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Two hybrid compounds constructed from Ni-tris(imidazolyl) complexes and Keggin clusters: Syntheses, structures and electrochemical properties

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ABSTRACT

By introducing different polyoxotungstates into the Ni-tib (tib = 1, 3, 5-tris (1-imidazolyl)benzene) system, two new polyoxometalate-based inorganic-organic hybrids with distinct architectures, $[Ni(Htib)_4][PW_{12}O_{40}]_2$ (**1**) and $[Nitib]_2(H_2O)_4](GeW_{12}O_{40})\cdot 2H_2O$ (**2**) have been synthesized under the same hydrothermal conditions. Their structures have been determined by single-crystal X-ray diffraction analyses and characterized by infrared spectra (IR), elemental analyses, powder X-ray diffraction (PXRD) patterns and thermogravimetic (TG) analyses. Structural analyses show that compound **1** is a dimer, in which two neighboring mono-connected $[PW_{12}O_{40}]^{3-}$ (PW_{12}) clusters are linked together by a $[Ni(Htib)_4]$ complex cation. In contrast to compound **1**, compound **2** presents a 2D grid layer formed by bi-connected $[GeW_{12}O_{40}]^{4-}$ (GeW_{12}) clusters and $[Ni_2(H_2O)_4(tib)_2]$ complex cations, and the adjacent layers are further linked together by the hydrogen bondings to form a highly opened 3D framework. The distinct structural features of two hybrids suggest that the charge of the Keggin anions should play a key role in the process of assembly. Additionally, the electrochemical properties of compounds **1** and **2** have been investigated, and the results indicated that **1** and **2** have good electrocatalytic activities towards reduction of nitrite and oxidation of ascorbic acid.

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1. Introduction

As a new generation of solid-state materials [1,2], inorganic-organic hybrid materials have various potential applications in different areas such as catalysis, medicine, molecular absorption, sensors, ion exchange, and photochemistry applications [3–6]. Polyoxometalates (POMs), as an outstanding class of inorganic metal-oxide clusters, with a nanosized, unique structural variety and interesting physicochemical properties, have been employed as inorganic building blocks for the construction of inorganic-organic hybrid materials [7,8]. Such POM-based hybrid materials can integrate the advantages of both POMs and common inorganic-organic materials [9,10]. Thus, the rational design and synthesis of POM-based organic-inorganic hybrid materials have become a significant area of research for chemists [11–13]. Up to now, hydrothermal synthesis method is a powerful technique for the preparation of the POM-based hybrid compounds [14,15]. Nevertheless, from the crystal engineering point of view for targeting syntheses, hydrothermal reactions are commonly termed as “black box” [16]. The structural control of the resulting POM-based hybrid compounds *via* hydrothermal synthesis is still a challenging work at present, because the structures of POM-based hybrids are frequently influenced by various factors, such as metal ions [17] and organic ligands [18,19]. It is well known that the charge of POM anions represents one of the important factors in self-assembly process, however, the investigation about the influences of POM anions on the structures of POM-based hybrid compounds is limited [20–26]. In the big family of POMs, the Keggin polyanions with the formula $[X^{x+}M_{12}O_{40}]^{(8-x)-}$ (M = W/Mo) [27], have been extensively studied due to their classical structures, interesting properties and applications in many fields. Especially, the central atoms X in the Keggin

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polyanions can be modulated by Ge^{4+}, P^{5+} cations and so on. This endows the $[X^{x+}M_{12}O_{40}]^{(8-x)-}$ clusters with different charge, and thus the Keggin polyanions with different central atoms are conveniently available to explore the influence of charge of POMs on the construction of the POM-based hybrid compounds. Taking this context into account, the $PW_{12}O_{40}^{3-}$ (PW_{12}) and $GeW_{12}O_{40}^{4-}$ (GeW_{12}) Keggin clusters are introduced into the Ni-tib reaction system (tib = 1, 3, 5-tris (1-imidazolyl)benzene) and we hope to obtain informative examples about the influence charge of POMs on the construction of hybrids. Such reaction system was selected based on following considerations: (i) unlike the most d-block metal ions with the various coordination modes, the Ni^{2+} ion generally possesses an octahedral coordination geometry, which could reduce the effect of the coordination geometries of metal ion; (ii) The volume and charge of Keggin clusters are obviously different and these differences will probably be expressed in the formation of distinct hybrids; (iii) the tib molecule as a rigid bridging ligand can exhibit diverse coordination modes (μ_1, μ_2 and μ_3, Fig. S1), which is in favor of formation complicated structures. Meanwhile, as far as we know, the POM-based hybrid compounds constructed by Ni-tib units have been never reported up to now. Consequently, the tib is a proper synthon for assembly of novel POM-based organic-inorganic hybrids.

Herein, two POM-based hybrids, namely $[Ni(Htib)_4][PW_{12}O_{40}]_2$ (**1**), $[Ni(tib)]_2(H_2O)_4](GeW_{12}O_{40})\cdot 2H_2O$ (**2**) have been synthesized under identical hydrothermal conditions except different Keggin anions, which shows that the charge of the Keggin anions is a key factor to control the dimension of the hybrid compounds. Furthermore, the electrochemical properties of the two compounds have been studied in detail.

