



Hybrid compounds of Keggin polyoxotungstate with transition metal ion as the central atom. Synthesis, structure and properties



Xiao-Min Li ^{a, b}, Ya-Guang Chen ^{a, *}, Tian Shi ^a

^a Department of Chemistry, Northeast Normal University, Changchun, Jilin, 130024, China

^b Department of Chemistry, Yili Normal University, Yining, Xinjiang, 835000, China

ARTICLE INFO

Article history:

Received 11 November 2015

Received in revised form

11 December 2015

Accepted 17 December 2015

Available online 22 December 2015

Keywords:

Polyoxotungstate

Cobalt

Nickel

4,4'-bipyridine

Magnetic property

ABSTRACT

The compounds (Hbipy)₂[Co(bipy)₂(H₂O)₄]₂(CoW₁₂O₄₀)·2bipy·7H₂O (**1**) and [Ni₂(Hbipy)₂(bipy)(H₂O)₄(H₂W₁₂O₄₀)]·5H₂O (**2**) (bipy = 4,4'-bipyridine) were synthesized hydrothermally and characterized by elemental analysis, IR spectroscopy, TG analyses, solid ultraviolet diffuse spectroscopy and single crystal X-ray diffraction method. In **1** the complex ions, [Co(bipy)₂(H₂O)₄]²⁺, construct a supramolecular layer through π-π stacking interaction. The heteropolyanions with central Co atom and supramolecular layers are linked by hydrogen bonds. In **2** a 2D structure is formed from metatungstate anions and binuclear Ni-bipy complexes through the coordination of metatungstate anions and bipy to Ni ions. Between the layers and bipyridine molecules are the hydrogen bond interactions. The formation of **1** and **2** shows that the solution acidity and metal ions influence greatly the structure of the compounds. Solid ultraviolet diffusion results indicate that the compounds **1** and **2** are potential semiconductor materials. In **1** and **2** there exists a weak antiferromagnetic interaction.

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1. Introduction

The inorganic-organic hybrid materials of polyoxotungstates containing transition metal have been attracting a lot of attention of people in recent years due to the diversity of structure and potential applications in various fields such as catalysis, medicine, magnetism and material science etc. [1–4]. In this field, Keggin-type polyoxometalates have occupied an important position [5] and much of inorganic-organic hybrid compounds of tungstosilicate and tungstophosphate were reported of in recent years [5–12]. The heteropolytungstates with a transition metal ion as central atom, for example, CoW₁₂O₄₀⁶⁻, FeW₁₂O₄₀⁵⁻, ZnW₁₂O₄₀⁶⁻, CuW₁₂O₄₀⁶⁻, have less stability and lower yield than tungstophosphate and tungstosilicate, therefore, their inorganic-organic hybrids are known relatively less [13–21] although the representative heteropolytungstate with a transition metal ion as central atom, CoW₁₂O₄₀⁶⁻ anion, was reported in 1950's [22]. In the reported inorganic-organic hybrids of polyoxometalate with a transition metal ion as central atom most of the compounds

contain tungstozincate anion [13,14,17–20] because of the electron configuration of zinc atom. d¹⁰ electron configuration of Zn²⁺ ion makes it easily adopt tetrahedral geometry (sp³ hybridization) required by the Keggin anionic structure and therefore, anion ZnW₁₂O₄₀⁶⁻ is more stable than other anion with transition metal ion (Co²⁺, Ni²⁺, Fe³⁺, Cu²⁺) as the central atom.

On the other hand, organic component plays an important role on the constructing inorganic-organic hybrids with high-dimensional structure. 4, 4'-bipyridine is used very commonly in synthesizing inorganic-organic hybrids with high-dimensional structure due to its high bridging coordination ability. The other organic component used in this work is 2-phosphono-acetic acid. It is two-functional and bridging ligand and has been rarely used in the synthesis of inorganic-organic hybrid materials of polyoxotungstates. In this work 4, 4'-bipyridine and 2-phosphono-acetic acid were chosen as organic ligands and transition metal ions (Co²⁺, Ni²⁺) and tungstate, as inorganic components to obtain inorganic-organic hybrid materials of polyoxotungstates with high-dimensional structure. As result, two unreported compounds containing transition ions, (Hbipy)₂[Co(bipy)₂(H₂O)₄]₂(CoW₁₂O₄₀)·2bipy·7H₂O (**1**) [Ni₂(Hbipy)₂(bipy)(H₂O)₄(H₂W₁₂O₄₀)]·5H₂O (**2**) (bipy = 4,4'-bipyridine) were obtained by using hydrothermal method. Herein their syntheses, structures and properties are

* Corresponding author.

