

SYNTHESIS AND CHARACTERIZATION OF METAL ORGANIC FRAMEWORKS (MOFs) DERIVED FROM 3,5-PYRIDINEDICARBOXYLIC ACID

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Abstract: Reaction between 3,5-pyridinedicarboxylic acid with four different metal salts which are cadmium nitrate tetrahydrate, cobalt acetate, zinc acetate hydrate and nickel chloride produced four novel metal organic frameworks (MOFs), with general formula given by elemental analysis as $\{(CdLNO_3 \cdot 2H_2O)CH_3OH\}_n$, $\{(CoL \cdot 2H_2O)\}_n$, $\{(ZnL \cdot 2H_2O)\}_n$ and $\{(NiL \cdot Cl_2)\}_n$ (where $L=C_7H_5NO_4$), respectively. These MOFs were synthesized using solvothermal techniques and fully characterized by using combination of Fourier Transform Infrared (FTIR) and Carbon, Hydrogen, Nitrogen Analyzer (CHN Analyzer). In the FTIR spectra of the MOFs, metal oxide bond peaks were identified at 1393 cm^{-1} , 586 cm^{-1} , 424 cm^{-1} and 471 cm^{-1} for Cd-O, Co-O, Zn-O and Ni-O, respectively. Characterization using Ultraviolet-Visible spectroscopy (UV-Vis) was unsuccessful due to limited solubility of MOFs in many solvents.

Keywords: Metal organic frameworks, 3,5-pyridinedicarboxylic acid, solvothermal, metal oxide, characterization.

Introduction

Abundant number of metal organic frameworks (MOFs) can be made from a combination of two building blocks consisting of inorganic metal ions and organic bridging ligands. MOFs can be shaped into diverse types of geometries such as linear, square-planar, tetrahedron, octahedron or square-pyramidal depending on the coordination number of the coordinated metal ion and organic linker. The involvement of amide group as organic linker has offered additional hydrogen-bonding sites which have enhanced MOFs applications in various areas such as gas storage, molecular sensing, catalysis and separations (Xiong *et al.*, 2013). This is due to the N site that play important roles as

hydrogen-bond donors resulting in attractive force between hydrogen and electronegative atom which lead to the formation of hydrogen bonding and Van der Waals interactions (Xu *et al.*, 2002; Raschka *et al.*, 2018).

Inspired by the use of amide containing group in MOFs, this study focused on the synthesis of MOFs utilizing 3,5-pyridinedicarboxylic acid (Figure 1) as organic linker. This type of ligand exhibits carboxylic groups which is important in the construction of MOFs or coordination polymers (Kumar *et al.*, 2018). Acid 3,5-pyridinedicarboxylic ($C_7H_5NO_4$) has three possible connected sites from hydroxyl group and nitrogen in the pyridine ring (Karmakar *et al.*, 2018).

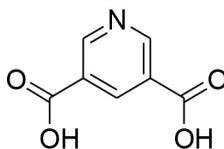


Figure 1: Chemical structure of 3,5-pyridinedicarboxylic acid

Materials and Methods

Apparatus, Chemicals and Materials

To conduct this research, the apparatus and glassware used were hot plate, beakers (100 ml, 250 ml and 500 ml), measuring cylinder (10 ml), vial tubes, filter funnel, spatula and dropper. The chemicals and solvents used were analytical grade and are used without any further purification. Chemicals used were the ligand 3,5-pyridinedicarboxylic acid and 4 types of metallic salts which are cadmium nitrate tetrahydrate, cobalt acetate, zinc acetate hydrate and nickel chloride.

Metal salts and the organic linker, 3,5-pyridinedicarboxylic acid ($C_7H_5NO_4$) were weighed in 1:1 mol ratio and mixed in small vials. The mixture was suspended in dimethylformamide and immersed into the heated plate which was filled with sand. The sand bath was heated up to $110^\circ C$ and the mixture was left to heat for 24 hours. This solution was kept to cool down at room temperature until the MOFs precipitated in another 24 hours. The precipitate was filtered off and dried under vacuum for an hour. The melting points of the products were high, showing the main properties of MOFs (Xu *et al.*, 2002).

