

## Synthesis and Characterization of New Metal-Organic Framework Derived from 6-(Methoxycarbonyl) Pyridine-2-Carboxylic Acid as Application for Hydrogen Storage Materials

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### Abstract

In this study, a new organic linker namely 6-(pyrimidin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L1) has been successfully synthesized. Along with this discovery, two metal-organic frameworks (MOFs) which derived from L1 and 6-(methoxycarbonyl)pyridine-2-carboxylic acid (L), have also been synthesized and characterized by using combination of spectroscopic techniques such as Infrared (IR), Nuclear Magnetic Resonances (NMR), Thermal Gravimetric Analysis (TGA) and X-ray crystallography. The formulations of these MOFs are confirmed by elemental analysis with formula molecules given as  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$  and  $\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$ , respectively. It was revealed from this study that reaction of both ligands with cadmium nitrate led to formation of one-dimensional MOFs. The hydrogen storage properties of these MOFs were investigated by Pressure Composition Temperature (PCT) analysis. The results showed that MOF  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$  can uptake 0.3wt. % hydrogen at 373 K and 60 bar. In contrast, MOF  $\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$  which is lacking of pyrimidine moieties at the pendant arm has zero adsorption when investigated by similar method.

**Keywords:** Hydrogen storage, 6-(methoxycarbonyl) pyridine-2-carboxylic acid, hydrogen uptake, tridentate ligand, metal-organic framework.

## INTRODUCTION

Hydrogen has long been considered as the best candidate to replace the fossil fuel as primary source of energy. This is due to the price of hydrogen that is cheaper compared to fossil fuel [1]. In order to promote safe storage of hydrogen gas, materials such as metal hydrides, carbon nanofibers and metal-organic frameworks (MOFs) [2,3,4,5,6] were investigated for hydrogen storage. MOFs are defined as compounds that consist of metal ions or clusters that coordinated to organic linker to form one-, two-, or three-dimensional structures [7]. These materials normally exhibit fascinating architectures such as sponge structure that allow for many application studies such as gas storage, chemical separation, heterogeneous catalysis and magnetic materials [8,9]. In order to generate a MOF that is suitable for hydrogen storage, the choice of organic linker is very important. Organic linker such as carboxylate and amide ligands are commonly employed in the construction of MOFs for hydrogen storage due to the presence of polar functional groups such as amine ( $\text{NH}_2$ ) and hydroxyl (OH) group that increase interaction with hydrogen atoms [10,11]. In this study, a rigid unsymmetrical amide ligand namely 6-(pyrimidin-2-ylcarbonyl)-pyridine-2-carboxylic acid methyl ester (L1) which derived from 6-(methoxycarbonyl) pyridine-2-carboxylic acid (L) is produced. Ligand L1 is occupied with additional two nitrogen atoms at the monopyridyl pendant arms in order to increase the polarity of the ligand and to promote the hydrogen uptake by its complexes. By using this new ligand (Figure 1), which has three nitrogen and three oxygen donor atoms, the potential of the MOF to uptake hydrogen in good amount is expected to be occurred.

## EXPERIMENTAL (MATERIALS AND METHODS)

Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Elemental analysis was performed by the Campbell Microanalytical Laboratory at the Universiti Malaysia Terengganu. Infrared spectra were collected on a Perkin Elmer Spectrum BX Infrared spectrometer as KBr disk in the spectral range of 4000-400  $\text{cm}^{-1}$ . All chemicals were obtained from commercial sources and used as received. TGA/SDTA 851e analyzer METTLER TOLEDO is used for the analyses of compounds with a range of temperature. The range used is between 20  $^{\circ}\text{C}$ -900  $^{\circ}\text{C}$  with the increment of heating rate at 10  $^{\circ}\text{C}$  /min. The mass of compounds change when the temperature increases. The de/rehydrogenation experiments were performed in a Sievert-type pressure-composition temperature (PCT) apparatus (Advanced Materials Corporation). The composite was loaded into a sample vessel. For the temperature-programmed-desorption (TPD) experiment, all the composites were heated in a vacuum chamber, and the amount of desorbed hydrogen was measured to determine the lowest decomposition temperature. The heating rate for the experiment was 5  $^{\circ}\text{C}$ /min, and the samples were heated from room temperature to 100  $^{\circ}\text{C}$ . The re/dehydrogenation kinetics measurements were performed at the desired temperature with the initial hydrogen pressures of 60 bars.

### X-RAY CRYSTALLOGRAPHY

In general, crystals were mounted under oil onto a plastic loop and X-ray data collected at low temperatures with Mo- $K\alpha$  radiation ( $\lambda=0.71073 \text{ \AA}$ ). Data was collected on a Bruker Apex II CCD diffractometer. Data were corrected for polarisation and Lorentzian effects, and absorption corrections applied using a multi-scan method. Structures were solved by direct methods using SHELXS-97 [12] and refined by full-matrix least squares on  $F^2$  by SHELXL-97 [13]. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. Diagrams were generated using the program X-Seed [14] as an interface to POV-Ray [15]. X-ray crystallography data of complex  $\{[\text{Cd}_3(\text{L}-\text{CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$ : Orthorhombic space group, crystal system  $Pbcn$ ,  $a=11.9144$ ,  $b=17.315$  and  $c=13.4072$  ( $\alpha=\beta=\gamma=90^\circ$ ). Volume= $2765.88 \text{ \AA}^3$ . Crystal dimension= $0.16\times 0.15\times 0.15 \text{ mm}^3$ . Theta range= $2.36- 29.95$ .  $R_2=0.2302$ .

