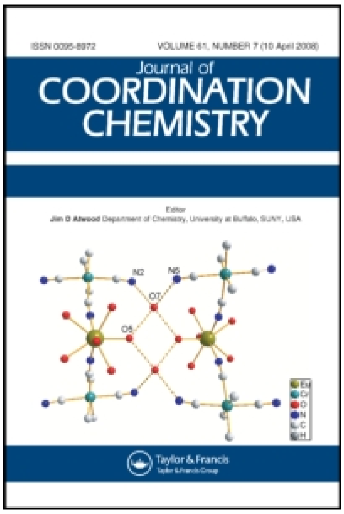

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A novel cobalt(II) complex with polyoxometalate-based ligand by virtue of coexistence of both a capped-Keggin anion and a neutral unit

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A novel cobalt(II) complex with polyoxometalate-based ligand by virtue of coexistence of both a capped-Keggin anion and a neutral unit

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A new bicapped Keggin heteropolyoxoanion derivative $[Co(bpy)_3]_2[PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2]$ $[\{Co(bpy)_2(H_2O)\}_2\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}] \cdot 8H_2O$ (**1**) (bpy = 2,2′-bipyridine), has been hydrothermally synthesized and structurally characterized by elemental analysis, single crystal X-ray diffraction, IR and X-ray photoelectron spectra. Complex **1** consists of two $[Co(bpy)_3]^{2+}$ cations, an anion of $[PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2]^{4-}$ and a neutral unit $[\{Co(bpy)_2(H_2O)\}_2$ $\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}]$ in which $\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}^{4-}$ is coordinated to two Co atoms through its terminal oxygen atoms of the two capping V atoms at opposite sites together with bipyridine and water ligands. The most interesting feature of **1** is that a polyoxoanion and a neutral component coexist in the crystal structure. Hydrogen-bonding contacts are also formed between different polyanions through the lattice water molecules.

Keywords: Organic–inorganic hybrid material; Hydrothermal synthesis; Polyoxometalate; Cobalt complex

1. Introduction

The rapid progress of exploring inorganic/organic hybrid materials is driven by interest in combining the different characteristics of the components to obtain unusual magnetic, electrical and optical properties for applications in the field of contemporary material science [1]. Using polyoxometalates (POM) as building blocks has become a fascinating direction that can expand the potential applications of POMs in areas of catalysis, medicine and materials [2–10]. Recently, a large number of POM-based organic–inorganic hybrid materials have been prepared as solid state coordination

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polymers, molecular crystals and ultrathin composite films, etc. [11–21]. There are two methods to prepare such POM-based hybrid materials. One is the use of simple starting materials, such as molybdate and tungstate (MoO_4^{2-} and WO_4^{2-}), such that the composition and structure of the product cannot be predicted. The other is by using POMs as the ligand, allowing the synthetic reaction to occur *via* linkage between external oxygen atoms (ligand atom) of POM anions and the other component. Obviously, the latter should be a favourable way to conduct the molecular design and structural prediction, because the ligand role of POM anion is manifest in the structure of the resulting product.

By means of the latter procedure, some coordination compounds containing both Keggin or pseudo-Keggin anions and other complex cations have been reported recently [22–28]. For instance, a dinuclear copper complex with a Keggin polyoxometalate $K_{14}[\{Cu_2(bpy)_2(ox)_3\}\{SiW_{11}O_{39}Cu(H_2O)\}]_2[SiW_{11}O_{39}Cu(H_2O)] \cdot 5H_2O$, consisting of corrugated chains of alternating $[Cu_2(bpy)_2(ox)_3]^{2+}$ and $[SiW_{11}O_{39}Cu(H_2O)]^{6-}$ building blocks [22]; a 1D POM-based composite compound $[\{Gd(NMP)_6\}(PMo_{12}O_{40})]_n$ (NMP = N-methyl-2-pyrrolidone), containing zigzag-type chains with both alternating $[Gd(NMP)_6]^{3+}$ cation and $[PMo_{12}O_{40}]^{3-}$ anions through Mo–Ot–Ga–Ot–Mo linkage [23]; a two-dimensional coordination compound $[Co(en)_2][Co(bpy)_2]_2[PMo_5^{VI}Mo_3^{V}V_8^{IV}O_{44}] \cdot 4.5H_2O$ [24], where pseudo-Keggin anions are linked by two types of complex fragments; $[\{Na(dibenzo\text{-}18\text{-}crown\text{-}6)(MeCN)\}_3\{PMo_{12}O_{40}\}]$ [25], in which a single MoO_3 from a Keggin anion is coordinated to three $[Na(dibenzo\text{-}18\text{-}crown\text{-}6)(MeCN)]^+$ cations; $[Ni(phen)_3][PMo_9^{VI}Mo_3^{V}O_{40}\{Ni(phen)\}_2]$ [26], in which the Keggin anion is capped by two Ni atoms through four bridging oxo groups; and $[\{Ba(DMSO)_5(H_2O)\}_2(SiMo_{12}O_{40})]$ and $[\{Ba(DMSO)_3(H_2O)_3\}\{Ba(DMSO)_5(H_2O)\}(GeMo_{12}O_{40})]$, in which the $\{Ba(DMSO)_5(H_2O)\}^{2+}$ cation is bonded with the Keggin anion [27]. These examples suggest that the negative charge density on the external oxygen atoms (ligand atoms) of a POM anion is a vital factor in ligand reactivity. From previous research, it is known that the central heteroatom in a Keggin anion could directly affect the charge density of an external oxygen of the POM anion. Therefore, the synthesis of this type of coordination compounds containing Keggin anionic clusters with different central heteroatoms is of considerable significance in finding the relationship of heteroatom-reactivity-structure. While more structural and functional properties of coordination compounds are needed, the synthesis and structural characterization of new polyoxoanion-based complexes still remain a challenge.

