



Ligands directed versatile cadmium-bis(triazole) metal–organic fragments to generate three new two dimensional complexes based on polymolybdenum phosphate

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ABSTRACT

Three new two dimensional (2D) polymolybdenum phosphate-based cadmium complexes, $[\text{Cd}_{2.5}(\text{btp})_2(\text{H}_2\text{O})_3][\text{Cd}_{0.5}(\text{PO}_4)(\text{HPO}_4)_3(\text{MoO}_2)_6(\text{OH})_3] \cdot 2\text{H}_2\text{O}$ (**1**), $[\text{Cd}(\text{Hbtb})(\text{H}_2\text{O})_4][\text{Cd}(\text{PO}_4)_4(\text{HPO}_4)_4(\text{MoO}_2)_{12}(\text{OH})_6] \cdot 6\text{H}_2\text{O}$ (**2**) and $[\text{Cd}(\text{H}_2\text{O})_2][\text{Cd}(\text{H}_2\text{O})(\text{Hbth})]_2[\text{Cd}_{0.5}(\text{H}_2\text{O})(\text{bth})]_2[\text{Cd}(\text{PO}_4)_4(\text{HPO}_4)_2(\text{H}_2\text{PO}_4)_2(\text{MoO}_2)_{12}(\text{OH})_6] \cdot 4\text{H}_2\text{O}$ (**3**) (btp = 1,3-bis(1,2,4-triazol-1-yl)propane, btb = 1,4-bis(1,2,4-triazol-1-yl)butane and bth = 1,6-bis(1,2,4-triazol-1-yl)hexane), have been synthesized and characterized by elemental analysis, IR, TG and single crystal X-ray diffraction. Single crystal X-ray diffraction analyses reveal that all the compounds are based on the polymolybdenum phosphate $[\text{P}_4\text{Mo}_6\text{O}_{28}(\text{OH})_3]^{9-}$ ($[\text{P}_4\text{Mo}_6]$) units, which are further connected into sandwich-type $[\text{Cd}(\text{P}_4\text{Mo}_6)_2]$ dimers by cadmium ions, and different multi-nuclear Cd^{II} subunits. There exist penta-nuclear subunits in **1**, which are further connected by btp ligands to form 1D chains; tetra-nuclear fragments in **2**; and a 1D zigzag Cd–O–P chains based on tri-nuclear Cd^{II} units in **3**, all of which are extended into different 2D networks by $[\text{Cd}(\text{P}_4\text{Mo}_6)_2]$ dimers. The $-(\text{CH}_2)_n-$ spacers of the bis(triazole)-based ligands play an important role in the formation of multi-nuclear Cd^{II} subunits and the ultimate 3D supramolecular frameworks. Moreover, the thermal stabilities, electrochemical properties of the title compounds have been investigated in this paper.

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1. Introduction

In the past decades, chemists have dedicated great effort to the design and construction of polyoxometalate (POM)-based metal–organic complexes (MOCs) not only for their novel molecular topologies but also for their potential applications in magnetism, catalysis, electrochemistry and functional materials [1–4]. As is known, a remarkable branch is to modify the POMs with versatile transition metal complexes (TMCs) [5–10]. However, introduction of multi-nuclear secondary building units (SBUs) as special TMCs to the POM's field are still limited [11–13]. At present, four main strategies have been developed for the construction of polymetallic SBUs in POM-based compounds: (i) the metal ions are bridged by halogen atoms to generate metal-clusters [14–16]; (ii) the metal–metal bond donates to form the polymetallic clusters [17–19]; (iii) the polycarboxylic acids act as organic linkages to connect the metal ions [20]; (iv) the metal ions are linked by the multidentate N-donor ligands to construct the polynuclear subunits [21]. To our knowledge, reports on the multi-nuclear SBUs modifying POMs are very limited, especially the reduced polymolybdenum

phosphate $[\text{P}_4\text{Mo}_6\text{O}_{28}(\text{OH})_3]^{9-}$ ($[\text{P}_4\text{Mo}_6]$) modified with polynuclear subunits [22], which is still a challenging work.

As is known, $[\text{P}_4\text{Mo}_6]$ is feasible to form sandwich-type dimers with transition-metal ions [23–25]. These $[\text{P}_4\text{Mo}_6]$ -based dimers present favorable properties for the construction of MOCs: (i) it possesses high negative charges due to the reduced Mo^{V} centers, which may joint more cationic units into complicated architectures; (ii) the eight projecting PO_4 units at both sides of the dimer may provide versatile coordination sites for forming the TMCs-modified networks [26–30]. On the other hand, the rational design and selection of suitable organic ligands is a crucial factor for the preparation of $[\text{P}_4\text{Mo}_6]$ -based MOCs. In the previous reports, the rigid pyridine derivatives, such as 2,2'-bipyridine, 4,4'-bipyridine or 1,10-phenanthroline were introduced into the P_4Mo_6 -based MOCs [31–33]. However, most of these MOCs were derived from some discrete metal centers, which may be due to poor flexibility and large steric effect of the rigid organic ligands. Thus, in this work, a kind of flexible bis(triazole) ligands with different spacer length were selected as the main ligands, which not only possess high flexibility, but also own more N-donors coordination sites and small steric effect to enhance their coordination ability, aiming at forming multi-nuclear SBUs for modifying $[\text{P}_4\text{Mo}_6]$ -based dimer. In addition, D,L- α -alanine was selected as a reductive reagent to promote the reduction of Mo^{VI} atoms from MoO_3 to Mo^{V} atoms

