

# A novel hybrid crystal of chiral racemic complexes coexisting with two kinds of polyoxomolybdates: synthesis and structure of $[\text{Co}(\text{bpy})_3]_2[\text{Mo}_6\text{O}_{19}] [\beta\text{-(H}_2\text{Mo}_8\text{O}_{26})] \cdot 4\text{H}_2\text{O}$

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## Abstract

A novel polyoxometalate-based organic–inorganic hybrid compound,  $[\text{Co}(\text{bpy})_3]_2[\text{Mo}_6\text{O}_{19}] [\beta\text{-(H}_2\text{Mo}_8\text{O}_{26})] \cdot 4\text{H}_2\text{O}$  (**1**), have been hydrothermally synthesized and structurally characterized by elemental analysis, single-crystal X-ray diffraction, IR and X-ray photoelectron spectra. Compound **1** represents the first example that racemic complexes coexisting with two kinds of polyoxomolybdate anions in the same crystal architecture, which should be of rare chance that four kinds of complexes crystallizes into a compound.

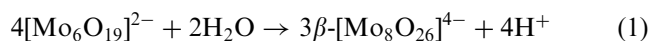
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**Keywords:** Hydrothermal synthesis; Racemic complexes; Polyoxometalates; Octamolybdate; Crystal structure

## 1. Introduction

Polyoxometalates (POMs) are an immense class of metal–oxygen cluster compounds, which exhibit compositional diversity and structural versatility, as well as molecular identity in both the solid state and the solutions [1]. Because of these above characteristics together with their remarkable physicochemical properties, POMs have attracted considerable attention on their academic significance and potential applications in a variety of fields, including catalysis, analytic chemistry, medicine, and materials science [2]. Recently, a great deal of research efforts have been paid to the functionalization of POMs with an organic component or transition metal complex [3], so that more organic–inorganic hybrid materials were successfully prepared by using POMs as building blocks.

It is well known that hexamolybdate anion  $[\text{Mo}_6\text{O}_{19}]^{2-}$  (Lindqvst-type structure) and octamolybdate anion  $\alpha$ - and  $\beta$ -isomer  $[\text{Mo}_8\text{O}_{26}]^{4-}$  have become effective building blocks in many POM-organic hybrids [4]. To rationally design and control the structures of the POM-organic hybrids, it is of great importance to establish the structural stabilities and convertibilities of these POM anions in aqueous solution. A lot of previous research literature provided various spectral and electrochemical data to elucidate the structural stabilities and convertibilities mechanism of  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and  $\alpha$ -,  $\beta$ - $[\text{Mo}_8\text{O}_{26}]^{4-}$  anions in aqueous solution, such as the following equation[5]:



but the direct crystallographic evidence, showing the coexistence of both  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  anions in the aqueous  $[\text{MoO}_4]^{2-}$  solution, has not been reported up to now, except that Hagrman et al.

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synthesized a crystalline compound containing both  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  anions from the starting material of  $\text{MoO}_3$  [6]. In fact, the pH-dependence and hydrolytic complexity of polymolybdates make the direct determination of such coexistence very difficult. Interestingly, while trying to synthesize a desired heteropolymolybdate with transition metal complex in the aqueous  $[\text{MoO}_4]^{2-}$  solution, we unexpectedly obtained a crystal hybrid in which racemic complexes  $(\pm)[\text{Co}(\text{bpy})_3]$  coexist with both  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  anions. Here, we report the hydrothermal synthesis and structural characterization of a novel organic–inorganic hybrid,  $[\text{Co}(\text{bpy})_3]_2[\text{Mo}_6\text{O}_{19}][\beta\text{-}(\text{H}_2\text{Mo}_8\text{O}_{26})]\cdot 4\text{H}_2\text{O}$  (**1**). Several previous reports by Müller and co-worker have indicated that the polymeric isopolyoxomolybdate species are possible to coexist in the aqueous  $[\text{MoO}_4]^{2-}$  solution [7,8]. Our result further suggests that by keeping an appropriate range of pH value, two or more kinds of POM anions may stably coexist in the solution, so that a crystal structure of the coexistence phase can form under rational reaction condition. This result also provides an useful information to develop crystal engineering based on POM building blocks.

