



Two new polyoxometalate-based hybrids: Structural transformation played by a secondary bridging ligand

Min Zhu, Jun Peng*, Hai-Jun Pang, Peng-Peng Zhang, Yuan Chen, Dan-Dan Wang, Ming-Guan Liu, Yong-Hui Wang

Key Laboratory of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun, Jilin 130024, PR China

ARTICLE INFO

Article history:

Received 10 December 2009
Received in revised form 8 July 2010
Accepted 12 July 2010
Available online 16 July 2010

Keywords:

Keggin polyoxometalates
Silver complexes
Secondary bridging ligand
Electrochemistry properties

ABSTRACT

Two new Keggin polyoxometalate-based compounds, $[\text{Ag}_4(\text{phnz})_6(\text{SiW}_{12}\text{O}_{40})]$ (phnz = phenazine) (**1**) and $[\text{Ag}(\text{phnz})_{1.5}][\text{Ag}(\text{phnz})(\text{pz})][\text{Ag}_2(\text{phnz})(\text{pz})(\text{H}_2\text{O})](\text{SiW}_{12}\text{O}_{40})$ (**2**) (pz = pyrazine), have been hydrothermally synthesized. Compound **1** is a discrete cluster in which the $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ (SiW_{12}) anion symmetrically connects two dinuclear $\text{Ag}_2(\text{phnz})_3$ fragments. All Ag^I in **1** adopt a trigonal geometry. By introducing the secondary bridging ligand “pz” into the above system, compound **2** was obtained. Compound **2** contains three kinds of silver complex subunits: $[\text{Ag}_2(\text{phnz})(\text{pz})(\text{H}_2\text{O})]^{2+}$, $[\text{Ag}_2(\text{phnz})_3]^{2+}$ and $[\text{Ag}(\text{phnz})(\text{pz})]^+$. The first one extends to a wave-like chain with SiW_{12} anions as bi-dentate suspenders, and the last two are counter cations. Furthermore, Ag^I ions in **2** exhibit three kinds of coordination modes. Their electrochemistry properties have also been studied.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The assembly of organic–inorganic hybrid materials through crystal engineering has been receiving significant interest originating not only from their intriguing architectures, but also from their widely exploitable properties such as catalysis, molecular absorption, photochemistry, electron-conductive, biochemical and magnetic materials [1,2]. One effective strategy to design and synthesize such hybrids includes selecting suitable inorganic building blocks and exploring appropriate organic ligands as structure-directing agents [3]. As is well known, polyoxometalates (POMs), as metal–oxygen cluster species, have become a kind of attractive and competent inorganic building blocks for the construction of novel hybrid materials, because they can provide plenty of terminal and bridging oxygen atoms to coordinate with metal complexes, leading to various unusual physical and chemical properties [4,5]. Hence, using POMs as inorganic building units has become an appealing and promising route to design novel organic–inorganic hybrids.

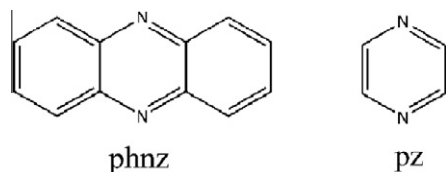
Up to now, most of POM-based hybrids, including Ag/POM-based hybrids [6], Cu/POM-based hybrids [7] and other metals/POM-based hybrids [8], contain a single kind of organic ligands. POM-based hybrids composed of mixed ligands are comparatively less reported, and these mixed ligands are focused on the following three types: –COOH donors plus N-donors [9]; N-donors plus small

organic amines [10]; two kinds of different N-donors [11]. For the third type, simultaneous utilizing of linear bridging ligand and chelate ligand is the most common. Our group and other groups have devoted many efforts on it and gained some interesting results [12,13], for examples: $[\text{Cu}^I\text{Cl}(4,4'\text{-bipy})_4][\text{Cu}^{II}(1,10\text{-phen})_2\text{Mo}_8\text{O}_{26}]$ [12a], $[\text{Cu}^I_2(2,2'\text{-bipy})_2(4,4'\text{-bipy})][\text{Cu}^{II}_{1.5}(2,2'\text{-bipy})-(4,4'\text{-bipy})_2][\text{H}_3\text{W}_{12}\text{O}_{40}]$ [12b], $\{\text{Ag}_3(2,2'\text{-bipy})_2(4,4'\text{-bipy})_2\}[\text{Ag}(2,2'\text{-bipy})_2][\text{Ag}(2,2'\text{-bipy})][\text{AlW}_{12}\text{O}_{40}]\cdot\text{H}_2\text{O}$ [12c] and $[\text{Ag}_3(4,4'\text{-bipy})_2(2,2'\text{-bipy})_2][\text{Ag}(2,2'\text{-bipy})_2]-[\text{Ag}(2,2'\text{-bipy})]\text{PW}_{11}\text{VO}_{40}$ [13c].

