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Room temperature synthesis and characterization of a Zn (II) based metal- organic framework with mixed ligands, 1, 4- benzenedicarboxylic acid and 1-methyle imidazole

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Abstract

A Zn (II) based metal-organic framework with ligands 1, 4- benzenedicarboxylic acid (H₂bdc) and 1-methyle imidazole (1-MI) has been synthesized by simple and economic, room temperature stirring method without heating. Crystals obtained were characterized by powder X-ray diffraction, FT-IR spectroscopy, CHNS, scanning electron microscopy, Thermogravimetric analysis and by Brunauer-Emmett-Teller based N₂ gas adsorption studies. A comparative study has been made between room temperature stirring method and conventional heating method in order to understand the efficiency of the methods. The studies show that the compound network contains two Zn center and each center displays a rare five-coordinated square pyramidal geometry.

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Keywords: Metal-organic framework; rigid ligand; Zn complex; carboxylate complex; imidazole; surface area; porosity studies.

1. Introduction

Metal-Organic Frameworks (MOFs) are a novel class of hybrid materials built from metal ions with well defined coordination geometry and organic bridging ligands. These fascinating materials are characterized by large internal surface areas, ultralow densities, and uniformly structured pores and channels and hence they have received a great attention in recent years, Ferey (2008), Tranchemontagne et al. (2009). In contrast to inorganic materials, the compositions and structures of MOFs are innumerable owing to the choice of a vast range of metal ions and organic linkers. Their diversity of possible topologies and useful properties allow possible application in areas such as host materials for molecular separation and storage, Banerjee et al. (2008), hydrogen storage, Rossi et al. (2003), molecular sieves, Bae et al. (2008), selective catalysis, Chae et al. (2004), Alkordi et al. (2008), magnetism, Sato et

al. (1996), nonlinear optical devices, Zhang et al. (2008) luminescence, Fernandez et al. (2007), ion exchange sensors, Katz (2008) and drug delivery, Horcajada et al. (2008), An et al. (2009).

The synthesis of MOFs is a process, which involves the self-assembling of molecular precursors leading to the formation of one-, two- or three dimensional structures depending on their starting materials. The synthesis of MOF can be influenced by many factors such as the nature of metal ions, Amabilino et al. (1995), Jung et al. (2000) and organic ligands, Eddaoudi et al. (2001) solvent system, Burrows et al. (2005) counterions as well as molecular interactions including hydrogen bonding and π - π interactions, Wang et al. (2012). Due to their excellent coordination capability and possibility of offering new functional materials, the study on MOFs has been well established, Eddaoudi, et al. (2001), Yaghi et al. (2003). Mixtures of carboxylates and amines or imines have also been used for the construction of porous MOFs, Delgado-Friedrichs et al. (2007). On the other hand, *N*-donor ligands with certain spacers between the two terminal coordination groups can also be used as ancillary ligand together with the carboxylate ligand to meet the requirement of coordination geometries of metal ions in the self-assembly process. Such *N*-donor ligands are good candidates to produce unique structural motifs with beautiful aesthetics and useful functional properties. There are several reports on the study using flexible bis(imidazole) and rigid multicarboxylate as mixed ligands to build multidimensional frameworks with varied structures and topologies. This is due to the nature of both flexible bis(imidazole) ligand and multicarboxylate to adopt a variety of coordination modes to satisfy the coordination geometry requirements of the metal ions, Qi, Y et al. (2008), Zhang et al. (2008), Liu et al. (2007). To gain more information about the coordination chemistry of mixture of ligands, we focus our attention on the construction of novel MOFs by using carboxylate ligand and *N*-donor ligands. MOFs are frequently synthesized by traditional hydro-/solvothermal methods: heating an organic linker (containing carboxylate link) and metal salt in a solvent system that usually contains formamide or water functionality, Tsao et al. (2007), Zhi et al. (2009), Wen et al. (2005). These methods often yield crystals suitable for single crystal X-ray diffraction analysis, but have the obvious disadvantage of being relatively slow. Reactions have to be carried out at a higher temperature for a prolonged period of time which can be in some cases as high as 8- 10 days as reported earlier in case of Be-btc. Furthermore, solvothermal conditions are unsuitable for thermally sensitive starting materials.

Here, we have made an attempt to synthesize MOF by a rapid, simple and high yielding room temperature reaction with mixture of ligands. Here, we are showing that heating to higher in order to carry out the reaction is not necessary and still by the reaction at room temperature highly crystalline MOFs can be produced. We illustrate this by the synthesis of MOF by both conventional heating and room temperature stirring methods. It has been reported earlier that the subsequent addition of triethylamine causes deprotonation of the organic linker to precipitate MOFs at room temperature, Tranchemontagne et al. (2008). This procedure involves no addition of triethylamine and the reaction takes place at room temperature under atmospheric pressure. The MOFs obtained were characterized by FTIR spectroscopy, X-ray diffraction (XRD), Thermogravimetric analysis (TGA) and by Brunauer-Emmett-Teller (BET) based N₂ gas adsorption studies.

