



Tin-porphyrin-assisted formation of coordination frameworks



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ABSTRACT

Novel 3D networks synthesized by two different methods are reported in this article. Structure **1** $\{[\text{CdL}_2] \cdot (\text{solvent})\}_n$ consists of Cd^{II} -single metallic nodes held together by coordinated isonicotinate ligands (**L**) to form a 3D chiral framework ($P4_12_12$). The resulting structure exhibits threefold-interpenetrated **dia** coordination networks. After a few weeks the crystals were re-measured to form **1a** $\{[\text{Cd}(\text{L})_2(\text{H}_2\text{O})] \cdot \text{DMF}\}_n$ with two interpenetrated **dia** nets which is thermodynamically more stable. On the other hand, the addition of the tin(IV)-porphyrin to the same reaction mixture led to the formation of 3D pseudo-isostructures, based on oxo-centered Cd^{II} and $\text{Mn}^{\text{II/III}}$ cluster nodes, **2** $\{[\text{Cd}_3(\text{OH})\text{L}_4(\text{H}_2\text{O})_3](\text{ClO}_4)\}_n$ and **3** $\{[\text{Mn}_3(\text{O})\text{L}_4(\text{DMF})_3](\text{ClO}_4)\}_n$. These structures represent topologically **bcg** nets. Possible synthetic mechanism was proposed to emphasize the role of the tin(IV)-porphyrin that led to the construction of oxo-centered trinuclear clusters in **2** and **3**.

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1. Introduction

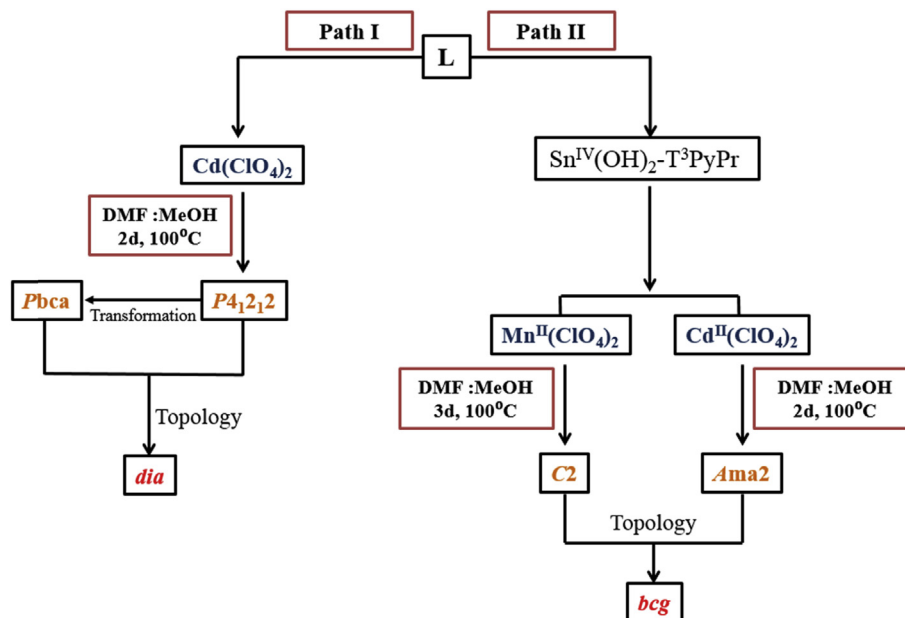
In the last few decades, metal-organic frameworks (MOFs) have gained a considerable attention due to their great potential in various applications [1,2]. MOFs are considered as a class of porous materials, where the stability lies on the strength of the coordinated ligands to suitable metal-ion nodes. MOFs with poly-nuclear metal cluster as secondary building unit (SBU) draw further scientific attention because of the fascinating topology of their structures [3]. Design of new SBUs is important to target robust open porous framework with predictable topology, and explore their specific chemical or physical properties. In addition, the use of poly-nuclear SBUs increases the odds of successful construction of multidimensional supramolecular architectures [4,5]. In this work the original intention was to incorporate isonicotinate in the axial positions into the tin(IV)-porphyrin scaffolds, in order to enhance the potential to involve more functional sites in the formulation of new types of coordination polymeric assemblies with different metal salts. This idea is based on my previous findings where the tin(IV)-porphyrin scaffolds were found to be held together through a series of non-covalent interactions [6,7]. The use of isonicotinic acid (**L**) as an axial ligand is particularly attractive, due to its nonlinear optical properties [8], blue fluorescence and luminescence properties [9]. This simple ditopic ligand is also known to display different coordination motifs [10]. However, the anticipated