In these compounds, 4,4'-bipy ligand acts as a linear bridging linkage, while 2,2'-bipy/phen exhibits a chelate coordination mode. We wonder if simultaneously using different N-donors with the same linear coordination mode, how the structures will be tuned. This should be a challenge for syntheses of POM-based hybrids. Thus, we choose phnz and pz ligands, as these two ligands possess the same coordination mode but distinct steric hindrances (Scheme 1). Firstly, we introduced phnz as a bridging ligand into the reaction system of SiW_{12} and Ag^I , and $[\text{Ag}_4(\text{phnz})_6(\text{SiW}_{12}\text{O}_{40})]$ (**1**) was obtained, which was a discrete cluster. Then we further introduced the secondary bridging ligand “pz” into the above reaction system, $[\text{Ag}(\text{phnz})_{1.5}][\text{Ag}(\text{phnz})(\text{pz})][\text{Ag}_2(\text{phnz})(\text{pz})(\text{H}_2\text{O})](\text{SiW}_{12}\text{O}_{40})$ (**2**) was obtained. The pz ligand successfully transfers the structure of $\text{SiW}_{12}/\text{Ag}$ hybrid from a discrete cluster in compound **1** to a wave-like chain in compound **2**. To the best of our knowledge, compound **2** represents the first Keggin polyoxometalate-based hybrid containing two kinds of linear bridging N-donors. Furthermore, their electrochemistry properties have also been studied.

* Corresponding author.

E-mail address: jpeng@nenu.edu.cn (J. Peng).



Scheme 1. The ligands used in the construction of organic–inorganic hybrids.

2. Experimental

2.1. Materials and methods

All reagents for synthesis were purchased from commercial sources and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. The IR spectra were obtained on an Alpha Centaur FT/IR spectrometer with KBr pallet in the 400–4000 cm^{-1} region. The TG analyses were performed on a DTG-60AH instrument in flowing N_2 with a heating rate of 10 $^\circ\text{C min}^{-1}$. Cyclic voltammograms were obtained with a CHI 660 electrochemical workstation at room temperature. Platinum gauze was used as a counter electrode and Ag/AgCl electrode was referenced. Chemically bulk-modified carbon paste electrodes (CPEs) were used as working electrodes.

2.2. Syntheses of compounds **1** and **2**

2.2.1. $[\text{Ag}_4(\text{phnz})_6(\text{SiW}_{12}\text{O}_{40})]$ (**1**)

A mixture of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.30 mmol), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (0.15 mmol), AgNO_3 (0.30 mmol), phnz (0.15 mmol) and H_2O (10 mL) was stirred for an hour. The pH was adjusted to 2.8–3.2 with 2 M HNO_3 , then sealed in an 18 mL Teflon-lined reactor and heated at 170 $^\circ\text{C}$ for 4 days. Yellow block crystals were filtered, washed with water, and dried at room temperature (yield 52%, based on W). *Anal. Calc.* for $\text{C}_{72}\text{H}_{48}\text{Ag}_4\text{N}_{12}\text{O}_{40}\text{SiW}_{12}$ (4386.84): C, 19.71; H, 1.10; N, 3.83. Found: C, 18.26; H, 1.29; N, 4.15%.

2.2.2. $[\text{Ag}(\text{phnz})_{1.5}][\text{Ag}(\text{phnz})(\text{pz})][\{\text{Ag}_2(\text{phnz})(\text{pz})(\text{H}_2\text{O})\}(\text{SiW}_{12}\text{O}_{40})]$ (**2**)

Compound **2** was synthesized in the same method except that additional pz (0.15 mmol) was added (yield 28% on W). *Anal. Calc.* for $\text{C}_{50}\text{H}_{38}\text{Ag}_4\text{N}_{11}\text{O}_{41}\text{SiW}_{12}$ (4114.52): C, 14.59; H, 0.93; N, 3.74. Found: C, 13.26; H, 1.15; N, 3.86%.

2.3. Preparation of **1**-CPE and **2**-CPE

Compounds **1**- and **2**-modified carbon paste electrodes **1**-CPE and **2**-CPE were prepared as follows: 90 mg of graphite powder and 8 mg of compounds **1** or **2** were mixed and ground together by agate mortar and pestle to achieve a uniform mixture, and then it was added 0.6 mL Nujol with stirring. The homogenized mixture was packed into a glass tube with 1.2 mm inner diameter, and the tube surface was wiped with paper. Electrical contact was established with copper rod through the back of the electrode.