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[34], which may combine with the second row transition metal cations Cd^{II} and H₃PO₄ to generate [Cd(P₄Mo₆)₂] dimer and Cd^{II}-organic fragments. As a result, three 2D [Cd_{2.5}(btp)₂(H₂O)₃][Cd_{0.5}(-PO₄)(HPO₄)₃(MoO₂)₆(OH)₃·2H₂O (1), [Cd(Hbtb)(H₂O)]₄[Cd(PO₄)₄(HPO₄)₄(MoO₂)₁₂(OH)₆·6H₂O (2) and [Cd(H₂O)₂][Cd(H₂O)(Hbth)]₂[Cd_{0.5}(H₂O)(bth)]₂[Cd(PO₄)₄(HPO₄)₂(H₂PO₄)₂(MoO₂)₁₂(OH)₆·4H₂O (3) (btp = 1,3-bis(1,2,4-triazol-1-yl)propane, btb = 1,4-bis(1,2,4-triazol-1-yl)butane and bth = 1,6-bis(1,2,4-triazol-1-yl)hexane) have been obtained under the hydrothermal conditions. The thermal stabilities and electrochemical properties of the title compounds have been investigated in this paper.

2. Experimental section

2.1. Materials and measurements

All reagents and solvents for syntheses were purchased from commercial sources and used without further purification. The ligands were synthesized by the literature method [35]. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 240C elemental analyzer. The FT-IR spectra with KBr pellet were taken on a Magna FT-IR 560 spectrometer. Thermogravimetric data for the title compounds were collected on a Pyris-Diamond thermal analyzer under nitrogen atmosphere. A CHI 440 Electrochemical Quartz Crystal Microbalance was used for the electrochemical experiments. The compounds **1**, **2** and **3** bulk-modified carbon paste electrodes (CPE) were used as working electrodes.

2.2. Syntheses of compounds 1–3

Compound **1** was synthesized from a mixture of MoO₃ (0.3 mmol), Cd(OAc)₂·2H₂O (0.6 mmol), D,L-α-alanine (0.9 mmol), btp (0.6 mmol), H₃PO₄ (0.3 mL) and 5 mL of H₂O. The pH value was adjusted to 2.8 by 1 M NaOH, and then the resulting suspension was transferred to a Teflon-lined stainless autoclave and kept under autogenous pressure at 160 °C for 4 days. After slow cooling to room temperature at a rate of 10 °C h⁻¹, orange block crystals of **1** were obtained (yield: 38% based on Mo). Elemental analysis (%) Calc. for C₁₄H₃₆Cd₃Mo₆N₁₂O₃₆P₄: C, 8.47; H, 1.83; N, 8.47. Found: C, 8.41; H, 1.87; N 8.43%. IR (KBr pellet, cm⁻¹): 1631.7(w), 1531.4(w), 1091(s), 1041.5(s), 977.8(s), 960.5(s), 738.7(m), 574(m).

A similar synthetic procedure to that of compound **1** was used for the synthesis of **2**, except for the ligand btb (0.6 mmol) was used instead of btp. The pH was adjusted to about 2.3 with 1 M NaOH, and then orange block crystals of **2** were filtered and washed with distilled water (yield: 42% based on Mo). Elemental analysis (%) Calc. for C₃₂H₆₈Cd₅Mo₁₂N₂₄O₇₂P₈: C, 9.85; H, 1.76; N, 8.61. Found: C, 9.83; H, 1.73; N, 8.59%. IR (KBr pellet, cm⁻¹): 3543.1(w), 3296.1(m), 3143.8(w), 1074.3(s), 1029.9(s), 964.3(s), 925.8(s).

For **3**, a similar synthetic procedure to that of compound **1** was used, except for the ligand bth (0.6 mmol) was used instead of btp. The pH was adjusted to about 2.2 with 1 M NaOH, and then orange block crystals of **3** were filtered and washed with distilled water (yield: 39% based on Mo). Elemental analysis (%) Calc. for C₄₀H₈₄Cd₅Mo₁₂N₂₄O₇₂P₈: C, 11.97; H, 2.11; N, 8.37. Found: C, 12.01; H, 2.15; N, 8.39%. IR (KBr pellet, cm⁻¹): 3122.5(m), 2941.2(w), 2862.2(w), 1018.3(s), 966.3(s), 933.5(s), 734.8(m), 715.5(m).

