

Short communication

Molybdovanadate $[\text{VMo}_7\text{O}_{26}]^{5-}$ cluster directed inorganic-organic hybrid: The highest coordination linkage and in situ isoniazid dimerizationYanqing Zhao ^{a,b}, Qiao Gao ^c, Ran Tao ^a, Fengyan Li ^a, Zhixia Sun ^a, Lin Xu ^{a,*}^a Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, PR China^b College of Basic Science, Jinzhou Medical University, Jinzhou, Liaoning 121001, PR China^c School of Pharmaceutical Sciences, Changchun University of Chinese Medicine, Changchun, Jilin 130117, PR China

ARTICLE INFO

Article history:

Received 30 November 2017

Received in revised form 21 January 2018

Accepted 26 January 2018

Available online 31 January 2018

Keywords:

Molybdovanadate

Isoniazid dimer

Crystal structure

Surface photovoltage

Semiconducting property

ABSTRACT

A new inorganic-organic hybrid based on both the new molybdovanadate species and the isoniazid dimer, $\text{H}_4\text{K}_2\text{Na}_2(\text{H}_2\text{O})_4(\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_2)(\text{VMo}_7\text{O}_{26})_2 \cdot 10\text{H}_2\text{O}$ (**1**), was synthesized and structurally characterized by single crystal X-ray crystallography, spectroscopic and thermogravimetric analyses. To our knowledge, compound **1** is the first example of inorganic-organic hybrid based on both polyoxometalate and isoniazid. In compound **1**, twelve surface oxygen atoms of $[\text{VMo}_7\text{O}_{26}]^{5-}$ cluster are utilized to make coordination linkage with other components; creating the highest coordination connection in molybdovanadates subfamily. Interestingly, the in situ isoniazid dimerization reaction could occur during the synthesis process, and then the in situ generated isoniazid dimer could function as a linker to join the coordination assembly of 3D architecture. Furthermore, the semiconducting property of compound **1** was investigated by photophysical measurements, demonstrating the characteristics of n-type semiconductor.

© 2018 Elsevier B.V. All rights reserved.

As a new type of solid state materials, inorganic-organic hybrid compounds with various structures and chemical compositions have been developed considerably in view of their potential applications in material science, industrial catalysis, energy storage, etc. [1,2]. Among them, hybrid compounds based on the inorganic building block of polyoxometalates (POMs) have recently received increasing attention. POMs is a rich family of inorganic metal-oxo cluster compounds (based mainly on Mo, V, Nb and Ta) with a unique structural variety and interesting physicochemical properties, showing wide applications in catalysis, molecular electronics, materials science and medicine [3–5]. In particular, recent researches have demonstrated that POMs of semiconducting property could also find applications in photovoltaic and energy storage devices such as solar cells and supercapacitor [6,7]. Furthermore, as spherical cluster anions, POMs can utilize their surface oxygen atoms to form coordination bonding with other components, which is favorable to assemble inorganic-organic hybrid architecture as well as crystal engineering.

In the large family of POMs, an important subfamily is the mixed molybdenum-vanadate metal-oxo cluster compounds (molybdovanadates) that may act as oxidative catalysts considering their highest oxidation ability. Meanwhile, molybdovanadates with structural flexibility will increase the linking versatility in coordination assembly of inorganic-organic hybrid

compounds. However, few molybdovanadates have been synthesized and structurally characterized, in contrast to other types of POMs, so that the development of molybdovanadate-based inorganic-organic hybrid materials is greatly limited. In 1979, Björnberg et al. firstly reported the crystal structure of molybdovanadate $[\text{V}_2\text{Mo}_6\text{O}_{26}]^{6-}$ [8], and then the similar species $[\text{V}_2\text{Mo}_6(\text{OH})_2\text{O}_{24}]^{4-}$ and $\{\text{Cu}(\text{en})_2\}[\text{V}_2\text{Mo}_6\text{O}_{26}(\text{Cu}(\text{en})_2)_2] \cdot 4\text{H}_2\text{O}$ were also synthesized by under hydrothermal conditions [9]. In 1999, Marina Cindric et al. reported the crown-shaped molybdovanadate $[\text{HMo}_6^{\text{V}}\text{V}^{\text{O}}\text{O}_{22}(\text{NH}_3\text{CH}_2\text{COO})_3]^{2-}$, in which the MoO_6 octahedra are in pairs bridged by glycine through its carboxylate group [10]. More recently, our group found two new molybdovanadates $[\text{V}_2\text{Mo}_{16}\text{O}_{58}]^{10-}$ and $[\text{VMo}_7\text{O}_{28}]^{9-}$, which were in coordination linkage assembled into multidimensional frameworks [11,12]. Significantly, the two molybdovanadates exhibited semiconducting behavior.

