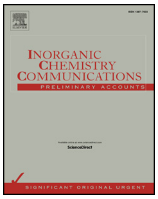
Inorganic Chemistry Communications 97 (2018) 74–78

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

journal homepage: www.elsevier.com/locate/inoche



Short communication

An unusual 2, 12-connected 3-D open framework based on $\{As_2Mo_6O_{26}\}$-type polyoxometallate and copper-pyrazole complex

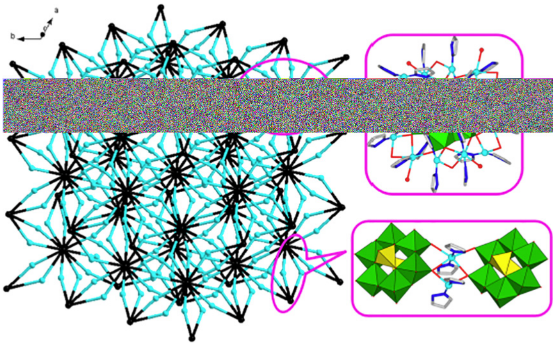
Maolin Zhang[a,b], Jinghua Lv[a], Kai Yu[a,b,*], Kunpeng Wang[a,b], Fanxue Meng[a,b], Baibin Zhou[a,b,*]

[a] Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, People's Republic of China

[b] Key Laboratory of Synthesis of Functional Materials and Green Catalysis, Colleges of Heilongjiang Province, Harbin Normal University, Harbin 150025, People's Republic of China

GRAPHICAL ABSTRACT

An unusual 2, 12-connected 3-D open framework with a new $\{2^6{\cdot}4^{48}{\cdot}6^{12}\}\{2\}_6$ topology based on $\{As_2Mo_6O_{26}\}$-type polyoxometallate and $\{Cu(pry)_2\}$ complexes has been hydrothermally synthesized. Compound **1** exhibits good fluorescent properties in solid state at room temperature and bifunctional electrocatalytic activities for oxidation of ascorbic acid (AA) and reduction of nitrite (NO_2^-).



[redacted]

ARTICLE INFO

Keywords:
$\{As_2Mo_6O_{26}\}$-type POM
Organic-inorganic hybrid
Electrocatalytic activity
Fluorescent property

ABSTRACT

An unusual 3-D organic-inorganic hybrid based on arsenomolybdate, $[\{Cu^I(pyr)_2\}_6(As_2Mo_6O_{26})]{\cdot}H_2O$ (**1**) (pyr = pyrazole) has been synthesized under hydrothermal conditions and structurally characterized by elemental analysis, IR, TG, PXRD, UV–vis, and single-crystal X-ray diffraction. In compound **1**, basic structural unit $\{As_2Mo_6O_{26}\}$ (abbreviated as $\{As_2Mo_6\}$) as dodeca-dentate ligand utilizes all of its terminal oxygen atoms (12) of $\{Mo_6O_{24}\}$ ring to connect with 12 $\{Cu(pyr)_2\}$ linkers at its periphery. Two $\{Cu(pyr)_2\}$ complexes are bonded together to form binuclear complex unit $\{Cu_2(pyr)_4\}$ via sharing two u_3-O atoms, which can be viewed as bidentate linker to further connect with adjacent two $\{As_2Mo_6\}$ clusters. The coordination number and modes of $\{As_2Mo_6\}$ cluster and Cu^+ ions together result in a 2, 12-connected 3D open-skeleton with a new $\{2^6{\cdot}4^{48}{\cdot}6^{12}\}\{2\}_6$ topology, which represents the highest connection of $\{As_2Mo_6\}$-based inorganic-organic hybrid. Compound **1** exhibits good fluorescent properties in solid state at room temperature and bifunctional electrocatalytic activities for oxidation of ascorbic acid (AA) and reduction of nitrite (NO_2^-).

---

[*] Corresponding authors at: Key Laboratory for Photonic and Electronic Bandgap Materials, Ministry of Education, School of Chemistry and Chemical Engineering, Harbin Normal University, Harbin 150025, People's Republic of China.