porphyrin-based MOFs have not been obtained in this work. Instead, 3D coordination polymers were formed by direct association of Cd- and Mn-ion centers to the **L** linker (compounds **1–3**), whether or not the (dihydroxy)tin(IV)-*meso*-5,10,15,20-*tetra*-(3-pyridyl)porphyrin ($\text{Sn}^{\text{IV}}(\text{OH})_2\text{-T}^3\text{PyPr}$) reagent was present in the reaction mixture (Scheme 1). Reaction of $\text{Cd}^{\text{II}}(\text{ClO}_4)_2$ with **L** in DMF/MeOH solution yielded structure **1**, which incorporates mononuclear tetrahedral metallic nodes linked to each other through the organic ligands. Structural transformation occurred with the crystals of **1** when left in the mother solution for a few weeks. A different structure **1a** was formed as a result of incorporation of the DMF molecules into these crystals, where the coordination environment around the cadmium centers transformed from tetrahedral (in **1**) to trigonal bi-pyramidal (in **1a**). When the supramolecular reaction between **L** and cadmium perchlorate was carried out in the presence of $\text{Sn}^{\text{IV}}(\text{OH})_2\text{-T}^3\text{PyPr}$ (Scheme 1, path II) a different 3D coordination framework (**2**) wherein the organic ligand is inter-linked *via* oxo-centered trinuclear cadmium clusters. Polymeric structure (**3**) of similar topology was obtained with the $\text{Mn}^{\text{II}}(\text{ClO}_4)_2$ reagent. It was found to contain as the inter-ligand metallic nodes oxo-centered mixed-valence manganese clusters, characteristic to materials that behave as single-molecule magnets [11].

2. Experimental section

In all reactions, commercially available reagents of analytical

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Scheme 1. A schematic representation of the synthetic approach, where paths I and II led to the construction of 3D supramolecular architectures based on either mono-nuclear or poly-nuclear metallic nodes, respectively.

grade were used without further purification. The FT-IR spectra were recorded in Bruker Tensor 27 system spectrophotometer in ATR mode. UV–vis spectra was recorded on a Perkin-Elmer UV–vis spectrometer. The synthesis of $\text{Sn}^{\text{IV}}(\text{OH})_2\text{-T}^3\text{PyPr}$ was prepared as detailed in the literature [6]. Complexes **1–3** were prepared as detailed below.

Compound **1** was synthesized by mixing **L** (0.024 mmol, 3 mg), and $\text{Cd}^{\text{II}}(\text{ClO}_4)_2 \cdot 5\text{H}_2\text{O}$ (0.036 mmol, 12 mg) in 2 mL 1:1 dimethylformamide (DMF)–methanol (MeOH) mixture. The mixture was sealed and heated for 48 h in a bath-reactor at 100 °C. After cooling the compound to room temperature, it yielded colorless crystals of complex **1**, yield 75%. IR (cm^{-1}): 1651 (s, $\nu_{\text{C}=\text{O}}$ free asymmetric), 1582 (s, $\nu_{\text{C}=\text{O}}$ coordinated asymmetric), 1396 (s, $\nu_{\text{C}=\text{N}}$ aromatic), 1321 (m, $\nu_{\text{C}=\text{O}}$ symmetric), 1093, 1061, 1021, 944, 881, 785, 691, 426.

Compound **1a** was obtained after a period of few weeks by leaving the crystals of **1** in the mother solution without disturbance in dark and ambient conditions.