Motivated by synthetic challenge and potential applicability, we attempt to continue the exploration of new molybdovanadates and further coordination assembly. Herein, we report a new molybdovanadate $\text{H}_4\text{K}_2\text{Na}_2(\text{H}_2\text{O})_4(\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_2)(\text{VMo}_7\text{O}_{26})_2 \cdot 10\text{H}_2\text{O}$ (**1**), in which the new molybdovanadate species $[\text{VMo}_7\text{O}_{26}]^{5-}$ is linked with organic isoniazid dimer, Na^+ and K^+ cations to form 3D architecture. Compound **1** was synthesized under conventional conditions and structurally characterized by elemental analysis, single crystal X-ray diffraction, IR spectrum, UV–Vis electronic spectroscopy, X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA). To the best of our knowledge, compound **1** is the first example of inorganic-

* Corresponding author.

E-mail address: linxu@nenu.edu.cn (L. Xu).

organic hybrid based on both polyoxometalate and isoniazid. The most interesting feature of compound **1** is that eleven terminal oxygen atoms from fourteen terminal oxygen atoms of $[\text{VMo}_7\text{O}_{26}]^{5-}$ cluster are bonded in coordination linkage with other components, creating the highest coordination connection in molybdovanadates subfamily. The another unexpected result is that an in situ isoniazid dimerization reaction could occur during the synthesis of compound **1**. Furthermore, the results of photophysical measurements demonstrate that compound **1** shows the property of n-type semiconductor.

Compound **1** was synthesized from $(\text{NH}_4)_2\text{MoO}_4 \cdot 4\text{H}_2\text{O}$, NaVO_3 , KCl and isoniazid at 80–90 °C and $\text{pH} = 1.5\text{--}2$ [13]. Single-crystal X-ray diffraction analysis revealed that compound **1** crystallizes in the monoclinic space group $C2/c$ [14]. The crystal structure of **1** contains molybdovanadate anion $[\text{VMo}_7\text{O}_{26}]^{5-}$, isoniazid dimer, Na^+ and K^+ cations as linker, coordination water molecule, and crystal water. Structural refinement of the population parameters indicates that a vanadium atom is of disordered occupy over three different positions of metal center. The molecular structure of $[\text{VMo}_7\text{O}_{26}]^{5-}$ is the same as that isopolymolybdate $\beta\text{--}[\text{Mo}_8\text{O}_{26}]^{4-}$ [15]. And the structure of the molybdovanadate anion $[\text{VMo}_7\text{O}_{26}]^{5-}$ is displayed in Fig. 1a. In compound **1**, the Mo–O_t (terminal oxygen) distance range is from 1.65(2) to 1.72(3) Å; the Mo–O_b (edge-sharing oxygen atoms) and Mo–O_c (corner-sharing oxygen atoms) distances are in the ranges of 1.73(2)–2.26(5) and 1.93(5)–2.39(5) Å, respectively; the Mo–O_{is} distance range is 2.14(2)–2.43(2) Å. However, V–O distances are indistinguishable due to the disordered occupy of the vanadium atom. The results of bond valence sum (BVS) calculation for **1** indicate that the oxidation states of all the Mo atoms are +6. The XPS measurements of compound **1** are also performed to identify the oxidation states of Mo and V atoms (Fig. S2). Two peaks at 232.3 and 235.4 eV are attributed to Mo 3d_{5/2} and Mo 3d_{3/2} level, respectively, and the peak at 523.0 and 516.8 eV are attributed to V 2p_{1/2} and V 2p_{3/2} level, indicating their oxidation states of +6 for Mo atom and of +5 for V atom. In addition, the charge balance in the formula of compound **1** can be explained as follows: Besides four alkali metal cations, the two pyridine N atoms in the isoniazid dimer $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$ are protonated due to the acidic aqueous solution, and thus the protonated organic cation $[\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2]^{2+}$ have two positive charges. Furthermore, the other four positive charges belong to the four protonated water molecules.

It was well known that the surface oxygen atoms (terminal oxygen atoms and edge-sharing oxygen atoms) of POM clusters could form coordination bonds with other metal centers; this is also the driving force for constructing POM-based inorganic-organic hybrid frameworks. However, previous researches indicated that achieving more coordination bonds of surface oxygen atoms generally need to employ the hydrothermal reaction system rather than the conventional synthesis

condition, suggesting the low reactivity of the surface oxygen atoms of POMs. Unexpectedly, although the synthesis reaction of compound **1** occurs under conventional condition, the molybdovanadate anion $[\text{VMo}_7\text{O}_{26}]^{5-}$ in compound **1** provides twelve surface oxygen atoms to act as coordination linkage points, in which eleven linkage points come from the terminal oxygen atoms and one linkage point from the edge-sharing oxygen atom (Fig. 1b). The use of twelve surface oxygen atoms making chemical bonds in compound **1** creates the highest coordination connection in molybdovanadates subfamily, suggesting the high reactivity of these surface oxygen atoms. We consider that the vanadium atom incorporated into isopolymolybdate cluster may increase the electron density of its surface oxygen atoms, thereby enhancing ligand reactivity.