### Synthesis of 6-(pyrimidin-2-ylcarbamoyl)-pyridine-2- carboxylic acid methyl ester (L1)

A suspension of 6-(methoxycarbonyl) pyridine-2-carboxylic acid (0.5 g, 2.0 mol) was heated at reflux in dichloromethane with thionyl chloride (0.5 mL) and dried DMF as catalyst for 1 h under nitrogen. After an hour, the dichloromethane was removed using rotaevaporator under reduced pressure and left in vacuum desiccators for another one hour to remove all the solvent. The acyl chloride (1.67 g, 3.5 mol) was dissolved in dichloromethane (40 mL) and amine, 2-aminopyrimidine (1.567 g, 3.5 mol) was added with distilled triethylamine (1.7 ml, 3.5 mol) before the mixture was further reflux for another 24 h. After the reaction was completed, the solvent was removed using rotavap. Then, the residue was dissolved with dichloromethane, washed with sodium hydrogen bicarbonate to remove unreacted starting material. Lastly, collected dichloromethane was dried over magnesium sulfate and the solvent was removed using rotavap under reduced pressure. The resulting residue was purified by column chromatography on silica gel with 1.5:9.5 methanol:dichloromethane solvent systems. The product was obtained as pale yellow precipitate in good yield.

### Synthesis of MOFs

Equimolar amount of  $\text{Cd}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  and ligand was dissolved in DMF (1 mL). The mixture was heated to  $110 \text{ }^\circ\text{C}$  for 48 hours in a sand bath. The resulting solution was slowly cooled down to room temperature, transferred to other vial containing methanol (0.5 mL) for slow diffusion. The reaction solution was capped, and left to stand from several weeks for crystallization. White solid was obtained after two weeks (0.054 g, 67.9 %). Similar method was used to prepare the MOF from 6-(methoxycarbonyl) pyridine-2-carboxylic acid (L) for structure comparison studies.

## RESULTS AND DISCUSSION

In this research study, a new ligand is synthesized for use as organic linker in MOF's formation. The new ligand, namely 6-(pyrimidin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L1), was prepared using acyl chloride reaction (Scheme 1) [16]. In this approach, the intermediate (i) was prepared from reaction between 6-(methoxycarbonyl) pyridine-2-carboxylic acid (L) and thionyl chloride in a mixture of dimethylformamide (DMF) and dichloromethane (DCM). This facile method gave 6-(pyrimidin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L1) as pale yellow precipitate isolated from flash chromatography. In the IR spectrum of ligand L1 (Figure 1), several distinctive peaks which assigned for CH<sub>3</sub>, N-H and C=O were identified at 2964 cm<sup>-1</sup>, 3331 cm<sup>-1</sup>, 1584 cm<sup>-1</sup>, 1572 cm<sup>-1</sup>, 1749 cm<sup>-1</sup> and 1724 cm<sup>-1</sup>, respectively. The N-H peak for pyrimidine compound was found shifted to the higher frequency compared to its precursor (L), due to the additional nitrogen at the pyridine group. The two important characteristic peaks (N-H and C=O) were appeared at common ranges for pyrimidine compounds [17,18]. The UV-Vis spectrum for ligand L1 was recorded in methanol (10<sup>-5</sup> M) with cut-off point of 205 nm. In the UV spectrum (Figure 2), the peaks which appeared at 227 nm and 265 nm represents n-π\* and π-π\* transitions. The electron transition by pyrimidine group occurred when electrons from the benzene ring π-system transferred to the C=O groups [19]. The absorbance peaks for pyrimidine was observed at 230-274 nm while pyridine at 260-320 nm, respectively [20,21]. The structure of the new ligand was also confirmed by NMR. In the <sup>1</sup>H NMR spectrum, the resonance for methyl proton was indicated at 4.07 ppm, benzene ring protons at range 7.13 ppm to 8.76 and amine proton at 10.73 ppm, respectively (Figure 3). The proton at pyrimidine ring depicts at the downfield region in the spectra due to electron-withdrawing effect by electronegative nitrogen [19,22]. From <sup>13</sup>C NMR spectrum, it can be observed that the resonance signal for CH<sub>3</sub> was indicated at 53.06 ppm. The resonance signals for pyridine were observed at 117.07-164.84 ppm while the C=O peaks were indicated at 157.34 ppm and 160.98 ppm, respectively. The effect of electronegative nitrogen from the pyrimidine had caused to the shifts of the resonance signal of carbon at downfield region. Combination data from IR and NMR have supported our expectation on the structure of L1 as shown earlier in Figure 1.