## 2. Experimental

### 2.1. Synthesis and characterization

The compound **1** in the form of light yellow crystals was prepared by the hydrothermal reaction of  $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ , Mo,  $\text{H}_2\text{SeO}_4$ ,  $\text{CoCl}_2$ , 2,2'-bipyridine and  $\text{H}_2\text{O}$  in a molar ratio 3:1:3:1:2:1500 at  $190^\circ\text{C}$  for 84 h (75% yield based on Mo). From the repeated synthetic experiments, we found the crystallization to be highly sensitive to pH value of the starting mixture, then the rational condition to successfully obtain crystals of **1** should be to keep the solution pH value in 2–3 range. Below the pH value, there were only microcrystals of **1**, but the product of **1** did not appear above pH 5. Although the starting material  $\text{H}_2\text{SeO}_4$  was not related with the composition of **1** and product **1** did not appear if replacing  $\text{H}_2\text{SeO}_4$  by  $\text{H}_3\text{PO}_4$ , the real role of  $\text{H}_2\text{SeO}_4$  in the synthesis is unknown at present. Elemental analysis (ICP-AES) showed that the mole ratio of Co:Mo was 1:7 and CHN analyses performed on a Perkin–Elmer 2400 Elemental Analyzer gave the results found: C, 22.64%; H, 1.80%; N, 5.15% (calculated: C, 22.57%; H, 1.83%; N, 5.26%).

IR spectra were obtained in the range  $400\text{--}4000\text{ cm}^{-1}$  on the Alpha centaure FT/IR spectrophotometer using KBr pellets. XPS analysis was performed on a VG ESCALAB MK II spectrometer with a  $\text{MgK}\alpha$  ( $1253.6\text{ eV}$ ) achromatic X-ray source.

### 2.2. X-ray crystallography

A single crystal of compound **1** with  $0.378 \times 0.874 \times 0.461\text{ mm}$  was mounted on a Rigaku R-AXIS RAPID IP diffractometer at  $293\text{ K}$  using a graphite-monochromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) and oscillation scans technique in the range of  $2.03^\circ < \theta < 27.48^\circ$ . The absorption correction has been performed using  $\psi$  scan technique during data collection. A total of 14175 (8664 unique,  $R_{\text{int}} = 0.0295$ ) reflections were measured. The structure was solved by the direct method and refined on  $F^2$  by full-matrix least-squares using the SHELXTL-97 program package giving a final  $R_1 = 0.0375$ ,  $wR_2 = 0.0954$  and  $\text{GOF} = 1.134$  with respect to 8664 unique observed reflections with  $I > 2\sigma(I)$ . The two free water molecules were refined as disorderly models, which occupied two equivalent positions with the same probability, respectively. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were generated in their idealized positions. A summary of the crystallographic data and structural determination for compound **1** is listed in Table 1. Selected bond lengths and angles are provided in Table 2. Atomic coordinates and equivalent isotropic displacement parameters are given in Table S1(ESI).

## 3. Results and discussion

Although some previous reports have observed the possible coexistence of two or more isopolyoxomolyb-

Table 1  
Crystal data and structure refinement

Molecular formula	$\text{C}_{60}\text{H}_{58}\text{Co}_2\text{Mo}_{14}\text{N}_{12}\text{O}_{49}$	
Formula weight	3192.18	
$T(\text{K})$	293(2)K	
$\lambda(\text{\AA})$	0.71073A	
Crystal system	P-1	
Space group	Triclinic	
Unit cell dimensions	$a = 10.708(2)\text{ \AA}$	$\alpha = 96.25(3)^\circ$
	$b = 10.847(2)\text{ \AA}$	$\beta = 102.10(3)^\circ$
	$c = 19.926(4)\text{ \AA}$	$\gamma = 104.41(3)^\circ$
$V(\text{\AA}^3)$	2159.8(7)	
$Z, \rho_c(\text{g cm}^{-3})$	2, 2.45	
$\mu(\text{mm}^{-1})$	2.434	
$F(000)$	1534	
Reflections collected	14175	
Indenpant reflections	8664 [ $R(\text{int}) = 0.0295$ ]	
Data/restraints/parameters	8864/0/627	
Goodness-of-fit on $F^2$	1.134	
Final $R$ indices		
$[I > 2\sigma(I)]^a$	$R_1 = 0.0375, wR_2 = 0.0954$	
$R$ indices (all data) <sup>a</sup>	$R_1 = 0.0416, wR_2 = 0.0979$	

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]^{1/2}$ .