Compound **2** was prepared also in solvothermal conditions. A mixture of **L** (0.024 mmol, 3 mg), $\text{Sn}^{\text{IV}}(\text{OH})_2\text{-T}^3\text{PyPr}$ (0.006 mmol, 5 mg) and $\text{Cd}^{\text{II}}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ (0.036 mmol, 12 mg) was dissolved in 2 mL of DMF:MeOH (1:1). The reaction mixture was heated for 48 h in a bath-reactor at 100 °C. After subsequent cooling to room temperature crystals of **2** were obtained, yield 42%. IR (cm^{-1}): 3233 (bs, $\nu_{\text{O}-\text{H}}$ coordinated water), 1649 (s, $\nu_{\text{C}=\text{O}}$ free asymmetric), 1584 (s, $\nu_{\text{C}=\text{O}}$ coordinated asymmetric), 1398 (s, $\nu_{\text{C}=\text{N}}$ aromatic), 1252 (m, $\nu_{\text{C}=\text{O}}$ symmetric), 1091, 1014, 862, 785, 864, 691, 595, 426, 385.

Compound **3** was obtained by replacing the $\text{Cd}^{\text{II}}(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ reagent with $\text{Mn}^{\text{II}}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.091 mmol, 33 mg) dissolved together with the porphyrin material in 2 mL of DMF:MeOH (1:1). The solution was heated for three days in a bath-reactor at 100 °C. Gradual cooling to ambient conditions yielded dark brown crystals of **3** (33%). IR (cm^{-1}): 3464 (bs, $\nu_{\text{O}-\text{H}}$ coordinated water), 1668 (s, $\nu_{\text{C}=\text{O}}$ free asymmetric), 1603 (s, $\nu_{\text{C}=\text{O}}$ coordinated asymmetric), 1410 (s, $\nu_{\text{C}=\text{N}}$ aromatic), 1308 (m, $\nu_{\text{C}=\text{O}}$ symmetric), 1064, 933, 789, 944, 708, 689, 494, 390.

2.1. Crystal structures determination

Single crystal measurements for compounds **1–3** were collected at 110 (2) K, using Bruker's Apex-Duo diffractometer with $\text{MoK}\alpha$ ($\lambda = 0.71075 \text{ \AA}$) radiation. Crystal structures were solved by direct methods and refined by full matrix least squares (SHELXT-2014 and SHELXL-2014) [12,13]. The crystallographic and experimental data for **1–3** are given in Table 1. All the non-hydrogen atoms were refined anisotropically except for the disordered oxygen atoms of the ClO_4 anions in **2** and **3**. The hydrogen atoms were located in calculated sites and were refined using a riding model. The intralattice voids in **1** and **2** were found to contain disordered solvent molecules which couldn't be reliably modeled by discrete atoms. Therefore, their contribution was subtracted from the diffraction pattern by the SQUEEZE technique in the PLATON software [14]. Despite the apparent disorder of the perchlorate anions and of the water solvent, the crystallographic evaluations afforded models of the coordinated networks of good precision. Structures **1–3** were refined as inversion twins.

3. Results and discussion

3.1. Crystal structure description

Compound **1** [CdL_2] $_n \cdot (\text{solvent})$ contains one organic linker in its deprotonated state (L^-) and tetrahedral Cd^{II} ion centers (located on special positions) in the asymmetric unit. The crystal structure is characterized by a chiral tetragonal space group $P4_12_12$, and it represents a 3D coordination network (Fig. 1). This reaction was carried out without the involvement of the tin(IV)–porphyrin component in the reaction mixture. In **1** four organic linkers were found coordinated to the Cd^{II} centers through the carboxylate and pyridyl ligating positions. The carboxylate functions are bound in an asymmetric chelating mode, occupying two sites of the tetrahedral Cd–environment. The other two positions are coordinated to the N-atoms of the pyridyl functions of other ligands. The resulting coordination distance ranges are $\text{Cd}^{\text{II}}-\text{O} = 2.272(6)\text{--}2.421(7) \text{ \AA}$, and $\text{Cd}^{\text{II}}-\text{N} = 2.289(7) \text{--}2.290(7) \text{ \AA}$. The topology of the polymeric

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