Inorganic Chemistry Communications 86 (2017) 22–25

Contents lists available at ScienceDirect

Inorganic Chemistry Communications

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

Short communication

Copper(II) and cadmium(II) complexes derived from Strandberg-type polyoxometalate clusters: Synthesis, crystal structures, spectroscopy and biological activities

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ARTICLE INFO

Article history:
Received 30 July 2017
Received in revised form 4 September 2017
Accepted 14 September 2017
Available online 18 September 2017

Keywords:
Polyoxometalate
Crystal structures
Spectroscopy
Cytotoxicity

ABSTRACT

Three Strandberg-type polyoxometalate compounds $[Cu(L)_2(H_2O)_2]_2H_2[P_2Mo_5O_{23}]\cdot 2CH_3OH$ **(1)**, $[Cu(L)_2(H_2O)]H_2[Cu(L)_2(P_2Mo_5O_{23})]\cdot 4H_2O$ (**2**), $[Cd(L)_2(H_2O)_2]_2H_2[P_2Mo_5O_{23}]\cdot 2CH_3OH$ (**3**), (L = pyridine-2-carboxamide) have been synthesized and structurally characterized by elemental analysis, spectroscopic methods (IR and UV–vis) as well as single crystal X-ray diffraction. Single-crystal X-ray structural analyses indicate that **1** and **3** are isostructural and crystallized in monoclinic, space group *I2/a*. Biological studies have indicated that compounds **1**–**3** exhibit broad and effective activities against the tested cells. A synergistic effect involving L, metal and P_2Mo_5 could probably explain the improved growth-inhibiting properties. Both coordination mode and the type of metal ion play significant roles in these compounds cytotoxicity.

Polyoxometalates (POMs), as early transition metal oxygen clusters, have been attracting an increasing attention owing to structural and compositional diversity and manifold potential applications in catalysis [1], material [2], electrochemistry [3], photochemistry [4], magnetism [5], biology [6] and medicine [7–9]. Some functionalized POMs have been used as inhibitors of HIV-1 protease [10] or the promoters of Aβ-binding activity [11–12]. Among the versatile POMs building blocks such as Keggin [13], Dawson [14] and Anderson [15] type polyoxoanions, Strandberg-type phosphomolybdates (abbreviated as $[P_2Mo_5O_{23}]^{6-}$) as a preminent building block seized our attention due to their unique properties and structures [16]. As an important member of POMs family, Strandberg-type polyanions have a relatively smaller size but higher charge densities compared to other POMs, which can induce more metal-organic compounds cationic units to enter the crystal structures of the final products [16]. Meanwhile, the $[P_2Mo_5O_{23}]^{6-}$ polyanion is widely used as templates or inorganic building subunits to construct inorganic-organic hybrid compounds with desired properties. To construct hybrid compounds based upon POMs, the selection of organic ligands plays an important role. Recently a series of compounds based on $[P_2Mo_5O_{23}]^{6-}$ through the linking of organoamine bases have been reported. However, most of this kind of compounds are obtained from polyoxometalate clusters and organoamine by strong hydrogen bonds which involve the oxygen atoms acceptors and stabilize the crystal structure [17]. The various topologies can be interpreted in terms of supramolecular synthons between organic moieties and water molecules along with $[P_2Mo_5O_{23}]^{6-}$ cluster [18–19]. An intelligent choice of POMs and metal coordination complexes may yield materials with fascinating structures and desirable properties [20–21]. Recently, many efforts have been made to modify POMs through altering their structure, polarity, charge and composition in order to obtain compounds with superior biological activity, higher physiological stability and lower toxicity [22–25].