2.3. Preparation of 1-, 2-, and 3-CPE

The compound **1** bulk-modified carbon paste electrode (**1**-CPE) was fabricated as follows [36]: 0.01 g of compound **1** and 0.1 g of graphite powder were mixed and ground together by an agate

mortar and pestle for approximately half an hour to achieve an even, dry mixture; to the mixture was added 0.20 mL of paraffin oil and the resulting mixture was stirred with a glass rod; then the homogenized mixture was used to pack a 3 mm inner-diameter glass tube to a length of 0.8 cm. Electrical contact was established with a copper stick, and the surface of **1**-CPE was wiped with weighing paper. In a similar manner, **2**- and **3**-CPE were prepared with compounds **2** and **3**, respectively.

2.4. X-ray crystallographic measurements

Single crystal X-ray diffraction (XRD) data for compounds **1–3** were collected on a Bruker Smart 1000 CCD diffractometer with Mo Kα radiation (λ = 0.71069 Å) by ω and θ scan modes at 296 K. The structures were solved by direct methods and refined on F² by full-matrix least squares using the SHELXL package [37]. A summary of the crystallographic data and structural refinements for compounds **1–3** are given in Table 1. Selected bond distances (Å) and angles (°) of the three compounds are listed in Table S1 (Supporting information). All non-hydrogen atoms were refined anisotropically, all the H atoms attached to carbon atoms were generated geometrically while the H atoms attached to water molecules were not located but were included in the structure factor calculations.

3. Results and discussion

3.1. Description of crystal structures

Single crystal X-ray diffraction analysis reveal that compounds **1–3** all contain a classical reduced polymolybdenum phosphate [P₄Mo₆] unit [26–30]. The basic building unit [P₄Mo₆] contains a coplanar ring of six edge-sharing MoO₆ octahedra and four PO₄ tetrahedra. The six oxygen-bridged molybdenum centers [Mo–O: 1.928(5)–2.354(5) Å] approximately in the same plane consist of alternating bonding Mo–Mo (av. 2.608 Å for **1**, 2.606 Å for **2**, 2.607 Å for **3**) and nonbonding Mo···Mo (av. 3.5459 Å for **1**, 3.554 Å for **2**, 3.542 Å for **3**) contacts. One PO₄ tetrahedron is located in the center, providing three oxygen atoms bridging the bonding Mo–Mo contacts, while each of the other three PO₄ groups provides two oxygen atoms to connect the non-bonding Mo···Mo contacts. The P–O bond length is in the range of 1.511(4)–1.580(3) Å for **1**, 1.508(6)–1.570(7) Å for **2** and 1.507(5)–1.586(4) Å for **3**. Two [P₄Mo₆] moieties are linked together by an octahedral Cd^{II} ion constructing a centrosymmetrical sandwich-shaped [Cd(P₄Mo₆O₂₈(OH)₃)₂]¹⁶⁻ ([Cd(P₄Mo₆)₂]) dimer, while the Cd–O bond distances are in the range of 2.238(5)–2.556(4) Å. According to the valence bond calculations [38,39], all Mo atoms are in the reduced oxidation state (+5), Cd atoms are +2. In addition, the μ₂-O atoms between non-bonding Mo atoms (O5, O13, O30 for **1**, O11, O26, O31 for **2**, O3, O10, O22 for **3**) and uncoordinated O atoms of PO₄ groups (O10, O19, O34 for **1**, O24, O31 for **2**, O14, O12 for **3**) are protonated. Therefore the molybdenum phosphate hexamer can be formulated as [(PO₄)(HPO₄)₃(-MoO₂)₆(OH)₃]⁶⁻ for **1**, [(PO₄)₂(HPO₄)₂(MoO₂)₆(OH)₃]⁷⁻ for **2** and [(PO₄)₂(HPO₄)(H₂PO₄)(MoO₂)₆(OH)₃]⁶⁻ for **3**.

Compound **1** is a 2D layered sheet, which is constructed from [Cd(P₄Mo₆)₂] building blocks and penta-nuclear cadmium subunits. There are four crystallographically independent Cd^{II} ions with octahedron coordination mode in compound **1** (see Fig. S1): Cd1 is coordinated by two nitrogen atoms (N7, N7#7) of two btp ligands with Cd–N bond distance of 2.261 Å, two oxygen atoms (O1, O1#7) of two PO₄ tetrahedron from different [Cd(P₄Mo₆)₂] dimers and two coordinated water molecules (O4W, O4W#7) with Cd1–O1, Cd1–O1#7, Cd1–O4W, Cd1–O4W#7 bond distances of

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