Synthesis of MOFs 1-4

Reaction of commercially available ligand, 3,5-pyridinedicarboxylic acid ($C_7H_5NO_4$) with

cadmium nitrate tetrahydrate, $Cd(NO_3)_2 \cdot 4H_2O$ forms MOF-1. As observed in the FTIR spectrum of MOF-1 (Figure 2), significant peak of metal oxide Cd-O was found at 1393 cm^{-1} (Arun *et al.*, 2015), while the original O-H bend of carboxylic acid at 3091 cm^{-1} disappeared due to complexation. The coordination of the carbonyl to cadmium, the C=O stretching 1720 cm^{-1} in the ligand spectrum disappeared. However, a broad peak of O-H water appeared at 3316 cm^{-1} . Comparison between the FTIR spectrum of 3,5-pyridinedicarboxylic acid with MOF-1 showed several chemical shifts. For example, the C=N stretching, was seen at 1600 cm^{-1} shifted to 1613 cm^{-1} . Similar chemical shift was identified for C-O, in which the peaks shifted from 1304 cm^{-1} to 1299 cm^{-1} .

MOF-1 was further analyzed by combustion analysis to determine the elemental percentage of carbon (C), hydrogen (H), and nitrogen (N) in the product. This analysis can be used to determine the purity of the compound and to confirm the formulation of the product obtain. Elemental analysis has confirmed the formation of MOF-1 from the reaction between 3,5-pyridinedicarboxylic acid ($C_7H_5NO_4$) and cadmium nitrate tetrahydrate $Cd(NO_3)_2 \cdot 4H_2O$. Table 1 shows the percentage for each element compared between theoretical and experimental values. Based on the elemental analysis, the product is confirmed to have formula molecule $\{(CdLNO_3 \cdot 2H_2O)CH_3OH\}_n$.

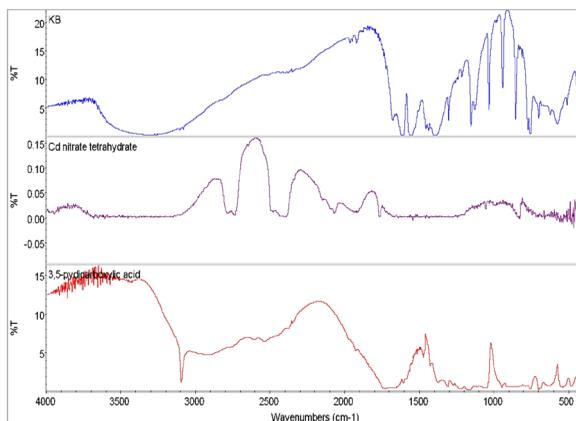


Figure 2: FTIR spectra of (a) MOF-1, (b) Cadmium nitrate and (c) Ligand

Table 1: Elemental analysis data of MOF-1

Element	Percentage of Element (%)		
	C	H	N
Theoretical	23.57	2.72	6.87
Experimental	26.79	2.74	5.27

Similar to the preparation of MOF-1, cobalt acetate to form MOF-2 with proposed 3,5-pyridinedicarboxylic acid was reacted with structure as follows:

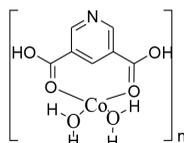


Figure 3: Chemical structure of MOF-2

From FTIR spectra in Figure 2, significant functional group peak of metal oxide Co-O was found at 586 cm^{-1} , similar to the reported range value (Hou *et al.*, 2017). Also, the O-H bend of carboxylic acid at 3091 cm^{-1} disappeared in MOF-2 spectrum and broad peak of O-H water at 3370 cm^{-1} was indicated (Figure 4).

Comparison between the FTIR spectrum of 3,5-pyridinedicarboxylic acid with MOF-2 showed several chemical shifts such as C=N stretching which was seen at 1600 cm^{-1} and shifted to 1632 cm^{-1} after complexation. Similar chemical shift was identified for C-O from 1304 cm^{-1} to 1275 cm^{-1} .