Pyridine-2-carboxamide has good pharmacological activity, possessing stronger anti-TB and antibacterial activities, therefore it can be used in the process of biology and medicine [26]. The carboxamide [—C(O)NH—] group of the primary structure of proteins represents an important construction unit in coordination chemistry and exhibits various biological activity [27–29]. Pyridine formamide with transition metal coordination, mainly include O-monodentate [30], O, O-bidentate ligands [31], N, O bidentate ligands [26,30] and N, O, O tridentate ligands [32]. A wide variety of pyridine-2-carboxamide ligands have been synthesized for investigating their coordination properties with metal ions. Structural investigation of some metal compounds of pyridine-2-carboxamide ligand (L) have been reported previously, including Cu(II) [33], Ni(II) [29], Zn(II), Cd(II) and Hg(II) [34]. In particular, pyridine-2-carboxamide copper complexes have good antibacterial activity [33]. Therefore, in order to obtain antitumor candidates of high efficiency and low toxicity, study of the pharmacological activity of POMs and pyridine derivative has important theoretical and practical significance [35].

In the present paper, we describe the synthesis, chemical characterization of three Strandberg-type inorganic-organic hybrid compounds, $[Cu(L)_2(H_2O)_2]_2H_2[P_2Mo_5O_{23}]\cdot 2CH_3OH$ **(1)**,

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https://doi.org/10.1016/j.inoche.2017.09.014
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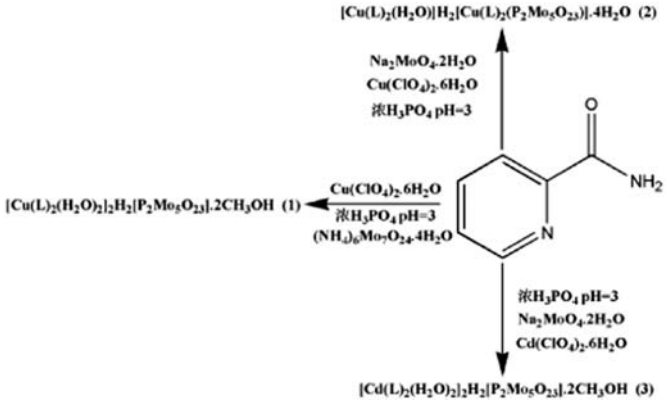

Scheme 1. The reaction scheme for the synthesis of **1–3.**

$[Cu(L)_2(H_2O)]H_2[Cu(L)_2(P_2Mo_5O_{23})]\cdot 4H_2O$ **(2)** and $[Cd(L)_2(H_2O)_2]_2H_2[P_2Mo_5O_{23}]\cdot 2CH_3OH$ **(3)**, (Scheme 1). The crystal structures of the complexes **1**, **3** have been determined by X-ray crystallography. The biological properties of **1–3** have been studied.

Complexes **1** and **3** were synthesized by solvent evaporation method [36], and **2** was prepared according to the literature method [37]. Crystals of **1** and **3** suitable for X-ray studies were obtained by slow evaporation of their methanol solutions.

Single-crystal X-ray structural analyses [38] reveals that **1** and **3** are isostructural (Fig. 1) and crystallized in the monoclinic, space group *I*2/*a*. Thus, only the structure of **1** is described in detail. Compound **1** is based on the P_2Mo_5 cluster. The P_2Mo_5 cluster is composed of five distorted MoO_6 octahedra with two capped PO_4 tetrahedra on each side. The five MoO_6 octahedra generate a pentagonal ring by sharing edges and corners and two PO_4 tetrahedra are connected to each side of the ring, sharing three oxygen atoms with different MoO_6 units [19]. The bond lengths of P—O and Mo—O range from 1.515(2) to 1.562(2) Å, 1.702(2) to 2.409(2) Å, respectively. All bond lengths and bond angles of the polyoxoanions are within the normal ranges [39–40]. As shown in Fig. 1a, compound **1** consists of one $[P_2Mo_5O_{23}]^{6-}$, two $[Cu(L)_2(H_2O)_2]^{2+}$ and two dissociative methanol molecules [41]. Two crystallography independent copper(II) ions with similar coordination environment, adopt a six-coordinated distorted octahedral geometry. The crystallographic analysis showed that each Cu(II) is coordinated by two N atoms, two O atoms from two L ligands and two O atoms from two water molecules with Cu—N bond lengths of 1.999(3)–2.008(3) Å, Cu—O bond lengths of 2.120(3)–2.153(2) Å, respectively.