Here we report the hydrothermal synthesis and structural characterization of an unexpected bicapped, Keggin-type derivative $[Co(bpy)_3]_2[PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2][\{Co(bpy)_2(H_2O)\}_2\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}] \cdot 8H_2O$ using the Dawson-type polyoxometalate of $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ as the starting material. To our knowledge, this is the first example that a polyoxoanion and a neutral component coexist in the same crystal structure.

2. Experimental

2.1. *Materials and methods*

All chemicals purchased were of reagent grade and used without further purification, and $H_6P_2Mo_{18}O_{62} \cdot nH_2O$ was prepared according to the literature method [29].

Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. P, Mo, V and Co were determined by a Leaman inductively coupled plasma (ICP) spectrometer. The IR spectra were obtained in the range $400–4000\,\mathrm{cm}^{-1}$ on the Alpha centaure FT/IR spectrophotometer using KBr pellets. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a Mg–Kα (1253.6 eV) achromatic X-ray source.

2.2. *Synthesis*

The title complex was hydrothermally synthesized under autogenous pressure. A mixture of $\mathrm{NH_4VO_3}$ (0.08 g), $\mathrm{H_6P_2Mo_{18}O_{62}\cdot nH_2O}$ (0.12 g), $\mathrm{CoCl_2}$ (0.024 g), 2,2′-bpy (0.03 g) and water (10 mL) was simply stirred and then sealed in a 15 mL Teflon-lined autoclave, which was heated to 180°C for four days. After slow cooling to room temperature at a rate of $10^{\circ}\mathrm{C\,h^{-1}}$, black block crystals of compound **1** separated as a major phase (65% yield based on Mo) together with an unidentified dark-green powder. Anal. Calc. for **1**: C, 21.6; H, 1.81; N, 5.06; O, 27.1; P, 1.12; Mo, 27.26; Co, 4.26; V, 11.07. Found: C, 22.0; H, 1.84; N, 5.31; O, 28.4; P, 1.07; Mo, 27.20; Co, 3.88; V, 10.30.

2.3. *X-ray crystallographic analysis*

The structure of compound **1** was determined by single crystal X-ray diffraction. A single black crystal with approximate dimensions of $0.45 \times 0.36 \times 0.28$ mm was mounted to the end of a glass fiber capillary. Data were collected on a Rigaku R-AXIS RAPID IP diffractometer at 293 K using graphite-monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å) and oscillation scans technique in the range of $0.84 < \theta < 24.00^{\circ}$. An empirical absorption correction was applied. A total of 17452 (10633 unique, $R_{\mathrm{int}} = 0.0555$) reflections were measured. The structure was solved by direct methods using the program SHELXS-97 and refined by Full-matrix least-squares methods on F^2 using the SHELXL-97 program package. All the non-hydrogen atoms were refined anisotropically. Structure solution and refinement based on 10633 independent reflections with $I > 2\sigma(I)$ and 1256 parameters gave $R_1(wR_2) = 0.0712\ (0.2017)$. In addition, the $\mathrm{PO_4}$ tetrahedra in **1** are disordered over two locations. The occupancies over two sites are 0.5, respectively. Crystal data for **1** are summarized in table 1. Selected bond lengths are given in table 2. CCDC reference number is 238133.