### Synthesis of metal-organic frameworks

The synthesis of metal complexes was attempted in two different approaches. In the first approach, ligand L which was the precursor was reacted with cadmium nitrate in DMF (Scheme 2). The solution was heated at 110 °C for 48 hours in a sand bath and cooled down before being transferred into a larger vial containing methanol for slow diffusion. Fortunately, the MOF was obtained as colorless needle-shaped crystals and suitable for X-ray crystallography. Crystals of MOF {[Cd<sub>3</sub>(L-CH<sub>3</sub>)·H<sub>2</sub>O]·5H<sub>2</sub>O}<sub>n</sub> crystallize in the orthorhombic space group *Pbcn* with a=11.9144, b=17.315 and c=13.4072 (α=β=γ=90°). The asymmetric unit of this structure comprises one molecule of hydrolyzed ligand, a cadmium atom and a coordinated water molecule in the asymmetric unit (Figure 5 (a)). In this structure, the methyl functional group of the ligand was absent and a tridentate O, N, O

donor atoms was formed. The decomposition of 6-(methoxycarbonyl) pyridine-2-carboxylic acid has been reported in many studies after being reacted with metal salts [23,24]. The obtaining *in situ* ligand coordinated to one cadmium atom, bridged by oxygen atoms leading to form infinite one dimensional network as shown in Figure 5(b). The polymeric structure is arranged in helical form, that when viewed down the helical axis (*b*-axis), has been contracted in one dimension and extended in the other, to form like a highly ordered beewax arrangement (Figure 5 (c)). The cadmium atoms have a distorted pentagonal bipyramidal geometry and are coordinated by five oxygen atoms, and two pyridyl donors (2.188 (2) and 2.199 (2) Å). In the central cadmium atom, the distorted octahedral environment is completed by the coordination of four oxygen atoms provided by the carboxamide moieties (Cd-O ranging from 2.723-2.465 Å). Another oxygen donor is provided by coordinated water and nitrogen atom from the pyridine carboxamide.

In crystal packing of this complex, a wide cavity (approximately Cd-Cd=2.465 Å and Cd-Cd=2.259 Å) was observed when viewed down the *ac* axis (Figure 5 (c)) indicating the possibility to accommodate gas molecule. This compares with the Cd-Cd distances in similar compounds reported by Wang and co-workers which is slightly longer at 3.605 Å. There were two similar structures of  $\{[\text{Cd}_3(\text{L}-\text{CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$  that have been reported with discrepancies in bond lengths, angles and crystal systems. These complexes crystallized in monoclinic space group, one in *C2/c* and another in *P2/c* space group [23,24]. The MOF of ligand L1 was prepared in the similar manner described for MOF  $\{[\text{Cd}_3(\text{L}-\text{CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$ . Since the compound was obtained in powder form, the obtained solid can only be characterized by IR and elemental analysis. In the IR spectrum, several important peaks for NH, C=O and N-O were detected at 3392  $\text{cm}^{-1}$ , 1655  $\text{cm}^{-1}$  and 1384  $\text{cm}^{-1}$ , respectively. In this complex, two new peaks representing Cd-O and Cd-N were indicated at 530  $\text{cm}^{-1}$ , 434  $\text{cm}^{-1}$  and 501  $\text{cm}^{-1}$ , as reported in many literature studies on tridentate ONO donor atoms [25,26]. The appearance of strong and broad band at 3400  $\text{cm}^{-1}$  indicates the presence of O-H...O hydrogen bonding between water molecules and also signifies the coupling of N-H and O-H stretching frequencies [27]. Based on the similarity in the IR spectra of the two MOFs (Table 1), ligand L1 was expected to coordinate with Cd (II) ion *via* tridentate O, N, O donors as the precursor (Figure 6). The structure is supported by the formula given by elemental analysis as  $\{[\text{Cd}_3(\text{L1}-\text{CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$ . The hydrolysis of 6-(methoxycarbonyl)pyridine-2-carboxylic acid to form *in situ* tridentate ligand is again occurred in this reaction in similar to our previous report [28] as well as by other groups [29]. In order to further determine the structure of the complex and its stability, the compound was subjected for thermal gravimetric analysis. As seen in Figure 7, the degradation process of  $\{[\text{Cd}_3(\text{L1}-\text{CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$  shows two degradation stages. At the first and second degradation stages, a mass loss of approximately 10 % between temperatures (150 °C-250 °C) represents the loss of methanol. The second degradation stage at (250 °C-500 °C) with mass loss of 40 % corresponds to the decomposition of ligand L1. The final compound obtained after the whole decomposition take place was cadmium. In particular, the degradation loss was consistent with the expected structure of the complex, as

proposed in this study. The two MOFs were further investigated for hydrogen storage potential using Pressure Isothermal Temperature (PCT) analysis. The result taken from the graph (Figure 8) shows that MOF  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$  has the ability to uptake hydrogen at 373 K. From the graph obtained, it was revealed that complex  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$  was not stable at the beginning of the analysis. It took approximately 90 minutes for the compound to get stable and then slowly adsorb hydrogen. After the analysis was completed,  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$  was found to adsorb 0.3 wt.% hydrogen at 373 K and 60 bar. The result from this study is comparable to some literature studies which has similar value [30,31]. In similar to MOF  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$ , the other investigated MOF,  $\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$  was analyzed by PCT at similar parameter and resulted to zero adsorption (Figure 9). The failure of  $\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$  to adsorb hydrogen was attributed to the lacking of the pendant pyrimidine ring which affect the pore properties (size and volume), surface area and chemical features [32,33]. The absence of pyrimidine pendant arm might as well attribute to the loss of Van de waals interaction between the hydrogen with the surface of the MOF which in return reduced the uptake of hydrogen by the MOF [34].