Table 2

Selected bond lengths (Å) and angles (°) for compound 1<sup>a</sup>

Mo(1)–O(5)	1.698(3)	Mo(1)–O(1)	1.700(3)
Mo(1)–O(11)	1.903(3)	Mo(1)–O(9) <sup>b</sup>	2.004(3)
Mo(1)–O(10) <sup>b</sup>	2.309(3)	Mo(1)–O(8)	2.333(3)
Mo(2)–O(2)	1.696(4)	Mo(2)–O(12)	1.899(3)
Mo(2)–O(8)	1.988(3)	Mo(2)–O(9)	2.383(3)
Mo(3)–O(3)	1.704(4)	Mo(3)–O(12)	1.927(3)
Mo(3)–O(13)	2.309(3)	Mo(3)–O(10)	2.479(3)
Mo(4)–O(4)	1.696(3)	Mo(4)–O(13)	1.748(3)
Mo(4)–O(8)	1.946(3)	Mo(4)–O(10)	2.397(3)
Mo(5)–O(15)	1.686(5)	Mo(5)–O(18)	1.868(4)
Mo(5)–O(19)	1.927(5)	Mo(5)–O(14)	2.320(4)
Mo(6)–O(16)	1.682(4)	Mo(6)–O(17)	1.864(4)
Mo(6)–O(21)	1.916(4)	Mo(6)–O(22)	1.930(4)
Mo(6)–O(18) <sup>c</sup>	1.984(5)	Mo(6)–O(14)	2.3237(12)
Co(1)–N(4)	1.929(4)	Co(1)–N(1)	1.935(4)
Co(1)–N(6)	1.935(4)	Co(1)–N(2)	1.936(4)
Co(1)–N(3)	1.941(4)	Co(1)–N(5)	1.949(4)
O(5)–Mo(1)–O(1)	104.75(18)	O(5)–Mo(1)–O(11)	100.75(17)
O(5)–Mo(1)–O(8)	86.73(14)	O(1)–Mo(1)–O(8)	165.27(15)
O(1)–Mo(1)–O(9) <sup>b</sup>	196.72(16)	O(11)–Mo(1)–O(9) <sup>b</sup>	147.83(13)
O(17)–Mo(6)–O(21)	89.6(2)	O(16)–Mo(6)–O(22)	104.9(2)
(17)–Mo(6)–O(22)	88.9(2)	O(21)–Mo(6)–O(22)	152.86(17)
O(16)–Mo(6)–O(14)	177.0(2)	O(17)–Mo(6)–O(14)	77.68(13)
N(4)–Co(1)–N(1)	86.67(17)	N(4)–Co(1)–N(6)	177.43(16)
N(1)–Co(1)–N(6)	95.59(16)	N(4)–Co(1)–N(2)	93.75(17)
N(1)–Co(1)–N(2)	83.29(16)	N(6)–Co(1)–N(2)	87.71(17)

<sup>a</sup>Symmetry transformations used to generate equivalent atoms:<sup>b</sup>–x; –y+2; –z.<sup>c</sup>x–1; y; z.

date species in the aqueous  $[\text{MoO}_4]^{2-}$  solution of low pH value, no conventional synthesis method could obtain a solid compound containing the coexistence of two isopolyoxomolybdate species. Taking account of both the preparation of compound **1** and the report of the Hagrman et al., it is obvious that hydrothermal reaction should be preferable to the conventional synthesis for stabilizing the coexistence, despite the molybdenum source being  $\text{Na}_2\text{MoO}_4$  or  $\text{MoO}_3$ . It is also very possible that under the pH value of 2–3 range,  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  are dominant species in the aqueous  $[\text{MoO}_4]^{2-}$  solution.

A single-crystal X-ray diffraction analysis revealed that compound **1** consists of four kinds of subunits:  $(\pm)[\text{Co}(\text{bpy})_3]$  complex,  $[\text{Mo}_6\text{O}_{19}]^{2-}$  anion,  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  anion, and uncoordinated water molecules (Fig. 1). The +6 oxidation state of molybdenum in **1** is consistent with the bond valance sum ( $\text{BVS}_{\text{ave}} = 5.94$ ) [9]. According to the results of the bond valance sum for all oxygen atoms in  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  anion, the two separate protons for the balancing charge should be attached to the two  $\mu_5$  bridge oxygen atoms (O10,  $\text{BVS} = 1.656$ ) of  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ . In compound **1**, the structure of  $[\text{Mo}_6\text{O}_{19}]^{2-}$  anion displays the well-known characteristic that consists of six  $\text{MoO}_6$  octahedra with three distinct types of Mo–O bond lengths. The Mo–O1 distances average 2.317 Å, the Mo=O distances aver-

