm-thick quartz cell. The results are displayed in figure 7, in which (a) and (b) depict the non-linear absorptive and refractive properties, respectively. The solid curve was obtained as a reasonably good fit between the experimental data and the theoretical curve. In accord with the observed α_2 and n_2 (α_2 and n_2 are effective third-order NLO absorptive and refractive coefficients, respectively), the modulus of the effective third-order susceptibility $\chi^{(3)}$ can be calculated by

$$|\chi^{(3)}| = \left[\left(9 \times 10^8 n_0^2 \varepsilon_0 c \lambda \alpha_2 / 8\pi^2\right)^2 + \left(n_0 c n_2 / 80\pi^2\right)^2\right]^{1/2} \tag{1}$$

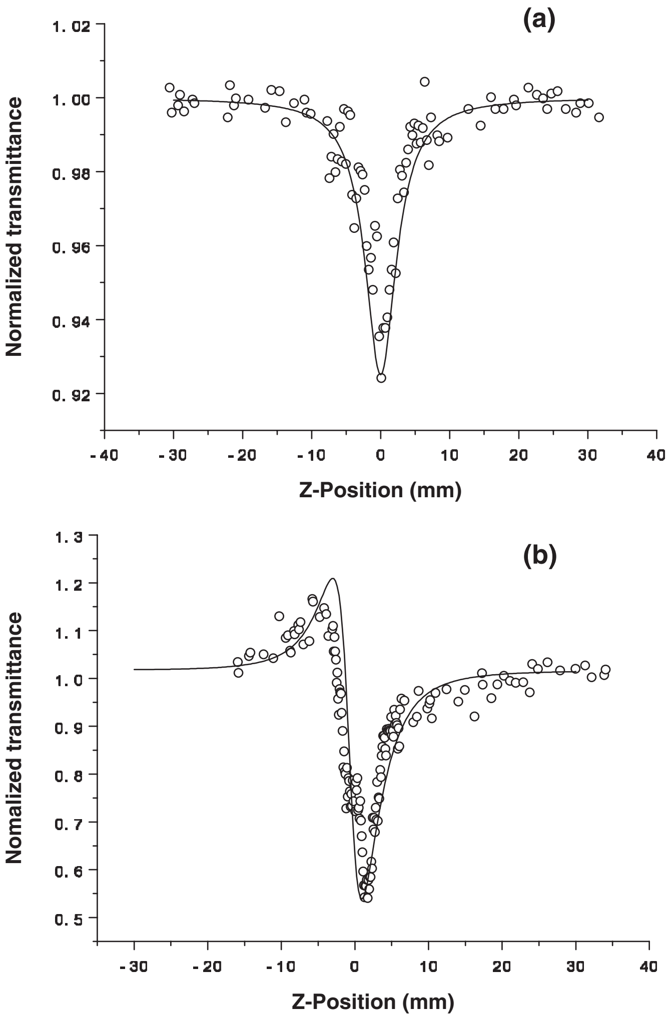


Figure 7. Z-scan data of 1.95×10^{-4} mol dm^{-1} of compound **1**. (a) Collected under the open aperture configuration (the solid curve is a theoretical fit). (b) Collected under the closed aperture configuration (the solid curve is a theoretical fit).

where λ is the wavelength of the laser light, n_0 is the linear refractive index of the sample (n_0 can be replaced by solvent if the concentration of the sample is very small), ε_0 and c are the permittivity and the speed of light in a vacuum, respectively. The corresponding modulus of the hyperpolarizability γ was obtained from $|\gamma| = |\chi^{(3)}|/\mathrm{NF}^4$ ($\mathrm{F}^4 = [(n_0{}^2 + 2)/3]^4$) in which N is the molecular number density of the compound in the sample and F^4 is the Lorents field correction factor.

The calculated results are listed in table 4. The $|\gamma|$ value of 2.834×10^{-29} esu for **1**, contrasts to other polyoxometalates [29]. Compound **1** exhibits third-order NLO property, and exhibits self-defocusing performance ($n_2 < 0$). Materials containing the self-defocusing property are excellent for applications in protection of optical sensors. With regard to the interrelation between structure and optical property, the nice

Table 4. Third-order non-linear optical property of the title compound.

Compounds	α_2 (mW^{-1})	n_2 ($m^2\ W^{-1}$)	$\chi^{(3)}$ (esu)	γ (esu)
Compound **1**	0.33×10^{-11}	-1.8×10^{-18}	1.1×10^{-11}	2.834×10^{-29}
$(C_9H_7NO)_4H_7PMo_{12}O_{40}\cdot3H_2O$ [29]			9.6×10^{-11}	3.6×10^{-29}
$(phen)_3H_7PMo_{12}O_{40}\cdot CH_3CN\cdot H_2O$ [29]			1.5×10^{-12}	8.86×10^{-31}

NLO property of compound **1** derives from the presence of larger delocalized space for electrons in the compound, provided by 1,10-phen ligands and the highly reduced polyoxoanion.