The crystal is stabilized by intramolecular and intermolecular hydrogen interactions. As shown in Fig. 1b, NH_2, CH_3OH and H_2O act as the proton donors, O atoms of $[P_2Mo_5O_{23}]^{6-}$ work as the proton acceptors with O—H···O (3.134(5) Å), N—H···O (2.851(3)–2.968(3) Å) and Ow—H···O (2.770(3)–3.091(4) Å), respectively.

In the infrared spectrum of compounds **1** and **3.** As seen in Fig. S1, the characteristic peaks at 3333–3452 cm^{-1} are attributed to the O—H stretching vibration of water [42]. The peaks at 3120–3197 cm^{-1} are related to the ν(N—H) of pyridine-2-carboxamide [43]. Bands in the region of 1112–1010 cm^{-1} are assigned to ν(P—O) stretching vibration [44]. While the characteristic peaks at (926–931, 890–892 cm^{-1}), 704–706 cm^{-1} are attributed to the ν(Mo═O_d) and ν(Mo—O—Mo), respectively [3].

As seen in Fig. S2, the UV spectra of **1** and **3** in aqueous solution (1×10^{-5} mol·L^{-1}) reveal two strong absorption bands at *ca*. 210

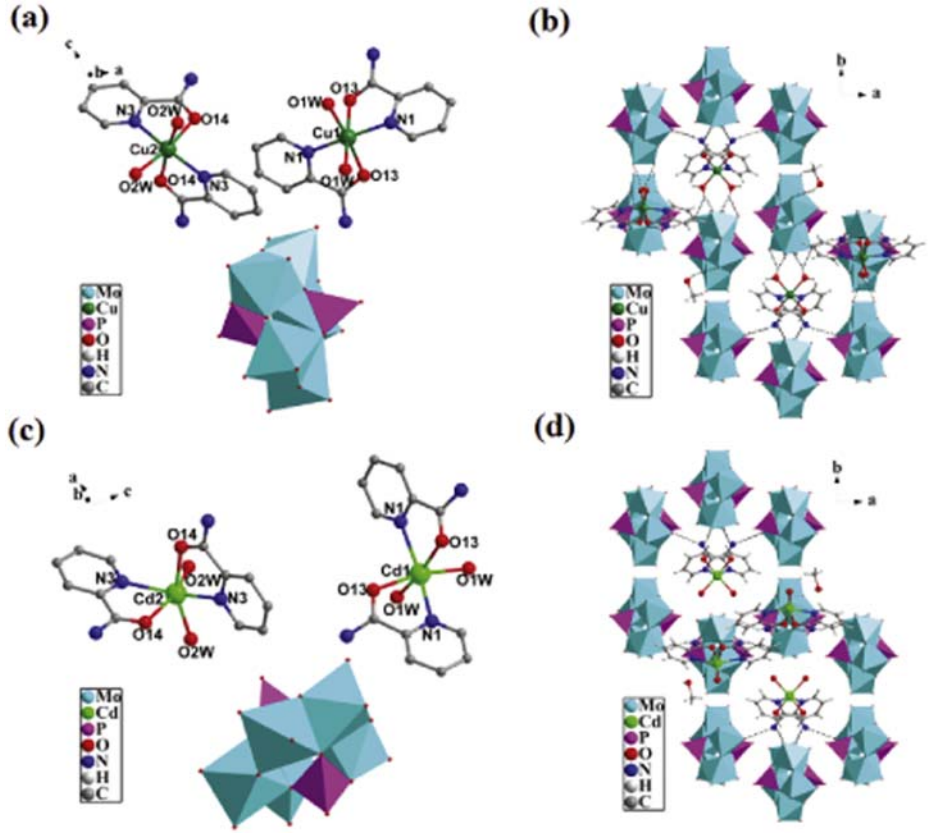

Fig. 1. (a) Structure of compound **1** with atomic numbering scheme (The hydrogen atoms and dissociative methanol molecules have been omitted), (b) The molecular packing projected intramolecular and intermolecular hydrogen interaction along the *c*-axis. (c) Structure of compound **3** with atomic numbering scheme (The hydrogen atoms and dissociative methanol molecules have been omitted), (d) The molecular packing projected intramolecular and intermolecular hydrogen interaction along the *c*-axis.