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Synthesis and characterization of infinite coordination networks from a hybrid ligand *N*-(4-pyridylmethyl)imidazole

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Abstract

Three cadmium(II) coordination polymers formed from pyim [pyim = *N*-(4-pyridylmethyl)imidazole], namely $^{2}_{4}[Cd(pyim)_2X_2]_n$ (X=Cl, **1**; Br, **2**; I, **3**), have been synthesized and characterized by IR, and fluorescence spectroscopy as well as TG analysis.

Keywords: Metal–organic compound; Hybrid; Unsymmetrical; Flexibility; Counter anions

Design and synthesis of organic and metal–organic compounds with unusual and tailorable structures are fundamental steps to discover and fabricate various functional supramolecular devices or technologically useful materials [1]. There has been much interest and progress recently in the study of crystal engineering of supramolecular architectures organized and sustained by means of ligands including pyridine and imidazole moieties. Herein, the ligand *N*-(4-pyridylmethyl)imidazole (pyim) is synthesized. Pyim can be considered as a hybrid of 4,4′-bipyridine and 2,2′-biimidazole, which are versatile N-donor ligands in transition metal chemistry [2]. Its chemistry, which has not been explored thoroughly [3], is our concern here. From a structural point of view, it should be pointed out that (1) this ligand, unlike the rigidity of bipyridine, possesses flexibility owing to the presence of a $–CH_2–$ spacer between the pyridyl ring and imidazole moiety; (2) if both N-donor sites can coordinate to the metal center, the pyim can act as μ_2-bridging ligand. Accordingly, a grid-like structure may be expected by introducing metal ions favoring tetra- or hexa-coordination mode, and the flexibility of pyim may result in a novel framework; (3) due to its unsymmetrical nature, pyim can be considered as a potential ligand for the construction of acentric solids based on two-dimensional (2D) grids [4]. Among our attempts, three polymers, namely $^{2}_{4}[Cd(pyim)_2X_2]_n$ (X=Cl, **1**; Br, **2**; I, **3**), were obtained as crystals suitable for single-crystal X-ray analysis.

The crystal structure of **1** is isomorphous with those of the bromide and iodine derivatives **2** and **3**. Reasonably, also the most relevant molecular and conformational parameters are similar, except for the small influence of the limited covalent radius of Cl vs. Br and I. Therefore, a complete analysis of the bromine and iodine derivatives were not performed.

The crystallographic analysis [5] reveals that compound **1** crystallizes in the centrosymmetric space group $P2_1/c$. The asymmetric unit contains one cadmium atom lying on a crystallographic twofold axis, one chlorine donor and one *N*-(4-pyridylmethyl)imidazole bridging group. In order to develop new second-order nonlinear optic materials, Thompson and co-workers [6] had reported an inorganic coordination polymer where molecules are aligned in a head-to-tail arrangement along the polymer backbone. This bridging ligand *N*-(4-pyr-

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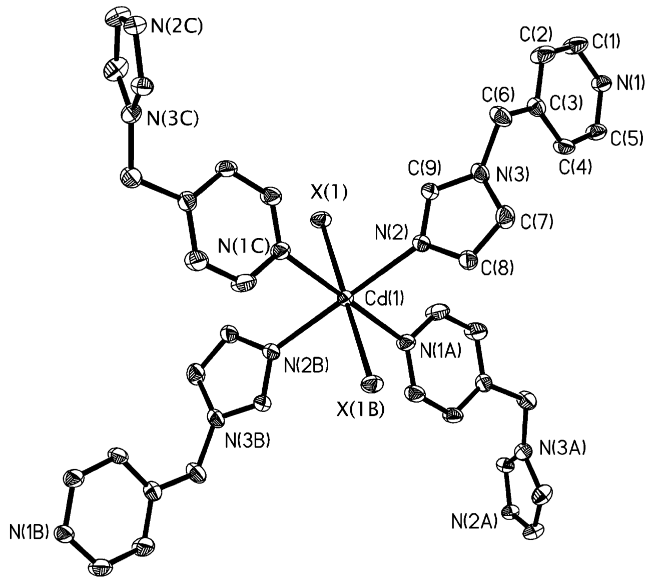