E-mail address: chenyaguang@tom.com (Y.-G. Chen).

reported.

2. Experimental section

2.1. Materials and instruments

All reagents were commercially purchased and used without any further purification. The IR spectra in KBr pellets were recorded in the range 400–4000 cm^{-1} with a Magna-560 FT/IR spectrophotometer. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN elemental analyzer and that of W, Co, Ni were carried out with a Leaman ICP spectrometer. Thermogravimetric analyses were carried out by using a NETZSCH STA 449F3 instrument, with a heating rate of 10 $^{\circ}\text{C min}^{-1}$ under a nitrogen atmosphere. Diffuse reflectance spectra were recorded with a finely ground sample on a Cary 500 spectrophotometer equipped with a 110 mm diameter integrating sphere in 200–800 nm. Barium sulfate (BaSO_4) was used as a standard with 100% reflectance. Variable temperature dc magnetic susceptibility measurements were performed on the polycrystalline samples in an applied magnetic field of 1000 Oe over the temperature range 2.0–300 K using Quantum Design XL-5 SQUID magnetometer.

2.2. Synthesis

$(\text{Hbipy})_2[\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]_2(\text{CoW}_{12}\text{O}_{40}) \cdot 2\text{bipy} \cdot 7\text{H}_2\text{O}$ (**1**) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.099 g, 0.300 mmol) and $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{COOH}$ (0.015 g, 0.107 mmol) were dissolved in 20 ml of distilled water and into it $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.029 g, 0.0996 mmol) and $\text{C}_{10}\text{H}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$ (0.019 g, 0.0988 mmol) were added with stirring. The pH value of the resulting solution was adjusted with a 0.1 mol L^{-1} HNO_3 solution to 5.0. The mixture was sealed in a Teflon-lined stainless steel autoclave, and then heated at 150 $^{\circ}\text{C}$ for 3 days. Green crystals of **1** were recovered in 35% yield based on tungsten. Compound **1** was proved to be air- and light-stable, and insoluble in water and common organic solvents. Anal Calc. for $\text{C}_{80}\text{H}_{94}\text{Co}_3\text{N}_{16}\text{O}_{55}\text{W}_{12}$ ($M_r = 4542.7$): C 21.29, H 1.79, N 4.97, Co 3.92, W 48.89%; found: C 22.07, H 1.64, N 5.05, Co 4.04, W 49.65%. IR (KBr, pellet, cm^{-1}): 3445(br, s), 3065(s), 1654(m), 1615(m), 1561(s), 1523(m), 1458(m), 1424(m), 1245(w), 945(s), 878(m), 767(s), 657(m), 585(m), 422(m) [$\text{Ni}_2(\text{Hbipy})_2(\text{bipy})(\text{H}_2\text{O})_4(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot 5\text{H}_2\text{O}$ (**2**).

The preparation of **2** was similar to that of **1** except that $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.024 g, 0.101 mmol) was used instead of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and the pH value of 3.0. Green crystals of **2** were recovered in 35% yield based on tungsten. Compound **2** was proved to be air- and light-stable, and insoluble in water and common organic solvents. Anal Calc. for $\text{C}_{30}\text{N}_6\text{Ni}_2\text{O}_{49}\text{W}_{12}\text{H}_{46}$ ($M_r = 3598.25$): C 10.05, H 0.93, N 2.34, Ni 3.27, W 61.54%; found: C 10.37, H 0.88, N 2.68, Ni 3.40, W 60.89%. IR (KBr pellet, cm^{-1}): 3446(br), 3070(s), 3010(s), 1648(m), 1615(m), 1544(m), 1483(m), 1415(m), 1217(s), 1079(s), 938(s), 874(s), 788(s), 749(m), 657(m), 515(w).

2.3. X-ray crystallography

X-ray diffraction data of **1** and **2** were collected on a SMART CCD diffractometer with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. Multi-scan absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least square on F^2 with the SHELXL-97 program package [23]. Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms on carbon and nitrogen atoms were calculated theoretically. A summary of the crystallographic data and structural refinement for **1** and **2** is listed in Table 1. Copy of the data (CCDC No. 1435823–1435824 for **1** and for **2**) can be obtained free of charge on application from CCDC, 12 Union Road,

Table 1

Crystal parameters and structure refinement data for **1** and **2**.