More interestingly, we attempt to use isoniazid as starting material in the synthesis reaction for creating inorganic-organic hybrid, but an isoniazid dimer $[\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_2]^{2+}$ appears unexpectedly in the resulting product, which has been proven by the data of single-crystal X-ray diffraction analysis. In 1953, Yale et al. reported the oxidative dimerization of isoniazid into *N,N'*-bis(isonicotinic acid) hydrazide by using HgO as oxidant (Fig. S3), suggesting that a suitable oxidant may induce the dimerization reaction of isoniazid [16]. In the synthesis process of compound **1**, ammonium molybdate and sodium metavanadate were firstly dissolved in HCl aqueous solution ($\text{pH} = 2$) with heating at 90 °C for 1.5 h, and then isoniazid was added into the solution. Thus we infer that POMs species could be produced firstly and then may become suitable oxidants to induce the dimerization reaction of isoniazid. The investigation on the reaction mechanism is in progress in our group, considering that the mechanism may direct a new route to the oxidative coupling of hydrazides into diacylhydrazines. As shown in Fig. 2, the in situ synthesized *N,N'*-bis(isonicotinic acid) hydrazide acts as a linker to form 2D layer conformation, in which the oxygen atom from the carbonyl group of *N,N'*-bis(isonicotinic acid) hydrazide is in coordination bond linked with the sodium atom, leading to the 2D interconnections of $[\text{VMo}_7\text{O}_{26}]^{5-}$ cluster anions. Furthermore, multipoint hydrogen bonds play an important role in the formation of 3D architecture, such as the representative hydrogen bonds O3w...O12w (2.97 Å), O3w...O5w (2.86 Å), O2w...O11w (2.88 Å), O10...O9w (2.96 Å), O2...O6w (3.07 Å), and O6w...O4w (2.66 Å).

As for compound **1**, the structure of anion $[\text{VMo}_7\text{O}_{26}]^{5-}$ is the same as that of anion $\beta\text{--}[\text{Mo}_8\text{O}_{26}]^{4-}$, and thus the IR spectra of compound **1** appear in the similarly characteristic vibrational features of Mo–O bonds with that $\beta\text{--}[\text{Mo}_8\text{O}_{26}]^{4-}$ structure, as shown in Fig. S3. The IR spectrum of **1** exhibited four strong bands at 939, 901, 824 and 720 cm^{-1} , which are attributed to $\text{M}=\text{O}$ and $\text{M}-\text{O}-\text{M}$ ($\text{M} = \text{Mo}$ or V) stretching vibrations. The bands in the 1700–1245 cm^{-1} region are ascribed to characteristic vibrations of the *N,N'*-bis(isonicotinoyl) hydrazide, further

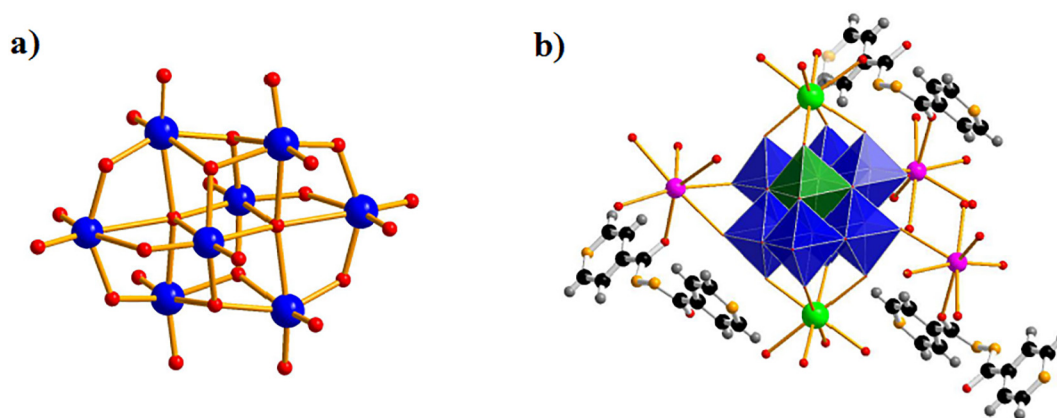


Fig. 1. (a) The structure of the molybdovanadate anion $[\text{VMo}_7\text{O}_{26}]^{5-}$ in compound **1**; The blue balls indicate the disordered V atom is partially occupied in all Mo atoms sites (V/Mo: blue; O: red). (b) The twelve coordination linkage points of $[\text{VMo}_7\text{O}_{26}]^{5-}$ (polyhedral representation) with Na^+ and K^+ cations, together with three isoniazid dimers. (VO_6 octahedra: green; MoO_6 octahedra: blue; K: green ball; Na: rosiness; O: red; C: black; N: ochre; H: grey; other components of compound **1** are omitted for clarity).

Download English Version:

<https://daneshyari.com/en/article/7748657>

Download Persian Version:

<https://daneshyari.com/article/7748657>

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