3. Results and discussion

3.1. *Structure description*

The crystal structure of complex **1** consists of two $[\mathrm{Co(bpy)_3}]^{2+}$ cations, a bicapped, pseudo-Keggin polyoxoanion $[\mathrm{PMo}_8^{\mathrm{VI}}\mathrm{V}_3^{\mathrm{V}}\mathrm{V}_3{}^{\mathrm{V}}\mathrm{V}^{\mathrm{IV}}\mathrm{O}_{40}(\mathrm{V}^{\mathrm{IV}}\mathrm{O})_2]^{4-}$, a neutral unit $[\{\mathrm{Co(bpy)_2(H_2O)}\}_2\{\mathrm{PMo}_8^{\mathrm{VI}}\mathrm{V}_3^{\mathrm{V}}\mathrm{V}^{\mathrm{IV}}\mathrm{O}_{40}(\mathrm{V}^{\mathrm{IV}}\mathrm{O})_2\}]$ and eight water molecules. The structure of the polyoxoanion $[\mathrm{PMo}_8^{\mathrm{VI}}\mathrm{V}_3^{\mathrm{V}}\mathrm{V}^{\mathrm{IV}}\mathrm{O}_{40}(\mathrm{V}^{\mathrm{IV}}\mathrm{O})_2]^{4-}$ (shown in figure 1a) is based on the Keggin structure capped with two additional $\{\mathrm{VO}\}^{2+}$ units similar to that in $[\mathrm{PMo}_6^{\mathrm{VI}}\mathrm{Mo}_2^{\mathrm{V}}\mathrm{V}_8^{\mathrm{VI}}\mathrm{O}_{44}]^{5-}$ [20] and $[\mathrm{PMo}_8^{\mathrm{VI}}\mathrm{V}_4^{\mathrm{VI}}\mathrm{V}_2^{\mathrm{V}}\mathrm{O}_{42}]^{5-}$ [31]. As shown in figure 1(b),

Table 1. Crystal data and structure refinement.

Formula	$C_{100}H_{100}Co_4Mo_{16}N_{20}O_{94}P_2V_{12}$
Formula weight	5529.98
T/K	293(2)
λ/Å	0.71073
Crystal system	$P\bar{1}$
Space group	Triclinic
Unit cell dimensions	$a = 12.996(3)$ Å $\alpha = 86.44(3)^\circ$ $b = 13.951(3)$ Å $\beta = 82.89(3)^\circ$ $c = 24.527(5)$ Å $\gamma = 63.08(3)^\circ$
V/Å^3	3934.6(14)
Z, D_c/g cm^{-3}	2, 2.334
μ/mm^{-1}	2.438
F(000)	2678
Reflections collected	17452
Independent reflections	10633 [R(int) = 0.0555]
Data/restraints/parameters	10633/0/1256
Goodness-of-fit on F^2	1.030
Final R indices [$I > 2\sigma(I)$][a]	$R1 = 0.0712$, w$R2 = 0.2017$
R indices (all data)[a]	$R1 = 0.0778$, w$R2 = 0.2093$

[a] $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

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

Mo(1)–O(1)	1.655(9)	Mo(1)–O(34A)	1.704(18)
Mo(1)–O(25)	1.800(9)	Mo(1)–O(15)	2.053(8)
Mo(1)–O(13)	2.054(8)	Mo(1)–O(23)#1	2.371(14)
Mo(2)–O(2)	1.646(8)	Mo(2)–O(37A)	1.697(15)
Mo(2)–O(33B)	2.009(19)	Mo(2)–O(13)	2.039(9)
Mo(2)–O(20)	2.053(9)	Mo(2)–O(44)	2.508(15)
Mo(3)–O(3)	1.636(8)	Mo(3)–O(26)	1.793(8)
Mo(3)–O(32B)	1.934(16)	Mo(3)–O(16)	2.029(8)
Mo(3)–O(20)	2.048(8)	Mo(3)–O(44)	2.360(13)
Mo(4)–O(4)	1.642(8)	Mo(4)–O(31)	1.786(9)
Mo(4)–O(18)	1.814(9)	Mo(4)–O(16)	2.047(7)
Mo(4)–O(15)	2.068(8)	Mo(4)–O(45)	2.433(13)
V(1)–O(11)	1.645(7)	V(1)–O(20)	1.904(9)
V(1)–O(16)	1.913(8)	V(1)–O(15)	1.919(8)
V(1)–O(13)	1.937(8)	V(2)–O(19)	1.599(8)
V(2)–O(34A)#1	1.845(19)	V(2)–O(26)	1.883(9)
V(2)–O(31)	1.898(10)	V(2)–O(33B)#1	1.95(2)
V(2)–O(23)	2.429(12)	V(3)–O(12)	1.596(8)
V(3)–O(18)	1.881(9)	V(3)–O(37A)#1	1.900(15)
V(3)–O(25)	1.918(9)	V(3)–O(32B)#1	2.041(17)
V(3)–O(44)#1	2.425(13)	P(2)–O(46)	1.449(12)
P(2)–O(45)	1.466(14)	P(2)–O(23)	1.601(13)
P(2)–O(44)	1.624(13)	Co(2)–O(11)	2.073(8)
Co(2)–N(9)	2.098(11)	Co(2)–N(7)	2.111(9)
Co(2)–OW1[a]	2.130(9)	Co(2)–N(8)	2.139(9)
Co(2)–N(10)	2.147(10)		