## CONCLUSION

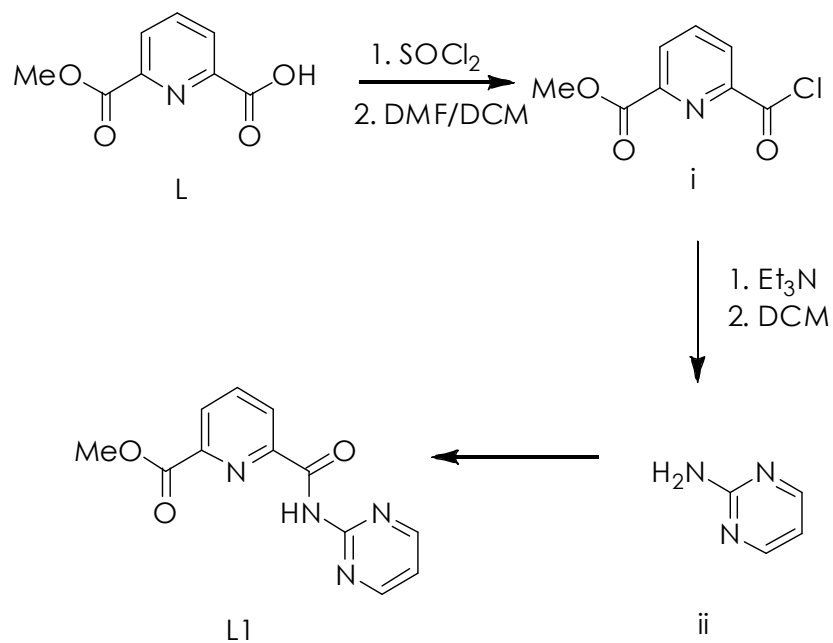
In conclusion, a new rigid ligand namely 6-(pyrimidin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester (L1) has been successfully synthesized and characterized. The ligand was reacted with cadmium nitrate to obtain a MOF with formula general formula  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$ . This complex was subjected for hydrogen storage analysis and the results revealed the potential of this MOF to store hydrogen up to 0.3 wt.% at 373 K and 60 bar. A MOF derived from the precursor,  $\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$  was found to exhibit zero hydrogen storage properties due to the lacking of pyrimidine moieties that contributes to the rise of electron density or polarity of the MOF that is important to establish interaction with hydrogen atoms.

## ACKNOWLEDGEMENTS

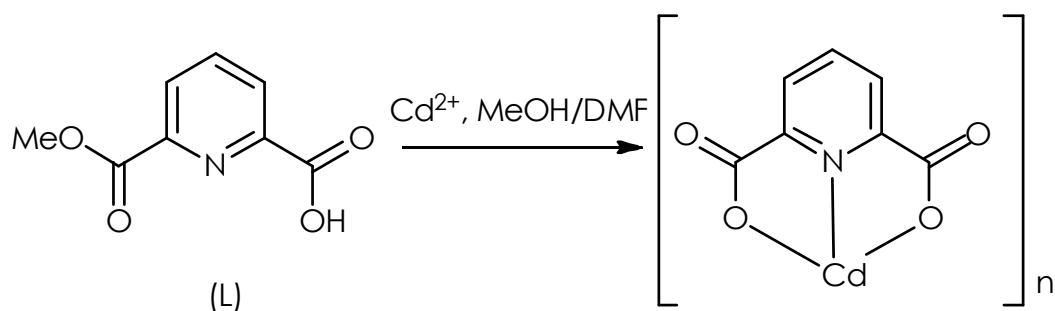
The authors greatly acknowledge the scientific support from Universiti Malaysia Terengganu. Christopher J Sumby from University of Adelaide is acknowledged for structure determination using X-ray crystallography. Ministry of Higher Education Malaysia (MOHE) is also acknowledged for financial support through Fundamental Research Grant Projects (FRGS) Vot 59293.