Fig. 1. Local coordination environment around Cd(II) atom in **1**, **2**, and **3** (X=Cl, **1**; Br, **2**; I, **3**). Selected bond lengths (Å) and angles (°): For **1**: Cd(1)–N(2) 2.318(4), Cd(1)–N(1A) 2.425(4), Cd(1)–Cl(1) 2.6208(13) and N(2B)–Cd(1)–N(1A) 94.68(15), N(2B)–Cd(1)–N(1C) 85.32(15), N(2)–Cd(1)–Cl(1B) 91.46(11), N(2)–Cd(1)–Cl(1) 88.54(11), N(1A)–Cd(1)–Cl(1B) 90.65(11), N(1A)–Cd(1)–Cl(1) 89.35(11). Symmetry operation: A $x - 1, -y + 3/2, z - 1/2$; B $-x + 1, -y + 2, -z + 1$; C $-x + 2, y + 1/2, -z + 3/2$; For **2**: Cd(1)–N(2) 2.341(4), Cd(1)–N(1A) 2.419(4), Cd(1)–Br(1) 2.7679(4) and N(2B)–Cd(1)–N(1A) 94.53(13), N(2B)–Cd(1)–N(1C) 85.47(13), N(2)–Cd(1)–Br(1B) 91.54(9), N(2)–Cd(1)–Br(1) 88.46(9), N(1A)–Cd(1)–Br(1B) 89.99(9), N(1A)–Cd(1)–Br(1) 90.01(9). Symmetry operation: A $x - 1, -y + 1/2, z - 1/2$; B $-x, -y + 1, -z + 1$; C $-x + 1, y + 1/2, -z + 3/2$; For **3**: Cd(1)–N(2) 2.362(4), Cd(1)–N(1A) 2.426(4), Cd(1)–I(1) 2.9895(3) and N(2B)–Cd(1)–N(1A) 94.02(16), N(2B)–Cd(1)–N(1C) 85.98(16), N(2)–Cd(1)–I(1B) 91.67(10), N(2)–Cd(1)–I(1) 88.33(10), N(1A)–Cd(1)–I(1B) 89.45(11), N(1A)–Cd(1)–I(1) 90.55(11). Symmetry operation: A $x + 1, -y + 1/2, z + 1/2$; B $-x + 1, -y + 1, -z + 2$; C $-x, y + 1/2, -z + 3/2$.

idylmethyl)imidazole, which is non-equivalent and assumes a head-to-tail arrangement, satisfies the fundamental requirements for NLO material. However, unfortunately, the compound crystallized in the centrosymmetric space group. According to the thoughts of rational design developed by Evans and Lin [7], we tentatively attribute the failure to the flexibility of pyim which might increase the potential packing complexity.

The Cd(II) center lies in an octahedral $\{CdN_4Cl_2\}$ environment with the axial positions occupied by two chlorine atoms and the equatorial positions occupied by two *trans* imidazolium nitrogen atoms and two *trans* pyridyl nitrogen atoms, each of which, respectively, belongs to four different *N*-(4-pyridylmethyl)imidazole ligands (Fig. 1). The bond angles about the Cd1 octahedron range from 85.32° to 94.68° and deviate slightly from those of a perfect octahedron. As predicted, this coordination fashion results in an infinite 2D rhombohedral grid containing 36-membered rings (Fig. 2). The grid-like $Cd_4(pyim)_4$ species can be viewed as the basic building block of the structure, in which the apices are occupied by cadmium ions and the sides are formed by pyim ligands. Each four $Cd_4(pyim)_4$ grids are joined together by sharing the cadmium apices to give the final 2D layer structure with a diagonal measurement of about 14.215 and 16.892 Å based on the metal–metal connections.

Noted that the basic grid is a highly distorted square. More accurately, the dimension of the grid can be described as hourglass-shaped. This shape is understandable, because the sp^3 configuration of C of –CH_2– spacer forces the pyim ligand to be non-linear, generating the nonlinear grid sides and thereby the dumbbell-shaped grids. Actually, the N–C–C angle of

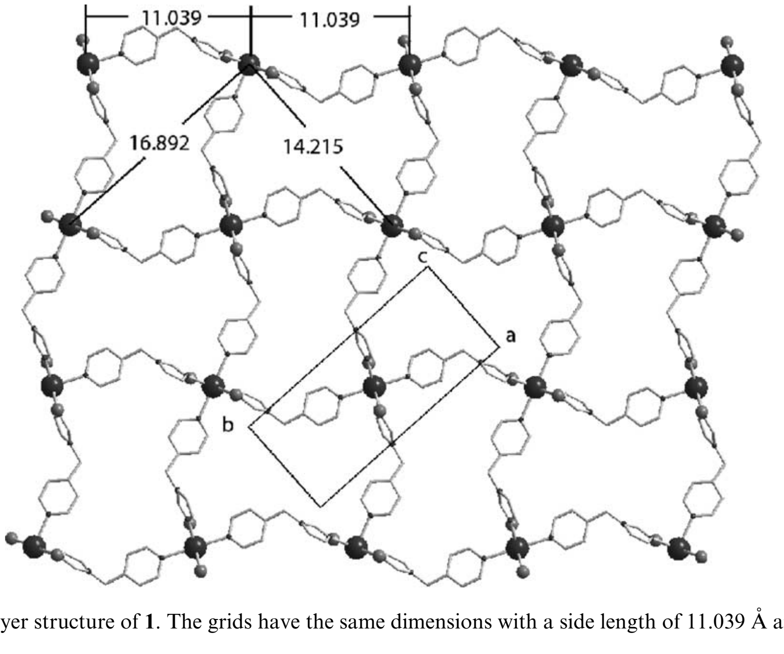

Fig. 2. The two-dimensional layer structure of **1**. The grids have the same dimensions with a side length of 11.039 Å and a diagonal measurement of about 14.215 × 16.892 Å.