

# Synthesis, Characterization, and Properties of Supported Tungstozincate Bridged by Co(II) Complex Fragment

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**Abstract**  $[\text{Co}^{\text{II}}(\text{phen})_3]_2[\{(\text{ZnW}_{12}\text{O}_{40})\text{Co}^{\text{II}}(\text{phen})_2(\text{H}_2\text{O})\}_2\text{Co}^{\text{II}}(\text{trien})_2(\text{NaH}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$  was synthesized via hydrothermal technique and characterized with elemental analyses, IR spectroscopy, TGA-DTA, and variable temperature magnetic susceptibility. The compound crystallized in the monoclinic system with the space group  $P2_1/n$ ,  $a=1.8210$  nm,  $b=2.3592$  nm,  $c=2.2932$  nm,  $\beta=110.31^\circ$ ,  $V=9.239$  nm<sup>3</sup>,  $Z=2$ ,  $R_1=0.0827$ . The compound consists of two coordination cations, three lattice water molecules, and a macroanion  $[\{(\text{ZnW}_{12}\text{O}_{40})\text{Co}(\text{phen})_2(\text{H}_2\text{O})\}_2\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)_2(\text{NaH}_2\text{O})_2]^{4-}$  in which each supported Keggin anion  $[(\text{ZnW}_{12}\text{O}_{40})\text{Co}^{\text{II}}(\text{phen})_2(\text{H}_2\text{O})]^{4-}$  acts as a ligand to coordinate to central bridging  $\text{Co}^{2+}$  ion via a terminal oxygen atom. Hydrogen bonds are responsible for the construction of 3D architecture of the compound. The compound is paramagnetic with a weak antiferromagnetic interaction ( $\theta=-46.796$  K).

**Keywords** Hydrothermal synthesis; Organic-inorganic hybrid; Supported Keggin structure; Cobalt complex; Tungstozincate

## 1 Introduction

Polyoxometalates(POMs), including POM-based organic-inorganic hybrids, are of great interest not only because of their various structures but also because of their potential application in different areas such as catalysis, materials science, and medicine<sup>[1–5]</sup>. As we know, the Keggin-type of POMs is one of the important building blocks in this field and is used for the preparation of sandwiching-type, capped or supported compounds. In most cases, these Keggin clusters supporting metal complexes are found in the ionic compounds<sup>[6–11]</sup> or in the polymer constructed from Keggin units as building blocks and metal complexes as bridging units<sup>[12–15]</sup>. Although many kinds of hybrids with Keggin-type clusters supporting metal complexes have been synthesized, the discrete macroanions with supported Keggin units linked by a metal complex fragment are still very rare. The synthesis and characterization of ionic organic-inorganic hybrid compound  $[\text{Co}^{\text{II}}(\text{phen})_3]_2[\{(\text{ZnW}_{12}\text{O}_{40})\cdot\text{Co}^{\text{II}}(\text{phen})_2(\text{H}_2\text{O})\}_2\text{Co}^{\text{II}}(\text{trien})_2(\text{NaH}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$  (trien=triethylenetetraamine) is reported in this article.

## 2 Experimental

### 2.1 General Procedures

All chemicals purchased were of reagent grade and were used without further purification. Elemental analyses(C, H, and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. Amounts of Zn, Co, and W were determined with a Prodigy ICP atomic emission spectrometer. IR spectrum(KBr pellets; 4000—400  $\text{cm}^{-1}$ ) was recorded on a Magna-560 FTIR Spectrophotometer. Thermal analysis was performed on a Perkin-Elmer TGA7 instrument in flowing air at a heating rate of 20  $^\circ\text{C}/\text{min}$ . Variable temperature magnetic susceptibilities were measured on a Quantum Design XL-5 magnetic property measurement system in a temperature range of 2—300 K at  $8\times 10^5$  A/m.

### 2.2 Synthesis of Compound 1

A mixture of 1 g(3 mmol) of  $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ , 0.0724 g(0.3 mmol) of  $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$ , 0.1514 g(0.6 mmol) of  $\text{Co}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$ , 0.041 g(0.3 mmol) of

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ZnCl<sub>2</sub>, 0.066 g(0.3 mmol) of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, 0.1 mL(0.6 mmol) of trien, 0.0589 g(0.3 mmol) of phen(phen=1,10-phenanthro line), and 16.2 mL(900 mmol) of H<sub>2</sub>O was stirred, and the pH value of the above mixture was adjusted to 5 with 2 mol/L HCl. The mixture was sealed in a 25 cm<sup>3</sup> Teflon-lined autoclave and heated to 160 °C for 120 h. Green tube crystals of 0.206 g(yield *ca.* 20% based on W) were collected by filtration. Elemental anal.(%) calcd. for C<sub>132</sub>H<sub>130</sub>Co<sub>5</sub>N<sub>28</sub>Na<sub>2</sub>O<sub>87</sub>W<sub>24</sub>Zn<sub>2</sub>(found): W 53.0(52.63), Co 3.7(3.51), Zn 1.5(1.56), Na 0.51(0.55), C 18.8(18.91), N 4.21(4.68), H 1.34(1.4). FTIR(KBr pellets),  $\tilde{\nu}/\text{cm}^{-1}$ : 935, 870, 759, 448 for Keggin anion and 1642, 1550, 1514, 1462, 1428, 1145, 1101 for organic ligands.