2.4. X-ray crystallography

Crystal data for compounds **1** and **2** were collected on a Bruker SMART-CCD diffractometer, with Mo $K\alpha$ monochromatic radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The structures were solved by the direct methods and refined by full matrix least-squares on F^2 using the SHELXTL crystallographic software package [14]. All the non-hydrogen atoms were refined anisotropically. Crystallographic

Table 1

Crystal data and structure refinements for compounds **1** and **2**.

Compound	1	2
Empirical formula	$\text{C}_{72}\text{H}_{48}\text{Ag}_4\text{N}_{12}\text{O}_{40}\text{SiW}_{12}$	$\text{C}_{50}\text{H}_{38}\text{Ag}_4\text{N}_{11}\text{O}_{41}\text{SiW}_{12}$
Formula weight	4386.84	4114.52
Crystal system	triclinic	orthorhombic
Space group	$P\bar{1}$	$Pbca$
a (\AA)	12.145(4)	24.018 (5)
b (\AA)	13.659(6)	20.361(5)
c (\AA)	14.766(3)	29.799(5)
α ($^\circ$)	81.692(3)	
β ($^\circ$)	71.271(3)	
γ ($^\circ$)	70.869(3)	
V (\AA^3)	2189(7)	14 573(5)
Z	1	8
λ (\AA^3)	0.71069	0.71069
D_{calc} (g cm^{-3})	3.327	3.749
μ (Mo $K\alpha$) (mm^{-1})	16.666	20.020
$F(0\ 0\ 0)$	1974.0	14648.0
Reflections collected	17 950	65 675
Independent reflections	11 921 ($R_{\text{int}} = 0.0273$)	19 800 ($R_{\text{int}} = 0.0716$)
Goodness of fit on F^2	0.967	0.840
R_1, wR_2 [$I > 2\sigma(I)$]	0.0419, 0.0928	0.0334, 0.0400
R_1, wR_2 (all data)	0.0546, 0.0966	0.0896, 0.0438

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)]}{\sum [w(F_o^2)]} \right\}^{1/2}$$

data are given in Table 1. Selected bond lengths and angles of the compounds are listed in Table S1.

3. Results and discussion

3.1. Structure description of compound **1**

Single crystal X-ray structural analysis reveals that compound **1** is constructed from one $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ (abbreviated to SiW_{12}) anion and two $[\text{Ag}_2(\text{phnz})_3]^{2+}$ fragments (Fig. 1). The SiW_{12} anion exhibits a classical α -Keggin configuration. The central Si atom is surrounded by a tetrahedron of four oxygen atoms. The Si–O distances range from 1.595(1) to 1.643(1) \AA . Each W atom shows $\{\text{WO}_6\}$ octahedral environment. According to the different coordination fashions of O atoms in the Keggin cluster, the W–O distances can be grouped into three sets: W–O_t (terminal, 1.640(2)–1.688(1) \AA), W–O_b (bridge, 1.840(2)–1.924(1) \AA) and W–O_c (central, 2.300(3)–2.460(3) \AA).

There are two coordinated dinuclear Ag^I fragments around each SiW_{12} anion. All the Ag^I adopt trigonal geometry contributed by two nitrogen atoms from two phnz molecules and one terminal oxygen atom of SiW_{12} anion. The Ag–N distances range from 2.153(4) to 2.229(0) \AA and the N–Ag–O angles are in the range of

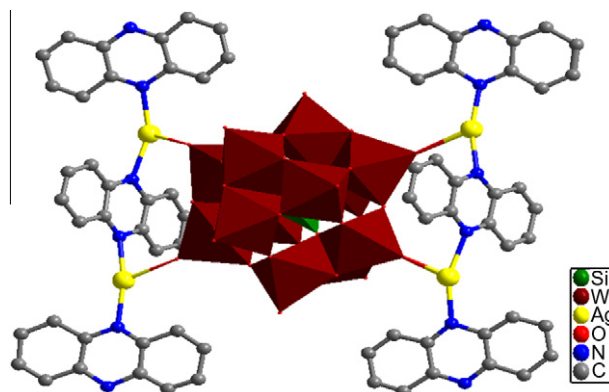


Fig. 1. Stick/ball view of the asymmetric unit of compound **1**.

Download English Version:

<https://daneshyari.com/en/article/1307856>

Download Persian Version:

<https://daneshyari.com/article/1307856>

[Daneshyari.com](https://daneshyari.com)