**Table 1:** The FTIR stretching for  $\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$  and  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$

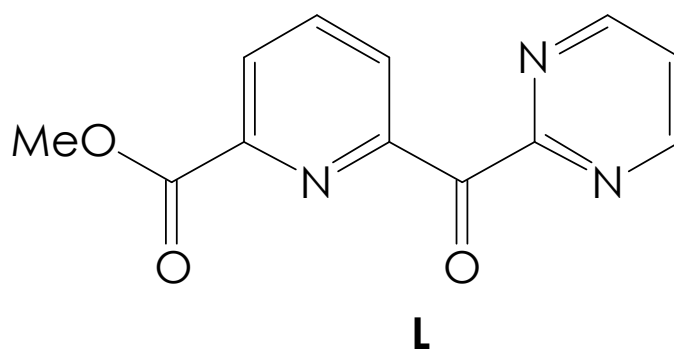
Stretching	$\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$	$\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$
N-Cd-O	520	530
N-Cd-N	434	434
O-Cd-O	733	734



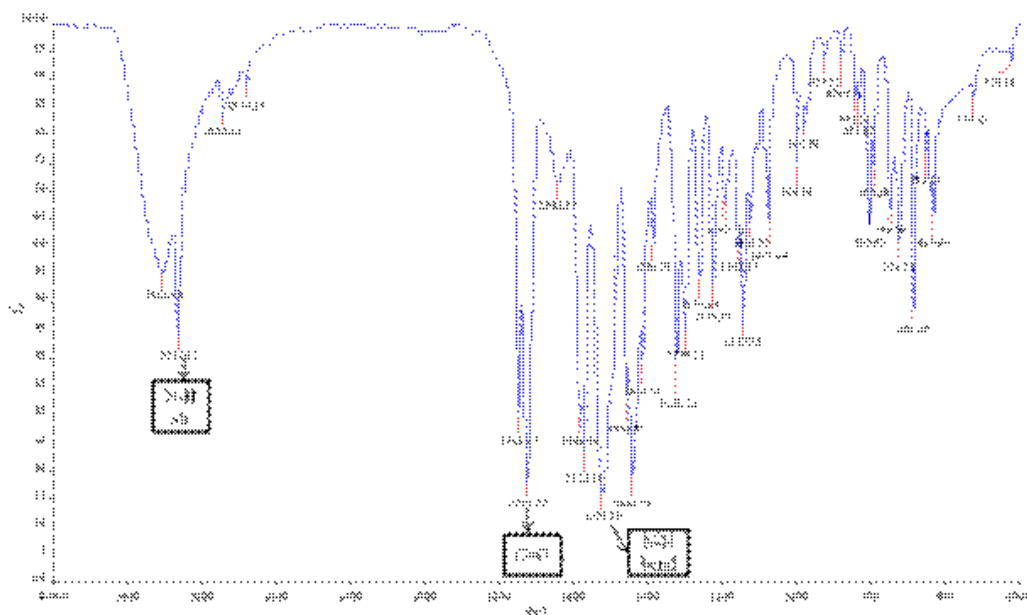
**Scheme 1.** Synthesis of ligand L1.



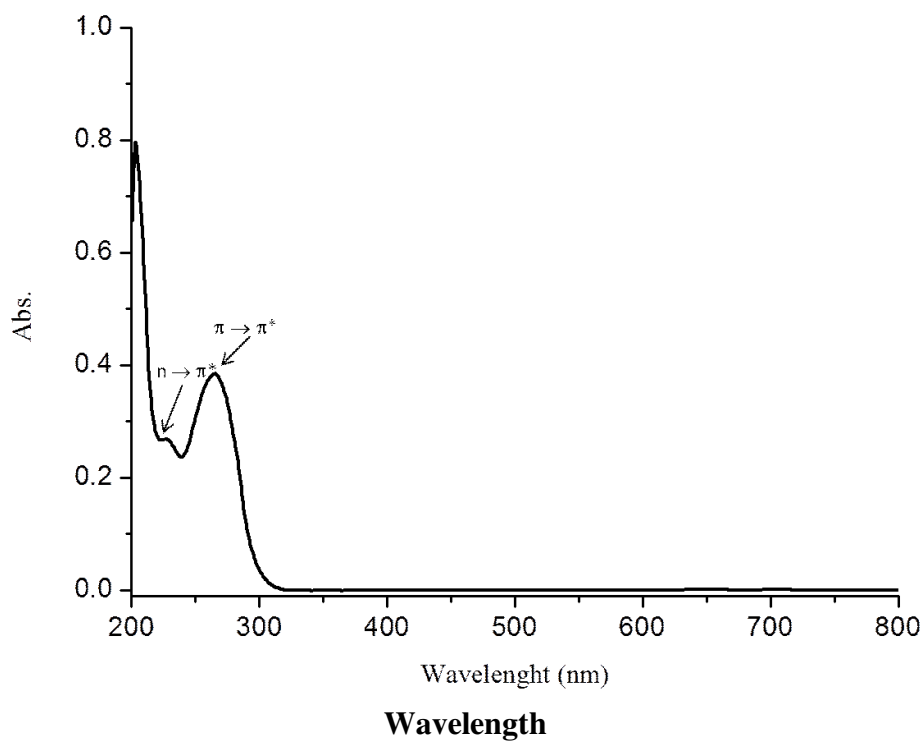
**Scheme 2.** Reaction of precursor (L) with cadmium nitrate.