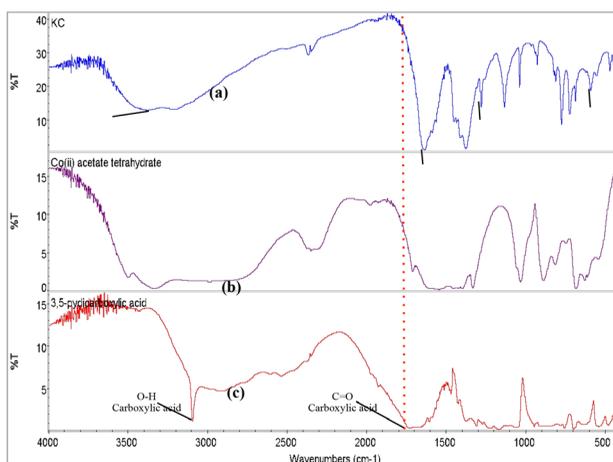


Figure 3: FTIR spectra of (a) MOF-2, (b) Cobalt acetate and (c) Ligand

Elemental analysis has confirmed the formation of MOF-2 with formula molecule $(\text{CoL}_2\text{H}_2\text{O})_n$ where $\text{L}=\text{C}_7\text{H}_5\text{NO}_4$. The results

show that the theoretical and experimental data had near value, with the formula suggested as $\text{Co}_1\text{C}_7\text{H}_9\text{O}_6\text{N}_1$ (Table 2).

Table 2: Elemental analysis data of MOF-2

Element	Percentage of Element (%)		
	C	H	N
Theoretical	31.97	3.42	5.32
Experimental	31.20	3.74	5.39

MOF-3 which was obtained from reaction of the ligand with zinc acetate was analyzed by FTIR and significant functional group peaks of metal oxide Zn-O was found at 424 cm⁻¹ (Muthukumar & Gopalakrishnan, 2012). Similar to MOF-1 and MOF-2, the O-H bend of carboxylic acid at 3091 cm⁻¹ was disappeared

in MOF-3 spectrum. As expected, the C=N stretching at 1600 cm⁻¹ was shifted to 1620 cm⁻¹. Similar chemical shift was identified for C-O from 1304 cm⁻¹ to 1299 cm⁻¹. Elemental analysis results proposed that the formula molecule of MOF-3 is Zn₁C₇H₉O₆N₁, as shown in Figure 4 and the FTIR spectra are shown in Figure 5.

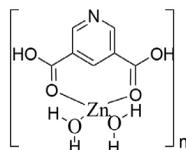


Figure 4: Chemical structure of MOF-3

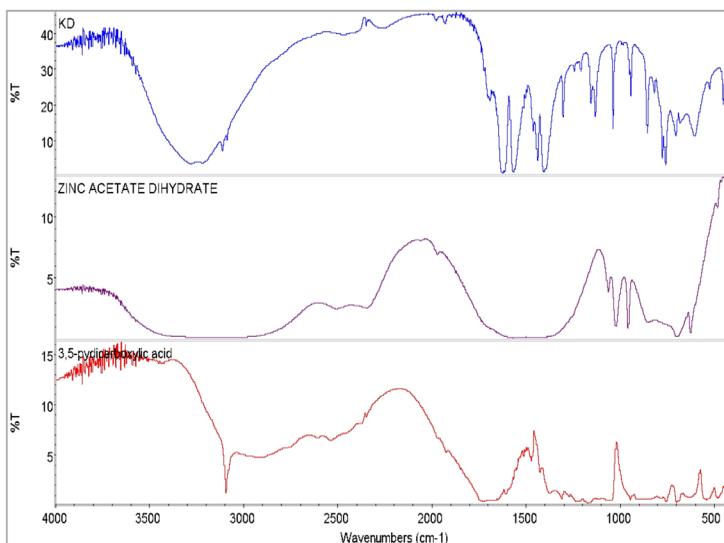


Figure 5: FTIR spectra of (a) MOF-4, (b) Zinc acetate and (c) Ligand

Elemental analysis has confirmed the formation of MOF-4 with formula molecule (NiL.Cl₂)_n (Table 3). The results show that the theoretical and experimental data had near value, with the formula suggested MOF-4 as Ni₁C₇H₅O₄N₁Cl₂.H₂O. The synthesized MOF-4

which was obtained from reaction between the ligand with nickel chloride was characterized by FTIR (Figure 6). The spectrum shows the presence of Ni-O observed at 471 cm⁻¹ (Subramanian *et al.*, 2008). Again, the O-H bend of carboxylic acid at 3091 cm⁻¹ has disappeared.