[a] Oxygen atom from water molecule.

two {Mo_4} layers and one {V_4} layer exist in the structure, which are distributed alternately. The vanadium atoms show two coordination environments, that is, the {VO_6} octahedron and the capped unit {VO_5} a distorted square pyramid. The bond lengths of V–O in the octahedron are in the range of 1.596(8)–2.429(12) Å and the

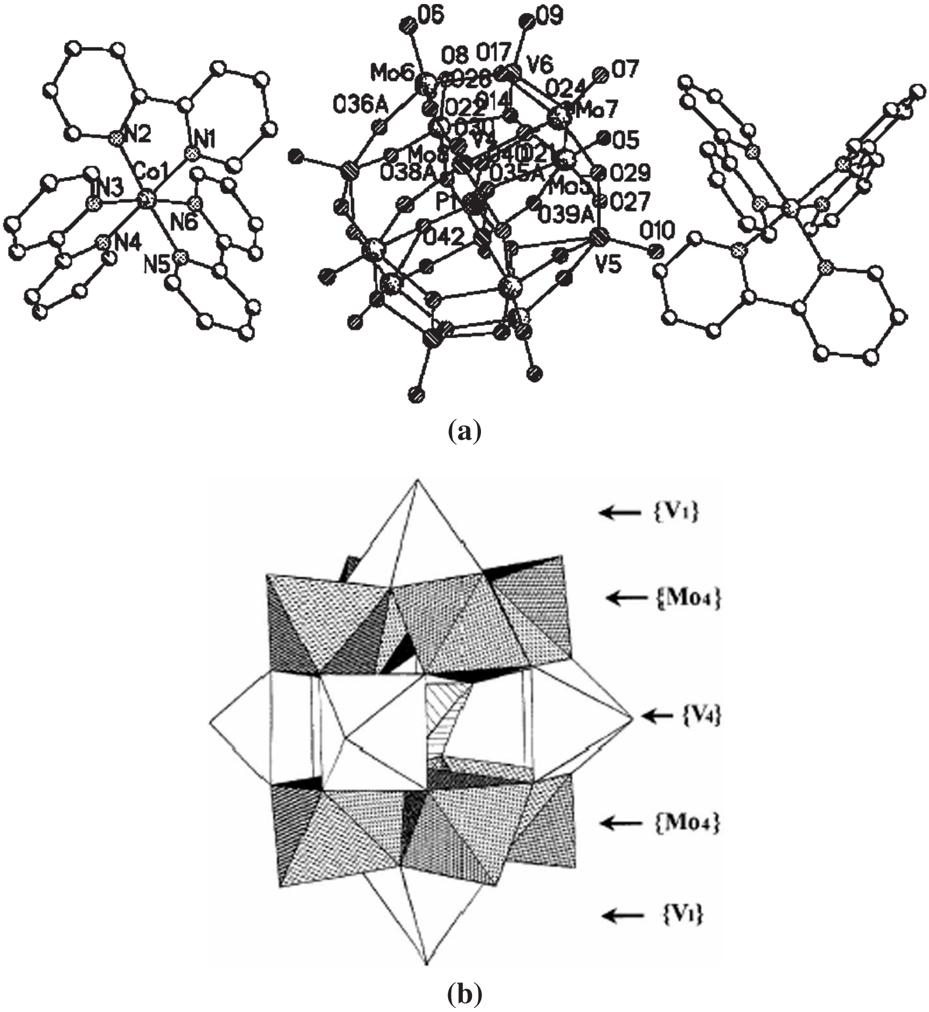

Figure 1. (a) An ORTEP view of the polyanion $\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}^{4-}$ and the cations $[Co(bpy)_3]^{2+}$.

