

Vibrational analysis and crystal structure of two new 1D Cu^{II} and Co^{II} coordination polymers, involving the ligands 2,5-dihydroxyterephthalate and glutarate



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ABSTRACT

Aiming to obtain metal-organic frameworks with high dimensionality, two new 1D coordination polymers with the general formula $\{[\text{Co}(\text{DHT})(\text{DMF})_2(\text{H}_2\text{O})_2]_n\}$ (**1**) and $\{[\text{Cu}(\text{GLU})(\text{DMF})]_n\}$ (**2**) have been obtained, where DHT = 2,5-dihydroxyterephthalate; GLU = Glutarate; and DMF = Dimethylformamide. Both coordination compounds involve simple chain formations in which the carboxylate groups from ligands adopt monodentate (for **1**) and bidentate (for **2**) coordination modes to the metal center. In this work, both polymers synthesized contain solvent molecules coordinated to metal centers, which represent potential open metal sites to allow postsynthetic modifications that may increase the dimensionality of the systems. The dinuclear group formation of type tetrakis (acetate) dicopper complexes, in the case of polymer (**2**), is worth mentioning. This unit may be categorized as a secondary building unit (SBU) like a paddlewheel formed in situ. Herein, Raman spectroscopy had an important role in its characterization. So, besides X-ray diffraction by single crystals, vibrational spectroscopy had been employed to reinforce the coordination modes analysis, especially through a good approximation of antisymmetric and symmetric shifts of vibrational modes from the carboxylate group of ligands (in comparison to the ionic form of the free ligand). Finally, we propose the removal of solvents coordinated to metal centers by activation for increasing the system dimensionality.

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1. Introduction

Coordination polymers (PCs) have been the subject of intense studies in the last decades [1–3]. A specific class of these materials are the metal-organic frameworks (MOFs) [4] that have as a main characteristic a high surface area and are modulated and tunable porous materials in which interesting structures can be formed [5,6]. MOFs are known as multifunctional porous materials because their applications range from gas adsorption/separation [7] to drug delivery [8], catalytic [9,10] and luminescent activities [11,12], and may show non-linear optical [13] and magnetic phenomena [14]. Recent studies have shown that synthetic pathways, solvents, temperature and time of reaction can affect directly the crystalline form and the architecture formed by a combination of organic ligands and metal centers [15,16].

The combination among these components leads to the self-assembly process, in which ligands and metal centers face successive associations and dissociations in aqueous solutions and finally form thermodynamically mostly stable structures [17–20]. These structures can form both discrete and more complex metallic units, such as 1D, 2D or 3D coordination polymers [21]. In this way, 3D MOFs can be formed directly by secondary building units (SBUs) with formation in situ or by a two-step process [22–24]. The latter means that some coordination compounds act as intermediary species when open binding sites are present, allowing the increase of system dimensionality [25,26]. Fig. 1 presents a scheme of different routes that may be considered in order to obtain tridimensional MOFs.

Therefore, the knowledge of predominant interactions on the crystalline state can ease the understanding of the self-assembly process in ways that hydrogen bonds and weak interactions like $\text{CH}\cdots\pi$; π - π stacking and others can form supramolecular assemblies using smaller or greater degrees of directionality [27,28]. At the same time, some authors have reported the

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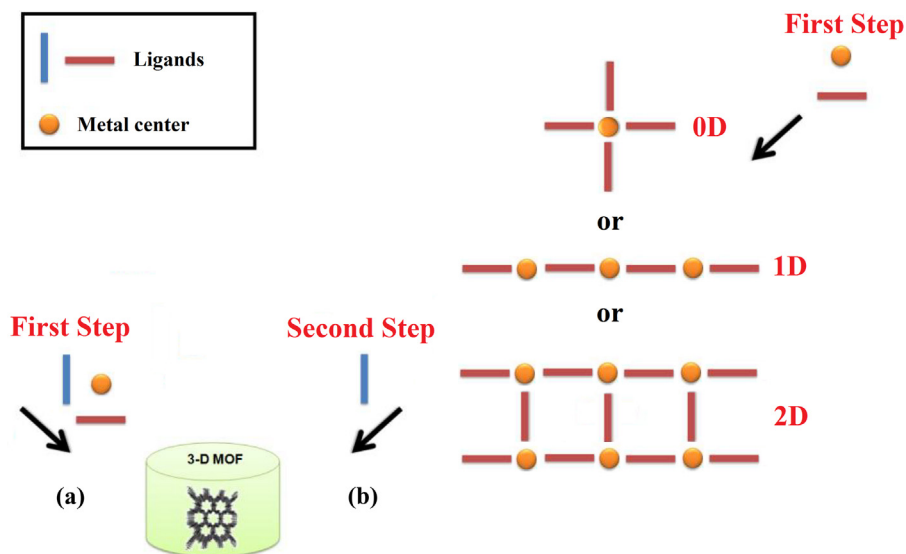