### 2.3 X-ray Crystallography

A single crystal with dimensions 0.39 mm×0.19 mm×0.18 mm of compound **1** was used for X-ray diffraction data collection on a Smart Apex CCD diffractometer at 293(2) K with graphite monochromated Mo *K* $\alpha$  radiation( $\lambda=0.071069$  nm). A total of 85828 reflections were collected in a range of  $3.02^\circ \leq \theta \leq 27.48^\circ$  ( $-23 \leq h \leq 21$ ,  $-27 \leq k \leq 30$ ,  $-29 \leq l \leq 29$ ). Empirical absorption correction(multiscan) was carried out. The structure of compound **1** was solved by direct method and refined by the full-matrix least squares on  $F^2$  with the SHELXTL-97 software<sup>[16,17]</sup>. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical models. A summary of the crystallographic data and structural refinement of compound **1** is shown in Table 1.

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

Empirical formula	C <sub>132</sub> H <sub>130</sub> Co <sub>5</sub> N <sub>28</sub> Na <sub>2</sub> O <sub>87</sub> W <sub>24</sub> Zn <sub>2</sub>
<i>M</i>	8384.43
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> , <i>b</i> , <i>c</i> /nm	1.8210(4), 2.3592(5), 2.2932(5)
$\beta/^\circ$	110.31(3)
<i>Z</i> , <i>V</i> /nm <sup>3</sup>	2, 9.239(3)
Calculated density/(Mg·m <sup>-3</sup> )	3.039
$\mu/\text{mm}^{-1}$	15.659
Independent reflections( <i>R</i> <sub>int</sub> )	21194(0.0897)
Completeness to $\theta=27.48^\circ$	0.994
Data/restraints/parameters	21073/5599/1228
Goodness-of-fit on $F^2$	1.024
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ $>2\sigma(I)$ ]	0.0827, 0.1541
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.1166, 0.1682

Crystallographic data for the structural analysis have been deposited in the Cambridge Crystallographic Data Center with CCDC reference number 275145.

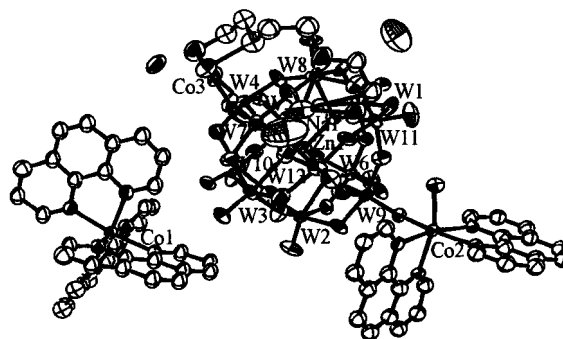
## 3 Results and Discussion

### 3.1 Aspects About Formation of Compound **1**

Many factors including starting materials, stoichiometry, acidity, temperature, pressure, and time of reaction exert a great influence on the formation and yield of the product and crystal quality. In our work, the crystalline product could not be obtained in the absence of acetate. The most reasonable explanation for this is that the acetate anion played a role of buffer in the reaction system and therefore restrained the acidity from a wide range of change, which benefited the formation and crystallization of compound **1**. Both the two kinds of nitrogen-containing ligands, phen and trien, have coordinated to Co atoms as we expected, but only two trien molecules appear in compound **1**, although its amount in the starting material was double of the amount of phen; and the coordination fragment of Co<sup>3+</sup> ion with *n*(Co):*n*(trien)=1:2 rather than 1:1(in which four nitrogen atoms of trien coordinate to one cobalt ion) was formed. The best explanation for these phenomena should be the nonrigidity of trien and asymmetric configuration of the 1:1 coordination fragment of trien.

### 3.2 Structural Description

Compound **1** consists of one macroanion [ $\{\text{ZnW}_{12}\text{O}_{40}\text{Co}(\text{phen})_2(\text{H}_2\text{O})\}_2\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)_2(\text{NaH}_2\text{O})_2\}^{4-}$ , two cations  $[\text{Co}(\text{phen})_3]^{2+}$ , and three lattice water molecules. Fig.1 shows the asymmetric unit of compound **1** in which Ow2 has a half site occupancy. The macroanion is composed of two  $\alpha$ -Keggin units  $[\text{ZnW}_{12}\text{O}_{40}]^{6-}$ , two cobalt(II) complex fragments  $[\text{Co}(\text{phen})_2(\text{H}_2\text{O})]^{2+}$  supported on the Keggin units through the terminal oxygen coordination and one complex fragment  $[\text{Co}(\text{C}_6\text{H}_{18}\text{N}_4)_2(\text{NaH}_2\text{O})_2]^{4+}$ ,



**Fig.1** ORTEP drawing of asymmetric unit of compound **1**

50% probability ellipsoids. All hydrogen atoms are omitted for clarity.

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