V–O distances in the capped units are in the range 1.581(8)–1.937(8) Å. The bond angles are 70.1(6)–167.79(6)°. All molybdenum atoms have a distorted $\{MoO_6\}$ octahedral environment with Mo–O distances 1.627(8)–2.508(15) Å and bond angles 65.0(4)–162.6(5)°. The P–O distances in the distorted PO_4 tetrahedron are 1.447(12)–1.637(13) Å and the O–P–O angles are 103.9(7)–112.3(7)°. The values of bond valence sum (BVS) calculations give the values 5.88, 6.11, 6.08 and 6.27 for Mo(1)–Mo(4) (2×), respectively. The calculated average value for the oxidation state of molybdenum is 6.08. The values of BVS for V(1)–V(3) (2×) atoms are 4.25, 4.82 and 4.39 with an average value of 4.48 (expected value 4.50 for $V_3^{V}V_3^{VI}$). It is thus obvious from the values that in the polyanion of **1**, all Mo centers show a +6 oxidation state, while the V centers are in a mixed-valence state.

An unusual feature of complex **1** is that it consists of a neutral unit $[\{Co(bpy)_2(H_2O)\}_2\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}]$, in which $\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}^{4-}$

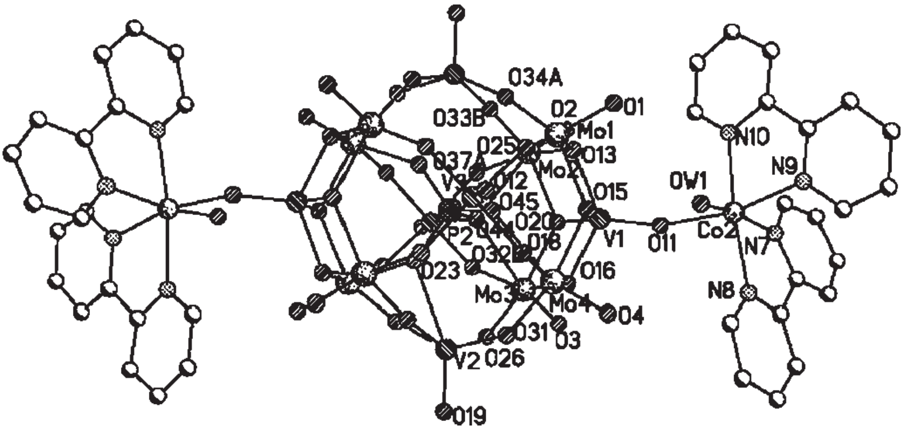

Figure 2. An ORTEP view of the neutral unit $[\{Co(bpy)_2(H_2O)\}_2\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}]$.

is coordinated to two Co atoms through its terminal oxygen atoms of the two capping V atoms at the opposite sites together with bipyridine and water ligands (figure 2). The coordination bond lengths for Co(2) range from 2.098(11) to 2.147(10) Å in which the Co–N bond lengths are longer than Co–O bond lengths. The bond valence sum (BVS) calculations give the values 5.80, 6.03, 6.34 and 6.13 for Mo(5)–Mo(8) (2×), with the average value 6.07, showing all Mo centers to be in the +6 oxidation state. The V centers with an average BVS value of 4.52 (expected value 4.50 for $V_3^{V}V_3^{VI}$) indicate that the V centers are also in a mixed-valence state.

The Co atoms in compound **1** have two coordination environments: In the cation $[Co(bpy)_3]^{2+}$, each Co is coordinated to six N atoms from three 2,2′-bipyridine molecules, while in the neutral part $[\{Co(bpy)_2(H_2O)\}_2\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}]$ the Co atom is linked with four N atoms from two 2,2′-bipyridine molecules, two oxygen atoms from both a water molecule and a Keggin anion with the distances of 2.111(9) Å for Co2–N7, 2.139(9) Å for Co2–N8, 2.098(11) Å for Co2–N9, 2.147(10) Å for Co2–N10, 2.078(8) Å for Co2–O11, 2.130(9) Å for Co2–Ow1.

