Journal of Basic and Environmental Sciences, 8 (2021) 29-31

ISSN
Online: 2356-6388
Print : 2536-9202

Research paper Open Access

Synthesis, Structure and Characterization of Some Metal Organic Framework Based on 4-Aminobenzoic Acid Schiff Base Linker

Reem G. Deghadi*, Ayman S. Eliwa, Wafaa M. Hosny
Chemistry Department, Faculty of Science, Cairo University, Giza, 12613, Egypt

Abstract

Due to their large surface area and porous structures, metal organic frameworks (MOFs) represent a desirable material as a result of array of nurturing features. In this article, a novel Schiff base ligand was prepared and then used as a linker for synthesis of novel Cd(II)-MOF and Cu(II)-MOF under ultrasonic condition. The newly synthesized Schiff base, Cd(II)-MOF and Cu(II)-MOF were characterized using different characterization tools such as infrared spectra and thermal analysis. The binding of the carboxylate group of the synthesized Schiff base was in monodentate manner to Cu(II) and Cd(II) ions as indicated from the IR spectra.

***Keywords*:** Cd(II)-MOF, Cu(II)-MOF, Schiff base linker, thermal analysis, IR
Received; 10 Oct. 2020, Revised form; 4 Dec. 2020, Accepted; 4 Dec. 2020, Available online 1 Jan. 2021.

1. Introduction

MOFs are defined as compounds that are consist of metal ions or clusters that coordinated to organic linker to form one, two, or three dimensional structures [1]. The unique properties of the MOFs can be adjusted by playing with their three main structural features: the metal, the organic ligand, and the framework. MOFs have some unique advantages compared to conventional porous materials such as zeolites and activated carbon including high specific surface area, adjustable pores and adjustable porous surfaces [2]. It is made through coordination bonds between organic ligands and metal ions that found to be an important class in material science due to their diversity in structure and function. MOFs have some unique advantages compared to conventional porous materials such as zeolites and activated carbon including high-specific surface area, adjustable pores and adjustable porous surfaces [3–5]. Construction of MOFs involves choosing of appropriate organic linker and inorganic metal. Also, the use of the organic ligand has been proven to spawn interesting topology that aids in adsorption. These materials normally exhibit fascinating architectures such as sponge structure that allow for many application studies such as optics [6], sensors [7–8], gas adsorption [9] and separation, gas storage [10–11], catalysis [12–16], drug delivery [17–19] and other fields. Schiff bases are compounds that have azomethine functional group which have been synthesized by the condensation of primary amines with active carbonyls materials (aldehyde or ketone). Particularly, the aromatic Schiff base dicarboxylate ligands, such as 2-(((4-carboxyphenyl)imino)methyl) benzoic acid (H_2L) which was newly prepared and characterized in this study, was well used in the preparation of two novel Cd-MOF and Cu-MOF with interesting structures and special topologies. Synthesis of nanoscale MOFs has also been attractive. Ultrasound irradiation is one of the simplest and most effective methods for preparation of nano or microstructures MOFs [20–21]. A new Cd(II)-MOF and Cu(II)-MOF were successfully synthesized via ultrasonic irradiation and characterized by using a combination of different techniques such as IR and thermal analysis [22–24].

2. Experimental

2.1. Materials and methods

All used chemicals were of analytical grade and bidistillated water was used throughout all experiments. 2-Carboxybenzaldehyde, 4-aminobenzoic acid, cadmium(II) acetate dihydrate and copper(II) acetate dihydrate were purchased from Sigma-Aldrich. Absolute ethyl alcohol was spectroscopic pure from BDH.

The instrument used in this work included FT-IR spectra were recorded on a Perkin-Elmer 1650 spectrometer (4000–400 cm^{-1}) as KBr pellets. ^1H NMR spectra, as a solution in DMSO-d_6, were recorded on a 300 MHz Varian-Oxford Mercury at room temperature using TMS as an internal standard. Mass spectra were recorded by the EI technique at 70 eV using MS-5988 GS-MS Hewlett-Packard instrument at the Microanalytical Center, National Research Center, Egypt. The thermogravimetric analyses (TG and DTG) were carried out from room temperature to 800 °C using a Shimadzu TG-50H thermal analyzer at a rate of 5 ºC/min. Microanalyses of carbon, hydrogen and nitrogen were carried out at the Microanalytical Center, Cairo University, Egypt, using CHNS-932 (LECO) Vario Elemental Analyzer.

2.2. Synthesis of Schiff base (H_2L) linker

The new Schiff base ligand (H_2L) was synthesized by mixing of saturated ethanolic solution of 2-carboxybenzaldehyde (5 g) and 4-aminobenzoic acid (5.47 g) by the ratio of 1:1. The aldehydic solution was added to the amine under stirring and refluxed for 5-7 hours. The resulting ligand was filtered and washed with cold ethanol several times until the filtrate became clear. The solid ligand was then dried over anhydrous calcium chloride in a desiccator.

2.3. Synthesis of Cd-MOF and Cu-MOF

The Schiff base ligand (H_2L; 1g, 3.7 mmol) was dissolved in 30 mL absolute ethanol. Cadmium acetate dihydrate (0.66 g, 2.48 mmol) or copper acetate dihydrate (0.287 g, 1.435 mmol) was dissolved in 25 mL ethanol. The molar ratio of metal ions to H_2L was 1:1.5. The solutions were mixed and then placed into a container mounted in a water bath and subjected to sonication for 60-75 min. The ultrasonic output was kept at 60W and precipitation of MOFs begins after 10 minutes of sonication. The products have been isolated by centrifugation and the precipitate has been washed with water and ethanol, then they were dried at 100 °C for 12 hours. The product was then cooled in air at ambient temperature.