2. Experimental section

2.1. Materials and general methods

All reagents were purchased commercially and used as received. Elemental analyses of C, H and N were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer and that of Ni and W were carried out with a Leaman inductively coupled plasma (ICP) spectrometer. IR spectra on KBr pellets were recorded on a Nicolet 170SX FT-IR spectrophotometer in the range 400–4000 cm^{-1}. The Powder X-Ray diffraction (PXRD) patterns were recorded with a Siemens D 5005 diffractometer with Cu-Kα ($\lambda = 1.5418$ Å) radiation. The thermal gravimetric analyses (TGA) were carried out on the Perkin–Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C/min. A conventional three-electrode system was used, with a carbon paste electrode (CPE) as a working electrode, a commercial Ag/AgCl as reference electrode and Pt wire as a counter electrode. The cyclic voltammetric behaviors for **1**-CPE and **2**-CPE have been investigated in 1.0 M H_2SO_4.

2.2. Synthesis of compound *1*

A mixture of $H_3PW_{12}O_{40}\cdot 12H_2O$ (350 mg, 0.11 mmol), tib (50 mg, 0.18 mmol), $NiCl_2\cdot 2H_2O$ (30 mg, 0.18 mmol), and H_2O (18 mL) was stirred for 1 h. The pH was adjusted to 3 with 1 mol L^{-1} HCl and then the mixture was transferred and sealed in a 20 mL Teflon-lined stainless steel autoclave, which was heated to 160 °C for 80 h. After the reactor was slowly cooled to room temperature at a rate of 10 °C/h, dark green block crystals were collected, yield: 44% (based on W). For $C_{60}H_{48}Ni_1N_{24}O_{80}P_2W_{24}$ (**1**) (6918.02): Anal. Calcd.: C, 10.42; H, 0.70; N, 4.86; Ni, 0.85; P, 0.9; W, 63.78% Found: C, 10.68; H, 0.78; N, 4.98; Ni, 0.76; P,1.13; W, 63.57%.

2.3. Synthesis of compound *2*

During this experiment process, compound **2** was similar to that of compound **1** except that $H_4GeW_{12}O_{40}\cdot 13H_2O$ (343 mg, 0.10 mmol) was used instead of $H_3PW_{12}O_{40}\cdot 12H_2O$, tib (86.2 mg, 0.41 mmol), and $Ni(CH_3COO)_2\cdot 2H_2O$ (0.25 mmol, 53.2 mg) was used as metal salt. After hydrothermal reaction, green block crystals of **2** were obtained in a yield of 48% based on W. Elemental analysis for $C_{30}H_{36}GeNi_2N_{12}O_{50}W_{12}$ (**2**) (3760.68): Anal. Calc.: C, 9.58; H, 0.96; N, 4.47; Ni, 3.12; Ge, 1.93; W, 58.66%; Found: C, 9.69; H, 1.02; N, 4.59; Ni, 3.0; Ge, 1.69; W, 59.5%.

2.4. Preparations of *1*-, *2*-CPEs

The compound **1** modified CPE (**1**-CPE) was fabricated as follows: 90 mg of graphite powder and 9 mg of **1**, were mixed and ground together by an agate mortar and pestle to achieve a uniform mixture, and then was added 0.1 mL of Nujol with stirring. The homogenized mixture was packed into a glass tube with a 1.5 mm inner diameter, and the tube surface was wiped with paper. Electrical contact was established with a copper rod through the back of the electrode. In a similar manner, **2**-CPE was made with compound **2**.

2.5. X-ray crystallography

X-ray diffraction analysis data for compounds **1**, **2** were collected with a Bruker Smart Apex CCD diffractometer with Mo-Kα ($\lambda = 0.71073$ Å) at 293 K [28]. The structures were solved by direct methods and refined on F^2 by full-matrix least squares methods using the *SHELXTL* package [29]. For the compounds, all the hydrogen atoms attached to carbon atoms were generated geometrically, while the hydrogen atoms attached to water molecules were not located but were included in the structure factor calculations. A summary of the crystallographic data and structural determination for them is provided in Table 1. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Number 1432039 for **1**, 1432038 for **2**.

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

Compounds	**1**	**2**
Empirical formula	$C_{60}H_{48}NiN_{24}O_{80}P_2W_{24}$	$C_{30}H_{36}GeNi_2N_{12}O_{50}W_{12}$
Mr	6918.02	3760.68
Crystal system	Triclinic	Triclinic
Space group	*P*-1	*P*-1
a, Å	12.313(6)	11.678(8)
b, Å	13.272(6)	12.737(8)
c, Å	18.883(8)	13.458(9)
α, deg	98.496(1)	69.95(1)
β, deg	94.809(1)	68.016(1)
γ, deg	93.163(1)	65.387(1)
V, Å^3	3034.3(2)	1645.5 (19)
Z	1	1
D_{calcd}, g cm^{-3}	3.779	3.783
Temperature K	293(2)	293(2)
F(000)	3038	1664
Goodness-of-fit on F^2	1.023	1.113
Final *R* indices [$I \geq 2\sigma(I)$]	R_1[a] = 0.0485	R_1[a] = 0.0979
	wR_2[b] = 0.1309	wR_2[b] = 0.2009

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

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