Fig. 1. Different ways to obtain tridimensional MOFs, through one step synthesis (a) and by multi-step preparation (b).

influence of the removal of solvents, coordinated on the structural dimensionality, as a way to form open metal sites, which can be available for new ligands for coordinating the metal center. In the literature, there is a wide array of ligands, which have been employed in the MOFs synthesis, as for example, carboxylate [29–32], azole [33–36], phosphonates [37–40], and pyridine derivatives [14,41], where the carboxylate ligands are most often used. Vibrational analysis is a complementary technique, powerful

and effective in the evaluation of structural features of MOFs. This is especially because it provides, in conjunction with other analysis techniques, insights into the coordination environment [42,43], composition [44–46], coordination modes [47,48], intermolecular interaction involving guest interaction or postsynthetic modification in the structure of MOFs [49]. In this way, carboxylate ligands can adopt a diversity of coordination modes. An example of this is what is observed in NTU-Z1-Z6 MOF, shown in Fig. 2, where from

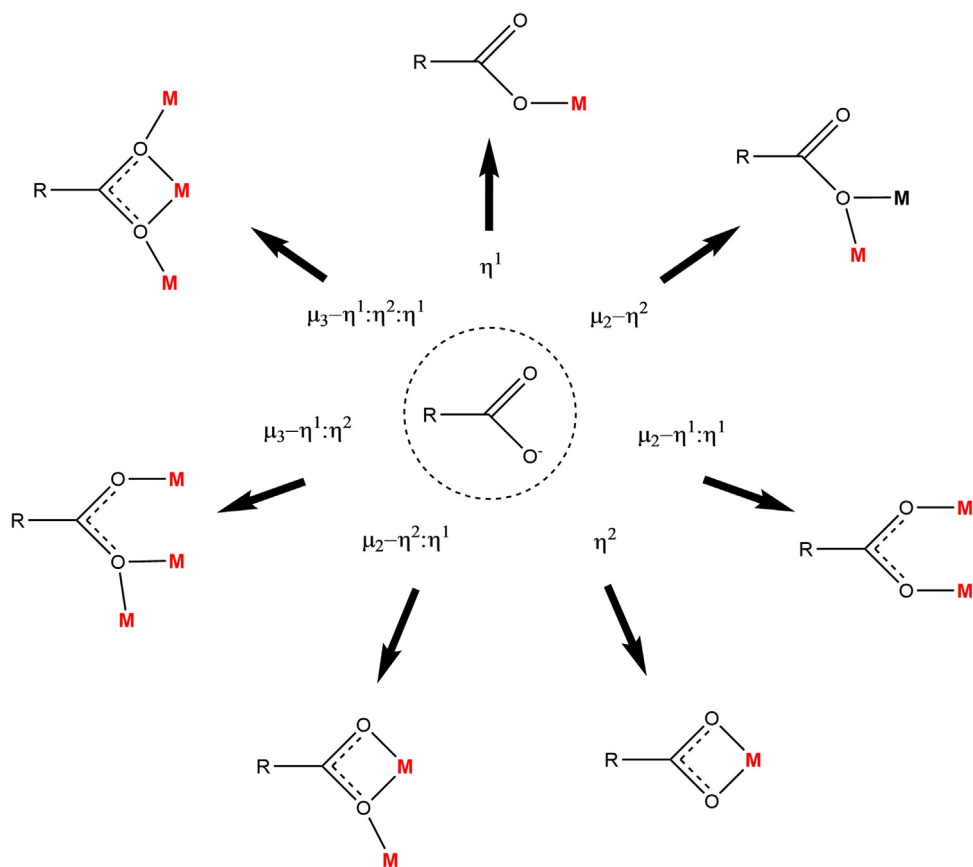


Fig. 2. Usual coordination modes of the carboxylic group also verified in carboxylate ligands of NTU-Z1-Z6 MOF [81]. Such “R” group represents the non-functionalized portion of 1,4-benzenedicarboxylate (BDC) or isophthalate (ITA) ligands.

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