Another noteworthy feature in **1** is that both the polyoxoanion $[PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2]^{4-}$ and the neutral unit $[\{Co(bpy)_2(H_2O)\}_2\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}]$ coexist in the same crystal structure. The possible reason is the modifying effect of the transition metal complex on the surface of polyoxometalates [26]. A similar case occurred in $K_3[\varepsilon\text{-}PMo_{12}O_{36}(OH)_4\{La(H_2O)_{4.25}Cl_{0.75}\}_4][\alpha\text{-}PMo_{12}O_{40}]\cdot 28H_2O$ [32]. Moreover, the structure of **1** shows an extended three-dimensional supramolecular network through π–π interactions and hydrogen bond contacts.

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

In the IR spectrum of compound **1**, four intense bands at 971, 939, 768 and 725 cm^{-1} can be attributed to $\nu_{as}(P\text{–}O_a)$, $\nu_{as}(M{=}O_d)$, $\nu_{as}(M\text{–}O_b\text{–}M)$ and $\nu_{as}(M\text{–}O_c\text{–}M)$ (M=Mo or V), respectively, indicating that the Keggin structure of POM still remains. In the X-ray photoelectron spectrum, as show in figure 3(a), the presence of Mo(3d5/2) satellite peak at 231.6 eV indicates the +6 oxidation state for molybdenum in

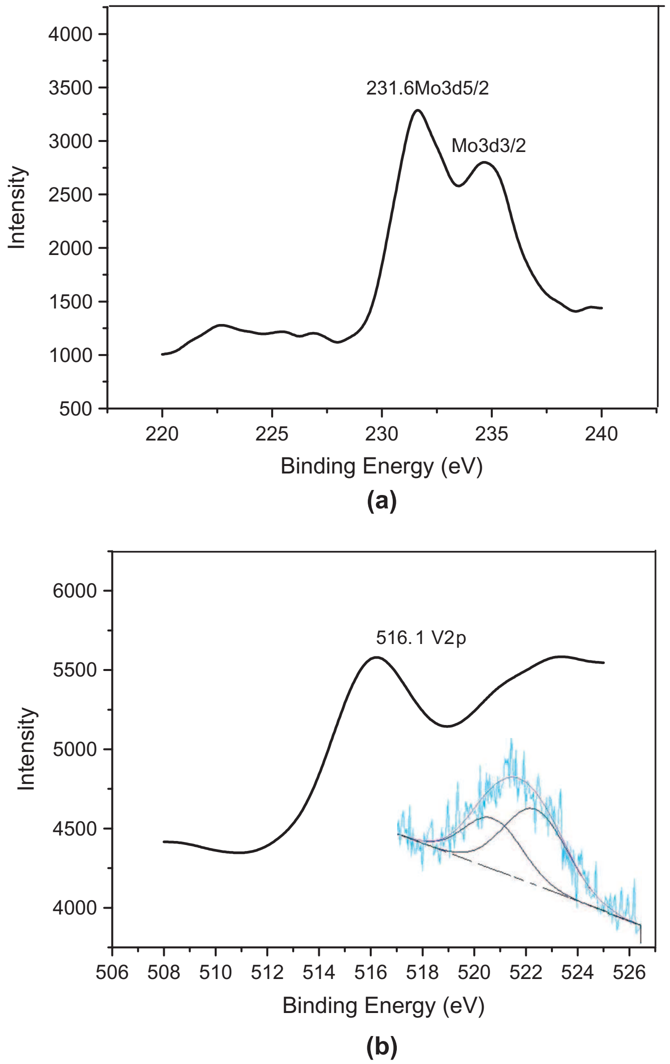

Figure 3. (a) XPS spectrum of Mo3d5/2 in compound **1** and (b) XPS spectrum of V2p in compound **1**.

compound **1** [33]. Two overlapped peaks at 515.4 eV and 516.7 eV (figure 3b) reveal that the mixed valences of V(V) and V(IV) coexist in compound **1** [34].

4. Conclusion

A new bicapped Keggin heteropolyoxoanion derivative $[Co(bpy)_3]_2[PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2][\{Co(bpy)_2(H_2O)\}_2\{PMo_8^{VI}V_3^{V}V^{IV}O_{40}(V^{IV}O)_2\}] \cdot 8H_2O$ has been hydrothermally synthesized and structurally characterized. In compound **1**, both the polyoxoanion and the neutral unit based on the polyoxoanion coexist in the same crystal structure. This is the first example that a polyoxoanion and a neutral component coexist in the same crystal structure. The successful preparation of this compound offers a valuable clue for the design and fabrication of POM-based solid-state materials with novel structures.

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