**Figure 1.** Molecular structure of ligand 6-(pyrimidin-2-ylcarbamoyl)-pyridine-2-carboxylic acid methyl ester.



**Figure 2.** FTIR spectrum for ligand L1



**Figure 3.** The UV spectrum for ligand L1



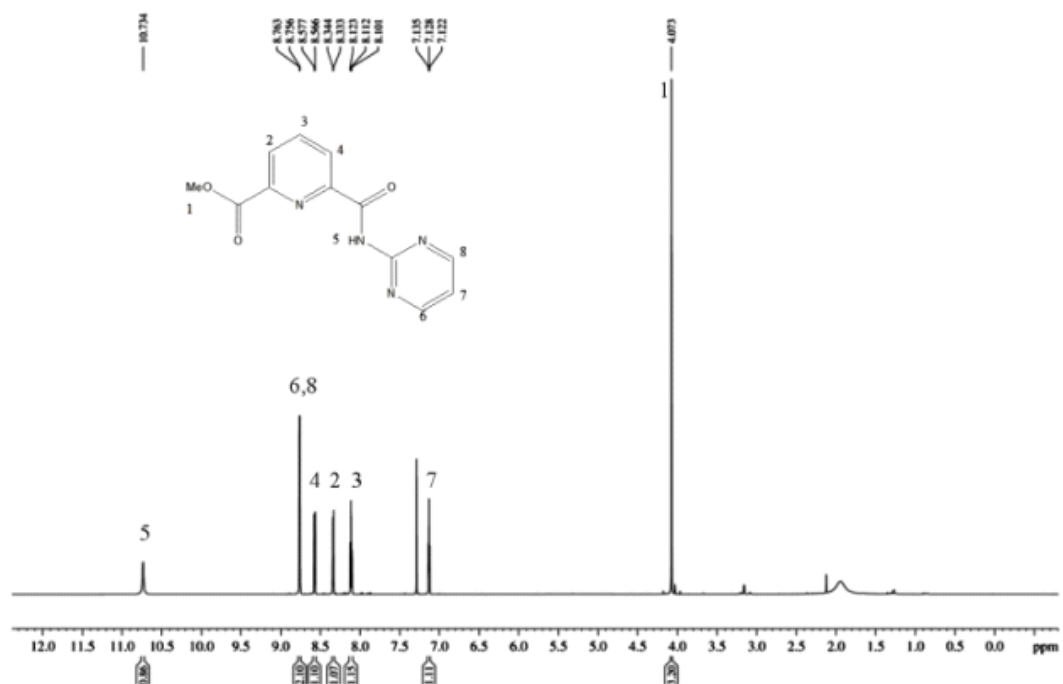
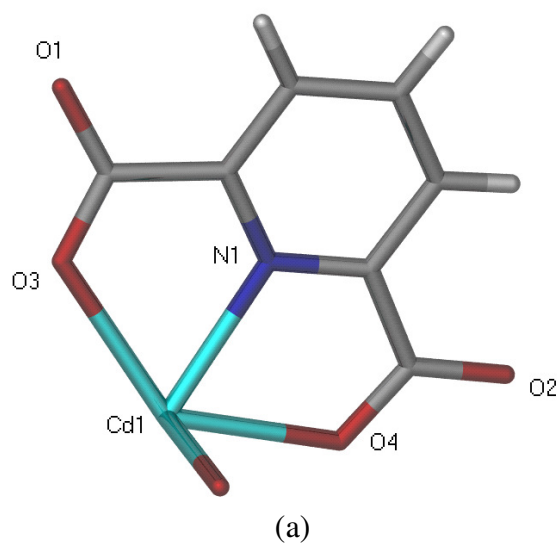
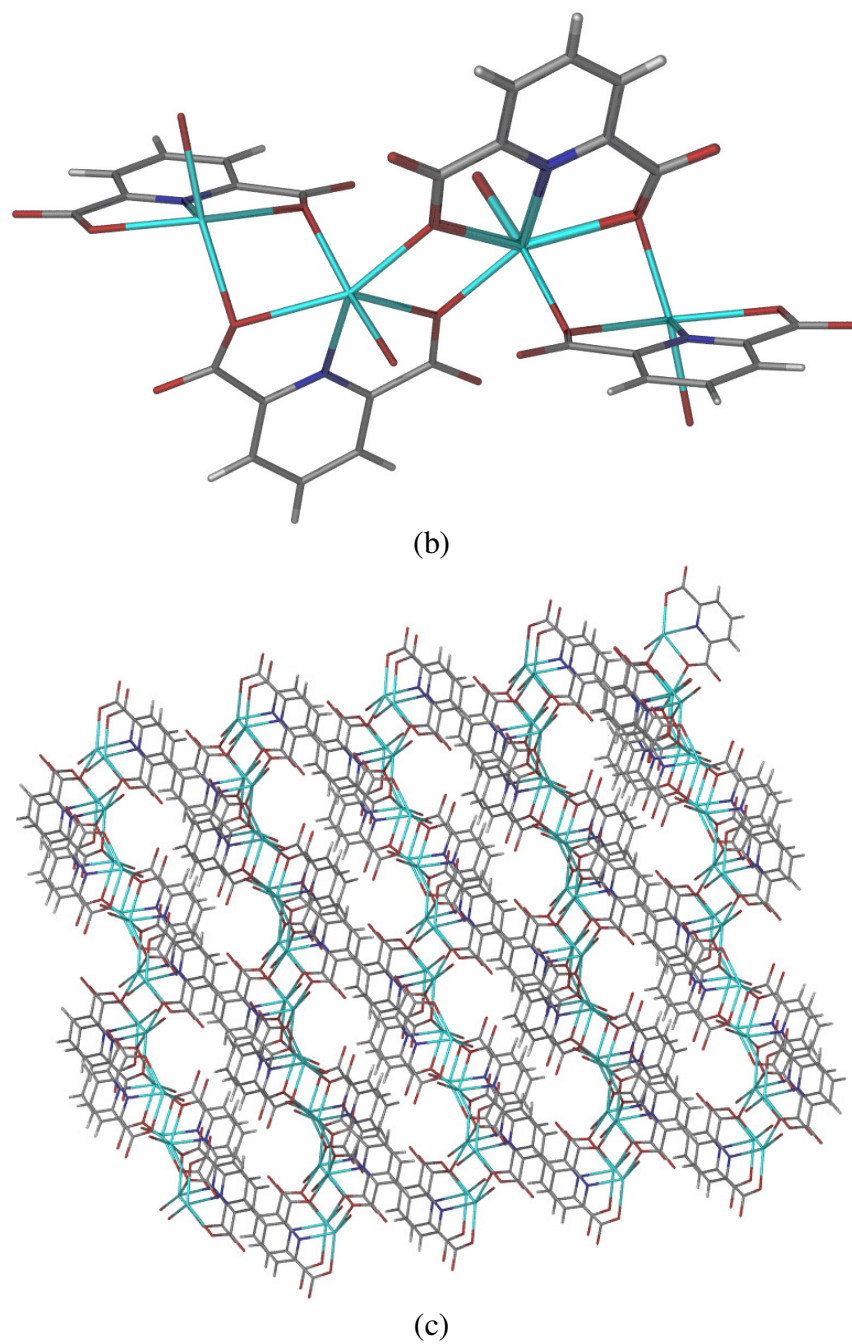
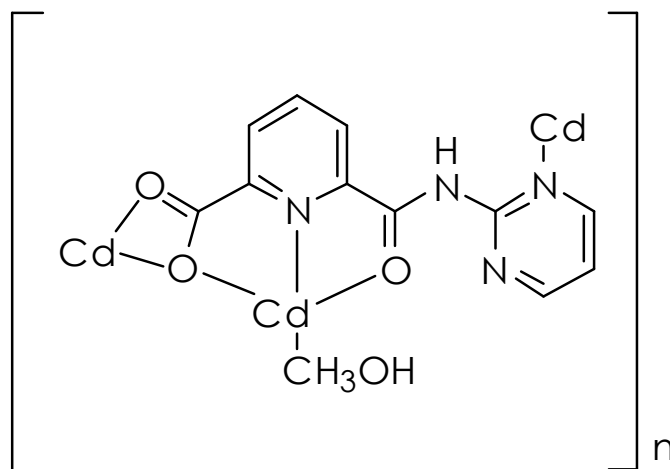