E-mail addresses: hlyukai188@163.com (K. Yu), zhou_bai_bin@163.com (B. Zhou).

https://doi.org/10.1016/j.inoche.2018.09.017
Received 14 July 2018; Received in revised form 4 September 2018; Accepted 12 September 2018

1. Introduction

The rapid development of polyoxometalates (POMs) is derived not only from their rich structure but also from their ideal properties, which give them wide applications in electrochemistry [1–3], photochemistry [4,5], catalysis [6–8], and adsorption [9–11]. At present, more and more researchers are interested in the construction of POM-based organic-inorganic hybrid materials. One of the important characteristics of these materials is the integration of POMs inorganic building blocks and organic ligands through establishing a linkage between the active oxygen atoms on the surface of POMs and organic ligand molecules or transition metal (TM) complexes [12–14]. The organic ligands are grafted into inorganic skeletons via this connection. Implantation of organic ligands dramatically enriches the structure of hybrid derivatives. The synergistic effect between organic and inorganic constituents endows hybrid derivatives with composite and novel properties. In addition, these kinds of hybrid compounds can be finely modulated on the molecular level, which are potential novel catalyst and ideal functional materials with photoelectric properties [15]. Many heteropolymolybdate hybrids have been reported recently due to the reversible redox properties of molybdenum [16,17]. Compared with many reported phosphomolybdate hybrids, arsenomolybdate analogues receive little attention. In particular, $[H_xAs_2Mo_6O_{26}]^{(6-x)-}$ (abbreviated as $\{As_2Mo_6\}$) clusters are still less common [18–27]. Since the $\{As_2Mo_6\}$-type POM cluster based on molybdenum organoarsonate was first synthesized by Pope, in 1976, A- and B-type $\{As_2Mo_6\}$ structures were analyzed by X-ray diffraction and characterization techniques [18–20]. Zubieta's and Ma's teams reported a series of organic-inorganic compounds based on $\{As_2Mo_6\}$ cluster and organic arsenic [21,22]. Then some extended hybrid materials based on inorganic arsenomolybdate clusters were reported by Wang and Niu et al. [23,24]. Recently, a series of hybrids based on $\{As_2Mo_6\}$ POMs and TM complexes were obtained using $NaAsO_2$ as raw material of arsenic by our group [25–27]. However, 3-D high-connected compound based on $\{As_2Mo_6\}$-type POMs has not yet been synthesized so far. Literature studies have shown that the maximum number of covalent connections for the kind of hybrids is no more than four. Thus, it would be a challenging and promising subject to synthesize this kind of derivatives.

In this work, $\{Cu(pyr)_2\}$ complexes are introduced into $\{As_2Mo_6\}$ skeleton to result in an unusual 2,12-connected 3-D open framework, $[\{Cu^I(pyr)_2\}_6(As_2Mo_6O_{26})]\cdot H_2O$ (**1**), which represents the highest connection of $\{As_2Mo_6\}$-based inorganic-organic hybrid.

Single-crystal X-ray diffraction analysis (Table S1) reveals [28,29] that the basic unit of compound **1** consists of a $\{As_2Mo_6O_{26}\}$ cluster, six $\{Cu^I(pyr)_2\}$ linkers, and a lattice water molecule, as shown in Fig. S1. The $\{As_2Mo_6O_{26}\}$ cluster is a highly symmetrical ring whose six $\{MoO_6\}$ octahedra and two $\{AsO_4\}$ tetrahedra are obtained by symmetric operations of one crystallographically independent Mo and As atom, respectively (Fig. S1). These $\{MoO_6\}$ octahedra are edge-connected to form a $\{Mo_6O_{24}\}$ ring, which was further capped by two $\{AsO_4\}$ tetrahedra on the both faces of the ring. Each $\{AsO_4\}$ terahedron links with six $\{MoO_6\}$ octahedra through three u_3-O atoms sharing by two molybdenum atoms and one arsenic center. The bond lengths of As—O and Mo—O are in the range of 1.65(3)–1.76(2) Å and 1.71(2)–2.348(19) Å, respectively. The bond angles of O—As—O and O—Mo—O are in the normal ranges (Table S2).