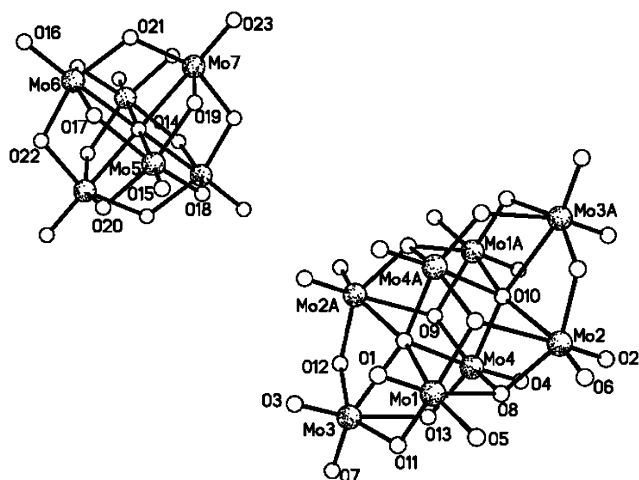


Fig. 1. A ball and stick drawing of the two POM anionic units in compound **1**. Water molecules,  $\text{Co}(\text{bipy})_3$  complexes and all hydrogen atoms are omitted for clarity.

age 1.677 Å, and the remaining Mo–O distances to the bridging oxygens average 1.924 Å. It can be seen from Fig. 1 that there are three types of molybdenum centers in  $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$  anion, in which all Mo atoms are six-coordinate but are not equivalent. Also, four types of oxygen can be found as terminal, two coordinate, three-coordinate, and five-coordinate atoms. The most

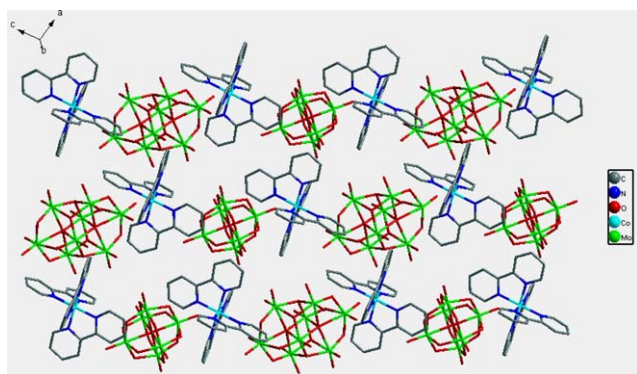


Fig. 2. A view of the sheet structure of **1** along the (1/2, 1/2, 1/2) plane, showing the alignment of the Co(bipy)<sub>3</sub> chiral moieties.

remarkable structural distinction of  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> from [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup> is that the former contains MoO<sub>6</sub> octahedron with two terminal O atoms, while the latter involves MoO<sub>6</sub> octahedron with only one terminal O atoms. According to the Pope's classification [10], the [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup> anion is obviously of type-I species in view of the presence of only a kind of MoO<sub>6</sub> octahedron including one terminal O atom, but the  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anion should be considered to be a type-III system because of the coexistence of both sorts of octahedra.

Another interesting aspect of **1** is that Co(bipy)<sub>3</sub> complex parts appear in racemic enantiomorphous pair architecture. As shown in Fig. 2, the two kinds of Co(bipy)<sub>3</sub> chiral enantiomorphs are located in alternate layer space but give the 1:1 molecular proportion. Such enantiomorphs complex generally results from bidentate chelating ligands. Each Co<sup>2+</sup> site in **1** is defined by six nitrogen atoms from three 2,2'-bipyridine molecules and formed a distorted CoN<sub>6</sub> octahedron with Co–N bond distances in the range of 1.929(4)–1.949(4), corresponding to mean Co–N length 1.937(4) Å. These bond distances of Co–N are comparable with those reported chiral Co(bipy)<sub>3</sub> compounds [11]. In the solid state, these three subunits are present in the respectively independent form, though there is O⋯H–O hydrogen bonding between  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anions mediated by free water molecules.

The IR spectrum of **1** exhibited three strong bands at 957, 800 and 765 cm<sup>-1</sup>, attributed respectively to the  $\nu(\text{Mo}=\text{O}_t)$ ,  $\nu(\text{Mo}-\text{O}_b-\text{Mo})$  and  $\nu(\text{Mo}-\text{O}_c-\text{Mo})$  in [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup> anion [12]. The absorption bands at 944, 915, 846, 713 and 667 cm<sup>-1</sup> were obviously characteristic of  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anion [4b]. The feature at 1604 and 1450 cm<sup>-1</sup> are characteristic of  $\nu(-\text{N}=\text{C})$  vibration for Co(II)-bipy complex, while other strong features at 765 cm<sup>-1</sup> is assigned as  $\nu(-\text{C}-\text{H})$  vibration in bipy. The vibration of  $\nu(-\text{N}=\text{C})$  at 1580 cm<sup>-1</sup> for the free ligand bipy was shifted to 1480 cm<sup>-1</sup> for **1**, showing the occurrence of a coordinate binding of bipy with a cobalt atom.