Figure 4.  $^1\text{H}$  NMR spectrum for L1

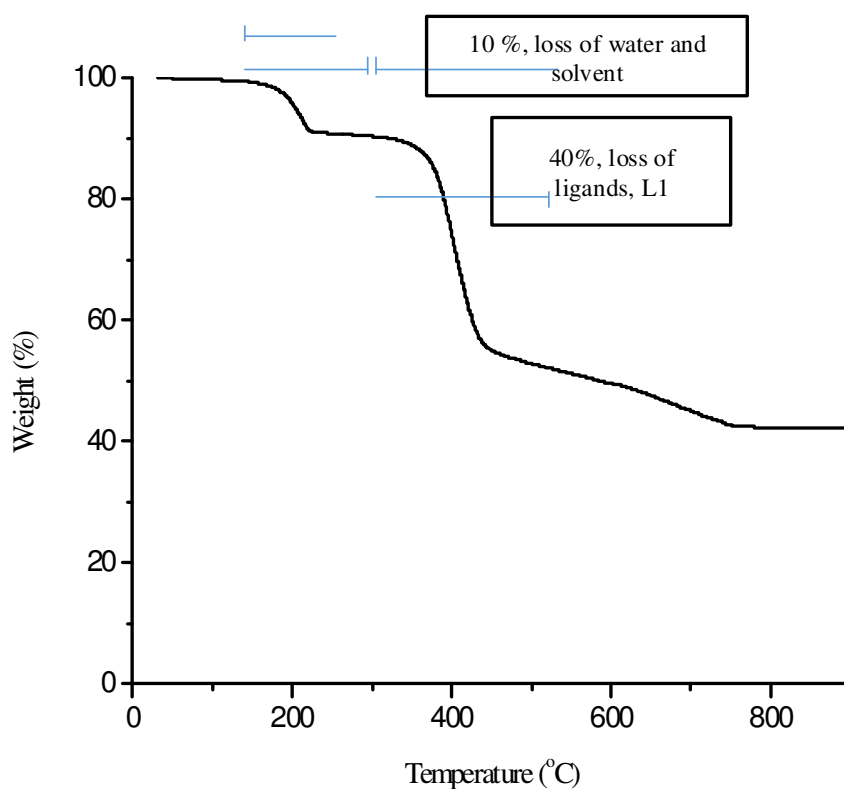




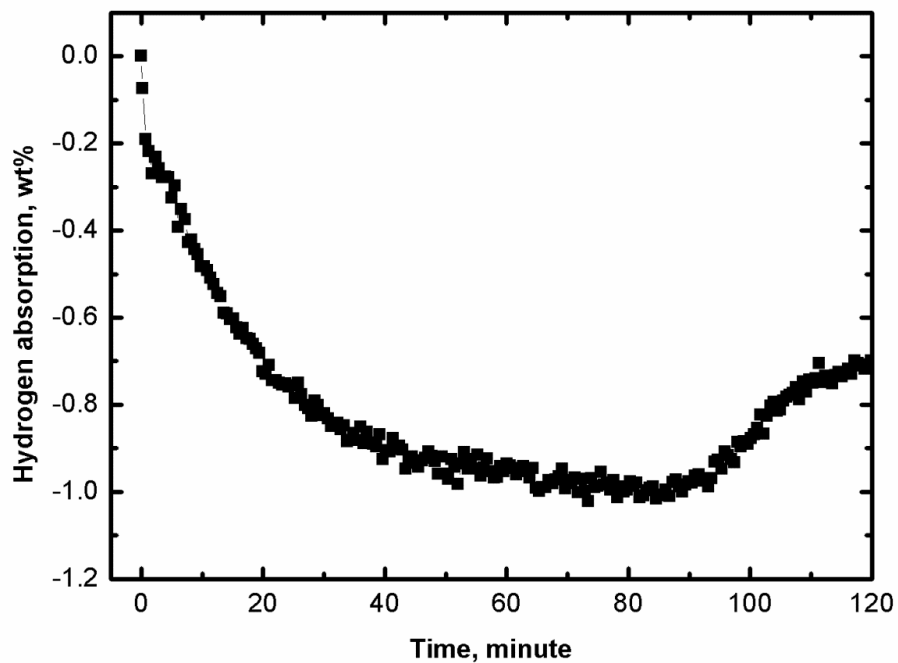
**Figure 5.** The perspectives view of (a) asymmetric unit of  $\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$  (b) extended structure of the MOF showing one dimensional arrangement (c) crystal packing when viewed from  $ac$  axis. Water molecule is omitted for clarity.



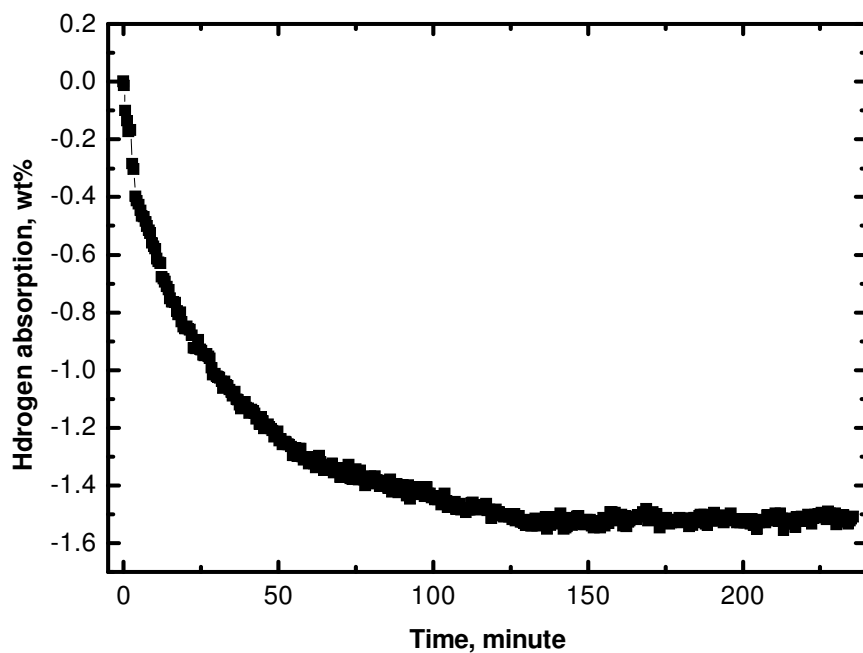
**Figure 6.** The structure of complex  $\{[Cd_3(L1-CH_3) \cdot CH_3OH]\}_n$  based on IR and elemental analysis.



**Figure 7.** A view for the TGA curve of  $\{[Cd_3(L1-CH_3) \cdot CH_3OH]\}_n$



**Figure 8.** A view for the absorption of hydrogen for  $\{[\text{Cd}_3(\text{L1-CH}_3)\cdot\text{CH}_3\text{OH}]\}_n$  analyzed at 373 K and 60 bar.



**Figure 9.** A view for the absorption of hydrogen for  $\{[\text{Cd}_3(\text{L-CH}_3)\cdot\text{H}_2\text{O}]\cdot 5\text{H}_2\text{O}\}_n$

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