Each $\{As_2Mo_6\}$ cluster as a dodeca-dentate ligand uses all of terminal oxygen atoms (12) of $\{Mo_6O_{24}\}$ ring to bond with peripheric twelve $\{Cu(pyr)_2\}$ segments (Fig. 1). There are two crystallographically independent Cu atoms exhibiting two kinds of coordination environments in compound **1**. Cu1 atom adopts a tetrahedron geometry which is defined by two nitrogen atoms from two pyr moleculars with the distance of Cu1–N2, 1.89(2) Å and two u_3-O atoms shared by two Cu atoms and one Mo atom with Cu1–O2, 2.41(3) Å. Each Cu2 center exhibits hexa-coordinated octahedron geometry defined by two nitrogen atoms from two pyr moleculars with Cu2–N1, 1.91(2) Å and two u_3-O atoms shared by two Cu atoms and one Mo atom, and two u_2-O atoms shared by a Cu atom and one Mo atom. The average bond length of Cu—O is 2.715 Å. Two $\{Cu(pyr)_2\}$ complexes are connected together to form binuclear complex unit $\{Cu_2(pyr)_4\}$, which acts as bidentate linker to connect adjacent $\{As_2Mo_6\}$ clusters. Each $\{As_2Mo_6\}$ cluster links with six binuclear complex units $\{Cu_2(pyr)_4\}$ via terminal O atom of $\{Mo_6O_{24}\}$ ring, in which four $\{Cu_2(pyr)_4\}$ linkers further connect four $\{As_2Mo_6\}$ clusters along 101 crystal to form 2-D layer (Figs. 2 and S2). The other two $\{Cu_2(pyr)_4\}$ units projecting from the 2-D layer, are linked to two $\{As_2Mo_6\}$ clusters of the adjacent two layers to give rise to a complicated 3D inorganic-organic hybrid network (Figs. 3 and S3).

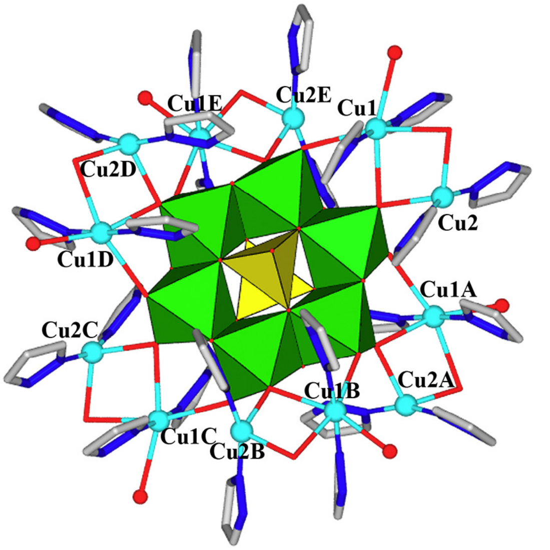


Fig. 1. The Coordination environment of $\{As_2Mo_6\}$ clusters in compound **1**; Symmetry code: A: y, −x + y, −z; B: −x + y, −x, z; C: −x, −y, −z; D: −y, x − y, z; E: x − y, x, −z.

In this 3-D structure, each $\{As_2Mo_6\}$ cluster links six peripheric analogs by six binuclear complex $\{Cu_2(pyr)_4\}$ linkers. Meanwhile each binuclear complex is shared by two $\{As_2Mo_6\}$ clusters. The structure of **1** can be simplified to a 2,12-connected 3-D topological framework with $\{2^6\cdot 4^{48}\cdot 6^{12}\}\{2\}_6$ topology (Fig. 4). In this simplification, the 12-connected nodes are $\{As_2Mo_6\}$ clusters, and the 2-connected nodes are Cu centers (Table 1).

Bond-valence sum (BVS) calculations [30] show As, Mo, and Cu

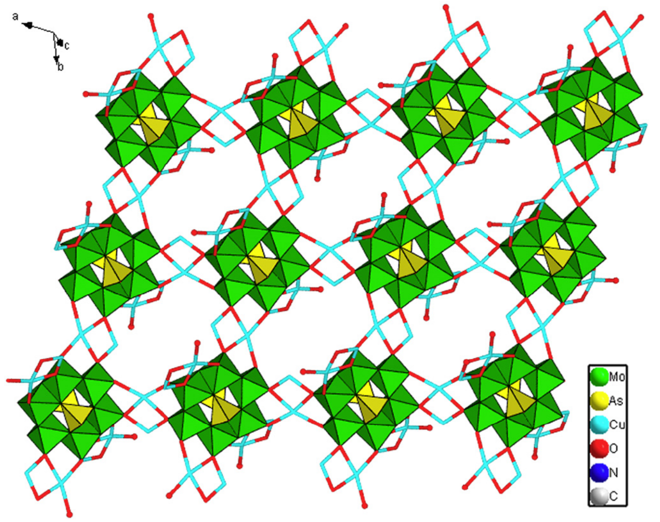


Fig. 2. The 2D layer of compound **1** linked by $\{Cu(pry)_2\}$ linker (pry ligands were omitted for clarity).