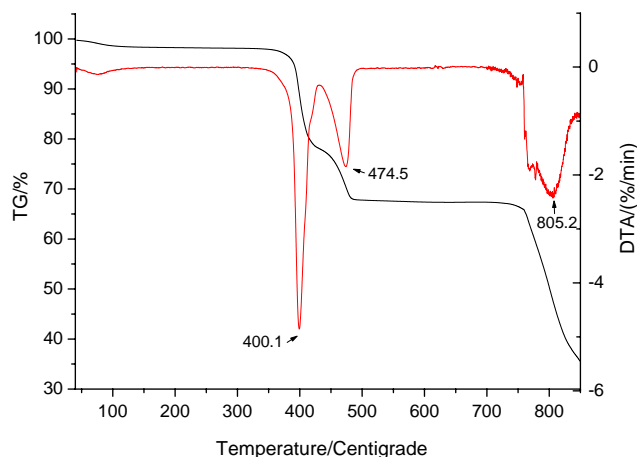


Fig. 3. The TG-DTA curves for compound **1**.

The formation of coordination bond and the oxidation states of cobalt and molybdenum have been investigated by X-ray photoelectron spectra (XPS). The measured Mo 3d<sub>5/2</sub> binding energy (BE) of 232.0 eV and the peak fashion suggests the assignment of Mo to +6 oxidation state. The presence of a Co(2p<sub>3/2</sub>) satellite peak at 782.3 eV is a obvious indication of the +2 oxidation state for cobalt in **1**. The N<sub>1s</sub> peak at 398.5 eV is attributed to the nitrogen atom of the N–Co coordination bond. Because of the possible occurrence of a N←Co feedback  $\pi$ -bond in the cobalt complex moiety of **1**, which often exists in some complexes with nitrogen ligand [13], the electron binding energy of N<sub>1s</sub> obviously decreases from 401.5 to 398.5 eV.

The TG-DTA curves are shown in Fig. 3. It can be seen from the TG-DTA curves that the thermal decomposition of compound **1** experiences four steps and accompanies four endothermic peaks. The first small endothermic peak at 78 °C results from the release of four water molecules (found 2.2%, calc. 2.3%). The second intense endothermic peak appears at 400.1 °C and corresponds to a mass loss of 19.9% (calc. 19.5% for four bipy molecules) on the TG curve between 378 and 434 °C, followed other endothermic peak at 474.5 °C resulting from the release of two bipy molecules (found 10.1%, calc. 9.8%). Beginning at 754 °C, Mo<sub>6</sub>O<sub>19</sub> and Mo<sub>8</sub>O<sub>26</sub> decompose gradually with the broad endothermic peak at about 805 °C. The final residue may be Mo and Co atom.

#### 4. Conclusion

In summary, we have hydrothermally synthesized and structurally characterized a novel polyoxometalates-based hybrid solid of **1**, which consists of racemic complexes ( $\pm$ )[Co(bipy)<sub>3</sub>] and both [Mo<sub>6</sub>O<sub>19</sub>]<sup>2-</sup> and  $\beta$ -[Mo<sub>8</sub>O<sub>26</sub>]<sup>4-</sup> anions. This solid state compound simultaneously possess

at least three kinds of intrinsic physicochemical properties coming from  $(\pm)[\text{Co}(\text{bpy})_3]$ ,  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and  $\beta$ - $[\text{Mo}_8\text{O}_{26}]^{4-}$  subunits; these properties will be possible in the potential application of catalyst and optical materials. The result not only shows that the  $[\text{Mo}_6\text{O}_{19}]^{2-}$  and  $\beta$ - $[\text{Mo}_8\text{O}_{26}]^{4-}$  anions could reach a coexistence equilibrium in the aqueous  $[\text{MoO}_4]^{2-}$  solution by keeping an appropriate range of pH value, but also suggests that two other kinds of POM anions are also possible to coexist together with racemic complexes in the same crystal structure. This provides an useful information to develop new organic–inorganic hybrid materials based on POM building blocks.

## 5. Supplementary material

Crystallographic data for the compound **1** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications (CCDC-244020). These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; <mailto:deposit@ccdc.cam.ac.uk>.]

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