Compounds	1	2
Formula	$\text{C}_{80}\text{Co}_3\text{H}_{80}\text{N}_{16}\text{O}_{55}\text{W}_{12}$	$\text{C}_{30}\text{H}_{33}\text{N}_6\text{Ni}_2\text{O}_{49}\text{W}_{12}$
M_r	4528.47	3585.18
crystal system	monoclinic	monoclinic
space group	Cc	$P2_1$
a (\AA)	15.881(5)	13.566(5)
b (\AA)	24.296(5)	14.964(5)
c (\AA)	31.979(5)	15.092(5)
α ($^{\circ}$)	90	90
β ($^{\circ}$)	102.604(5)	96.703(5)
γ ($^{\circ}$)	90	90
V (\AA^3)	12042(5)	3042.8(18)
Z	4	2
D_c (g cm^{-3})	2.489	3.914
μ , mm^{-1}	11.901	23.294
$F(000)$, e	8324.0	3184.0
R_{int}	0.099	0.0625
R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.1025$ $wR_2 = 0.2471$	$R_1 = 0.0569$ $wR_2 = 0.1282$
R indices (all date)	$R_1 = 0.1424$, $wR_2 = 0.2688$	$R_1 = 0.0782$, $wR_2 = 0.1366$
GOF on F^2	1.028	1.028

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}, \quad ^b wR_2 = \left(\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)]} \right)^{1/2}.$$

Cambridge CB2 2EZ, UK (Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). A summary of the crystallography date and refinement parameters for compounds **1** and **2** are listed in Table 1.

3. Results and discussion

3.1. Crystal structure description

3.1.1. $(\text{Hbipy})_2[\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]_2(\text{CoW}_{12}\text{O}_{40}) \cdot 2\text{bipy} \cdot 7\text{H}_2\text{O}$ (**1**)

As shown in Fig. S1, compound **1** consists of one $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anion, two $[\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$ cations, four bipy molecules and seven H_2O molecules. The bond lengths of W–O in $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anion are in the range of 1.670(2)–2.227(2) \AA , consistent with that in ref [15], showing that $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anion has a Keggin structure. Co1 atom is in the center of the anion in form of tetrahedron CoO_4 , the Co–O/N bond lengths and bond angles are shown in Table S1.

In complex cation $[\text{Co}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$, the Co^{2+} ion is in the center of octahedron, CoN_2O_4 , two bipy molecules are in the para-positions and basically in a same plane, forming a lathy complex cation. These complex cations stack in a way as shown in Fig. 1, forming a supramolecular layer. The distances between the parallel pyridine rings are in the range of 3.30–3.40 \AA , that is, there is strong π - π stacking interaction between pyridine rings ($d_{C79-C87} = 3.330 \text{ \AA}$, $d_{N10-C84} = 3.46 \text{ \AA}$, $d_{C17-C9} = 3.30 \text{ \AA}$, $d_{C74-C19} = 3.41 \text{ \AA}$, $d_{C2-C89} = 3.46 \text{ \AA}$). Such a supramolecular layer is rarely reported.

There are many hydrogen bonds between oxygen atoms (O27, O14, O23, O16, O25, O37) of the $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anions and nitrogen atoms of bipy (N5, N15), between the coordination water molecules and free water molecules, and between free water molecules and $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anions (Table S2). The $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ anions and complex ion layers were connected into a 3D structure (Fig. 2) by these hydrogen bonds.

3.1.2. $[\text{Ni}_2(\text{Hbipy})_2(\text{bipy})(\text{H}_2\text{O})_4(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot 5\text{H}_2\text{O}$ (**2**)

Compound **2** is composed of one $[\text{Ni}_2(\text{Hbipy})_2(\text{bipy})(\text{H}_2\text{O})_4]^{6+}$ cation, one $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ anion and five H_2O molecules. The bond lengths and bond angles of $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ anion are consistent with that in ref [24,25]. Comparing the W–O distances of **2** with those of $\text{TMA}_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 9\text{H}_2\text{O}$ [24], the W–Ot, W–Ob, W–Oc and W–Oa lengths are a little shorter, indicating $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ is slightly

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