Comparison between the FTIR spectrum of 3,5-pyridinedicarboxylic acid with MOF-4 indicated several chemical shifts such as C=N stretching from 1600 cm⁻¹ to 1637 cm⁻¹. Similar

chemical shift was identified for C-O from 1304 cm⁻¹ to 1276 cm⁻¹. The chemical shifts for all functional groups for all MOFs are listed in Table 4. Meanwhile, the chemical structure for MOF-4 is shown in Figure 7.

Table 3: Elemental analysis data of MOF-4

Element	Percentage of Element (%)		
	C	H	N
Theoretical	26.70	2.23	4.45
Experimental	26.61	4.5	4.51

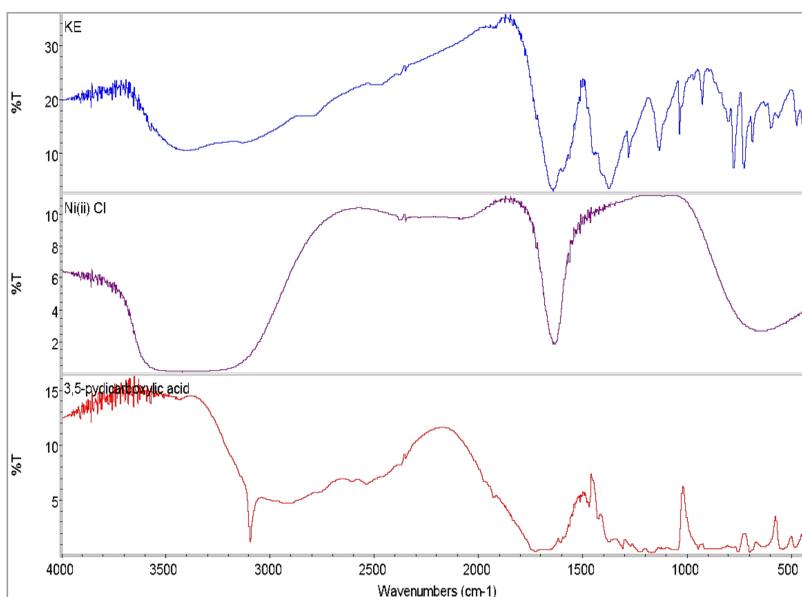


Figure 6: FTIR spectra of (a) MOF-4, (b) Nickel chloride and (c) Ligand

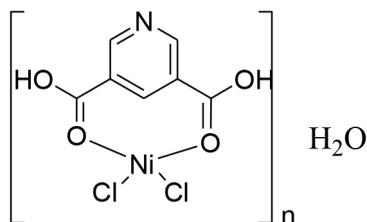


Figure 7: Chemical structure of MOF-4

Table 4: The list of functional groups observed in the ligand and MOFs 1-4

3,5-pyridinedicarboxylic Acid		MOF-1	MOF-2	MOF-3	MOF-4
Type of Vibration	Wavenumber cm ⁻¹				
C-H	753	808	808	808	724
C-O	1304	1299	1275	1299	1276
M-O	-	1393	586	424	471
C=C	1508& 1466	1556& 1435	1553& 1430	1556& 1400	1558 & 1468
C=N	1600	1613	1632	1620	1637
C=O	1720	-	-	-	-
O-H	3091	3316	3370	3391	3340

M-O =, M= Metal ions

Conclusion

In conclusion, four novel metal organic frameworks have been successfully synthesized and characterized. Synthesis of metal organic frameworks has its own challenges. Increasing synthesis scale requires further study on some parameters that may affect the reaction such as volume and pressure. The characterization methods that have been applied to this novel product were infrared spectroscopy (FTIR) and Carbon, Hydrogen, Nitrogen Analyzer (CHN Analyzer). It is common that MOFs have limited solubility in many solvents thus UV analysis cannot be carried out.

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