4. Conclusion

A novel mixed molybdenum–vanadium polyoxometalate supporting two transition metal complexes: $\{[Co(phen)_2]_2C_2O_4\}\{H_2PMo_3^{VI}Mo_5^{V}V_8^{IV}O_{44}[Co(phen)_2H_2O]_2\}\cdot7H_2O$ **1**, has been prepared by using hydrothermal synthesis techniques and thoroughly characterized. From the structure of **1**, the addition of transition metal moieties to the surface O atoms of a polyoxometalate provides an attractive strategy to decorate the periphery of these anions and thus alter their physical properties. The study of magnetic and NLO properties indicate that compound **1** exhibits antiferromagnetic coupling interactions and nice third-order NOL property with self-defocusing performance ($n_2 < 0$).

Supplementary data

Crystallographic data for the structures reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 217164. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336033: E-mail: deposit@ccdc.cam.ac.uk) or also from the author Ji-Qing Xu.

Acknowledgements

This work was supported by The State Key Basic Research Program of China (No. 2001 CB 108906), National Science Foundation of China (Nos. 20271021 and 20333070).

References

[1] M.T. Pope. *Herteropoly and Isopoly Oxometalates*, Springer-Verlag, Berlin (1983).
[2] V.W. Day, W.G. Klemperer. *Science*, **228**, 533 (1985).
[3] M.T. Pope, A. Müller. *Angew. Chem., Int. Ed. Engl.*, **30**, 34 (1991).
[4] M.T. Pope, A. Muller. *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer Academic Publishers, Dordrecht, and The Netherlands (1994).
[5] C.L. Hill. *Chem. Rev.*, **98**, 1 (1998).
[6] L.C.W. Baker, D.C. Glick. *Chem. Rev.*, **98**, 3 (1998).

[7] Y.P. Jeannin. *Chem. Rev.*, **98**, 51 (1998).
[8] P. Gouzerh, A. Proust. *Chem. Rev.*, **98**, 77 (1998).
[9] N. Mizuno, M. Misono. *Chem. Rev.*, **98**, 199 (1998).
[10] A. Müller, F. Peters, M.T. Pope, D. Gatteschi. *Chem. Rev.*, **98**, 239 (1998).
[11] E. Coronado, C.J. Gomez-Garcýa. *Chem. Rev.*, **98**, 273 (1998).
[12] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem., Int. Ed.*, **38**, 2638 (1999).
[13] J.Q. Xu, R.Z. Wang, G.Y. Yang. *Chem. Commun.*, 983 (1999).
[14] Y. Xu, J.Q. Xu, K.L. Zhang, Y. Zhang, X.Z. You. *Chem. Commun.*, 153 (2000).
[15] R.G. Finke, M.W. Droege. *J. Am. Chem. Soc.*, **106**, 7274 (1984).
[16] M. Pohl, Y. Lin, T.J.R. Weakley, K. Nomiya, M. Kaneko, H. Werner, R. Finke. *Inorg. Chem.*, **34**, 767 (1995).
[17] C.L. Pan, J.Q. Xu, G.H. Li, X.B. Cui, L. Ye, G.D. Yang. *Dalton Trans.*, 517 (2003).
[18] R.G. Finke. In *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, M.T. Pope, A. Müller (Eds.), p. 267, Kluwer Academic Publishers, Dordrecht, The Netherlands (1994).
[19] C.L. Pan, J.Q. Xu, D.Q. Chu, L. Ye, Z.L. Lü, T.G. Wang. *Inorg. Chem. Commun.*, **6**, 233 (2003).
[20] C.M. Liu, D.Q. Zhang, D.B. Zhu. *Cryst. Grow. Des.*, **3**, 363 (2003).
[21] G.Y. Luan, Y.G. Li, S.T. Wang, E.B. Wang. *J. Chem. Soc. Dalton Trans.*, 233 (2003).
[22] Y. Xu, H.G. Zhu, H. Hu, X.Z. You. *Chem. Commun.*, 787 (1999).
[23] Y. Xu, D.R. Zhu, Z.J. Guo, Y.J. Shi, K.L. Zhang, X.Z. You. *J. Chem. Soc., Dalton Trans.*, 772 (2001).
[24] I.D. Brown. In *Structure and Bonding in Crystals*, Vol. 2, p. 1, Academic Press, New York (1981).
[25] C.M. Liu, D.Q. Zhang, M. Xiong, D.B. Zhu. *Chem. Commun.*, 1416 (2002).
[26] D. Gatteschi, L. Pardi, A.L. Barra, A. Müller, J. Döring. *Nature*, **354**, 463 (1991).
[27] A.L. Barra, D. Gatteschi, L. Pardi, A.L. Barra, A. Müller, J. Döring. *J. Am. Chem. Soc.*, **114**, 8509 (1992).
[28] A. Müller, R. Sessoli, E. Krickemeyer, H. Bögge, J. Meyer, D. Gatteschi, L. Pardi, J. Westphal, K. Hovermeier, R. Rohlfing, J. Döring, F. Hellweg, C. Beugholt, M. Schmidtmann. *Inorg. Chem.*, **36**, 5239 (1997).
[29] Y.S. Zhou, E.B. Wang, J. Peng, J. Liu, C.W. Hu, R.D. Huang, X.Z. You. *Polyhedron*, **18**, 1419 (1999).