3. Results and discussion

3.1. Characterization of Schiff base ligand

The results of elemental analysis (C, H and N) of the synthesized Schiff base (H_2L; Figure (1) showed carbon percent 67.10% (calcd. = 66.91%), nitrogen 5.36% (calcd. = 5.20%) and hydrogen 4.20% (calcd. = 4.12%). IR spectrum of the free ligand (H_2L) showed the appearance of a new band for ν $(CH=N)_{azomethine}$ at 1601 cm^{-1} [25]. Stretching bands of $\nu_{asym}(COO^-)$ and $\nu_{sym}(COO^-)$ were appeared at 1468 cm^{-1} and at 1321 cm^{-1}, respectively [26]. The ^{1}H-NMR spectrum of the ligand showed signals at 5.8 ppm (singlet, 1H, HC=N), 12.3 ppm (singlet, 2H, carboxylic protons) and multiplet signals at 6.5-7.9 ppm which attributed to the aromatic protons. The mass spectrum of the Schiff base ligand exhibited a clear parent peak at m/z = 269.07 amu as indicated from elemental analysis that was corresponding to the ligand moiety $C_{15}H_{11}NO_4$ with atomic mass 269.25 amu.

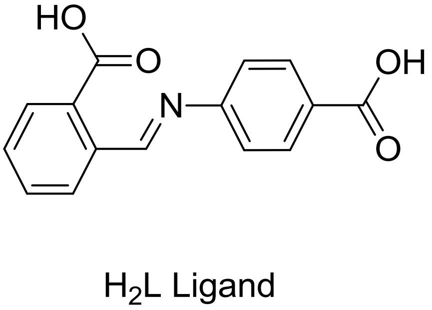

Fig (1): Structure of the synthesized organic linker Schiff base

3.2. Characterization of Cd-MOF

The strong absorption band in the range of 3612-3545 cm^{-1} was corresponded to the O-H vibrations of water molecules that present in the crystal structure of the prepared MOF [27]. The existence of the bands close to 1500 cm^{-1} and 1323 cm^{-1} can be directed to the existence of dicarboxylate $(O\text{-}C\text{-}O)^-$ functionalities within the synthesized Cd-MOF, which related to asymmetric and symmetric vibrations, respectively [28]. The shift in the band position of the symmetric and asymmetric carboxylate of the prepared MOF can be assigned to the binding of carboxylate group to the cadmium ions in monodentate mode [29]. In Cd-MOF, new peak representing Cd-O was observed at 516 cm^{-1} (Figure 2) [30].

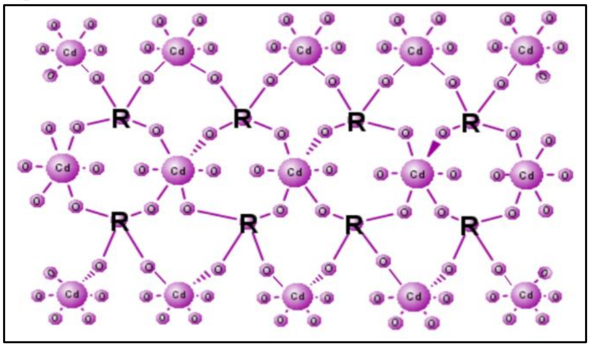

Fig (2): Structure of synthesized Cd-MOF

Thermal decomposition of the synthesized Cd-MOF displayed with a first weight loss of 16.61% in the temperature range 80-300 °C. The second and third weight losses of 57.13% were found in the temperature range 300-765 °C. These decompositions consistent with the release of the solvent molecule per formula at first step and thermal decomposition of the organic component in the other steps, leaving CdO as residue.

3.3. Characterization of Cu-MOF

The O-H vibrations of water molecules that present in the crystal structure of Cu-MOF was found as strong absorption band in the range of 3325-3056 cm^{-1} [27]. The bands found in the IR spectrum at 1540 cm^{-1} and 1468 cm^{-1} can be assigned to dicarboxylate $(O\text{-}C\text{-}O)^-$ functionalities within the synthesized Cu-MOF, which related to asymmetric and symmetric vibrations, respectively [28]. The shift in the band position of the symmetric and asymmetric carboxylate from the free ligand can be assigned to the binding of carboxylate group to the metal ions in monodentate. Peak that represented to Cu-O was observed at 506 cm^{-1} (Figure 3) [30].

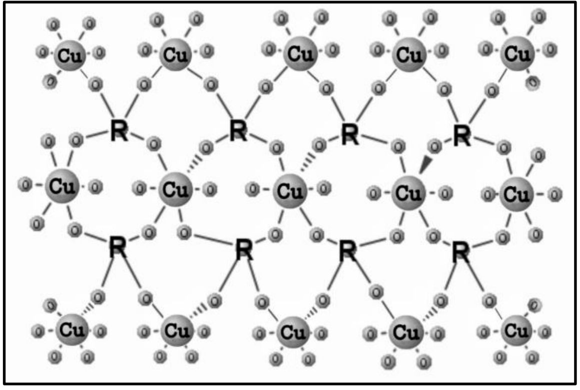

Fig (3): Structure of synthesized Cu-MOF

Thermal decomposition step of the synthesized Cu-MOF exhibited with a first weight loss of 74.31% in the temperature range of 35-425 °C, attributed to the release of solvent molecule per formula and the thermal decomposition of the organic part of the MOF. Resulting of the formation of the stoichiometric amount of CuO as residue.

4. Conclusion

New Schiff base ligand 2-(((4-carboxy phenyl) imino) methyl) benzoic acid (H_2L) was successfully synthesized and characterized to be used in the preparation of new Cd-MOF and Cu-MOF via ultrasonic irradiation and then characterized by using combination of different techniques.

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