2. Experimental Section-

3. 2.1. Materials

All the chemicals, such as Zinc nitrate hexahydrate, 1-4 benzene dicarboxylic acid (Terephthalic acid), *N,N*-dimethylformamide (DMF) etc., used in this research work were purchased from s d fine Chem. Ltd. of analytical-grade. 1-methyleimidazole and chloroform obtained from Spectrochem pvt. Ltd. They all were of reagent grade and used as they received without further purification. The reactors used were stainless steel autoclaves with Teflon

liners of 60 ml capacity.

2.2. Synthesis Processure

Compound was synthesized under room temperature conditions with-out heating the reaction. In a typical reaction, 1 gm of hexahydrated Zinc nitrate and 0.7 gm of terephthalic acid were dissolved separately in 15 ml of DMF with mild stirring. The clear solution of Zinc nitrate hexahydrate, terephthalic acid in DMF added along with 0.5 ml of 1-methyle imidazole. The system was sealed and stirred at room-temperature for 3 h. Now the reaction had kept without touching for overnight. Resulting crystals were collected after continuous washing with DMF and chloroform followed by drying at room temperature. Figure 1 shows the synthesis of MOF with the reactants at room temperature. We had also performed the same reaction under similar reaction conditions by solvothermal route.

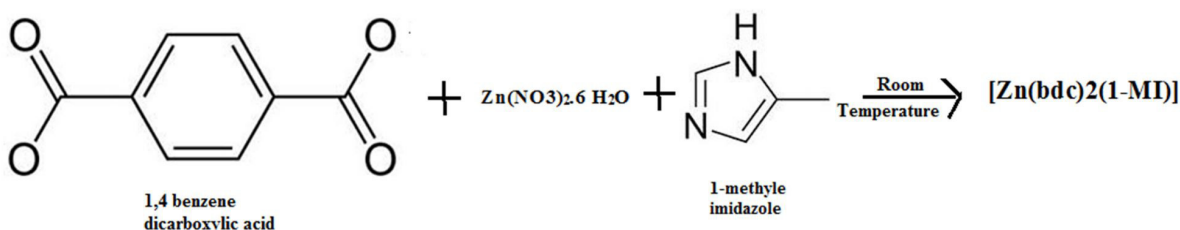


Figure1. Reaction scheme for the formation of Zinc metal organic framework.

2.3. Characterization Techniques

As obtained colorless crystals were characterized by powder X-ray diffraction (PXRD) analysis which has inferred about the purity and phase structure and nature (crystalline or amorphous) of the product. The PXRD patterns were obtained on Bruker D8 Advance powder X-ray diffractometer with $\text{CuK}\alpha$ radiation, at $\lambda = 0.1541874$ nm. The vibrational properties of the MOF material was studied by using FTIR, an 8400S Shimadzu spectrophotometer in the range from 4000 to 400 cm^{-1} using KBr pellets. Elemental analysis was performed by Elementar Vario MICRO VI.9.7 analyzer to study the purity and composition of the products. The morphologies of the samples were observed through JEOL model JSM 6490 LV scanning electron microscope (SEM). Thermogravimetric analysis (TGA) was performed using a Thermal analysis (TA) SDT-Q600 simultaneous DTA/TGA system. For TGA, the samples were taken in alumina crucible and heated under a flow of air or nitrogen at a rate of 20 $^{\circ}\text{C}/\text{min}$ up to 800 $^{\circ}\text{C}$. Also, Brunauer-Emmett-Teller (BET) based N_2 gas adsorption studies were made using NOVA – 2000 Ver. 2.00, a BET surface area measurement instrument.

4. Result and discussion

The colorless crystals of Zinc metal-organic framework so obtained by the reaction of 1,4-benzene dicarboxylic acid and 1-methyl imidazole in *N,N*-dimethylformamide were well characterized and compared with the ones synthesized by solvothermal procedure. The Figure 2 (a) and (b) respectively show the FTIR spectra of the so obtained MOF synthesized at room temperature and conventional heating at higher temperature. The absorption band in the region 3200-3100 cm^{-1} in the spectra is due to $-\text{C}-\text{H}$ stretching vibration mode originating from benzene ring of 1,4-benzenedicarboxylic acid. The second absorption band is observed in the region 2980 - 2940 cm^{-1} is due to $-\text{C}-\text{H}$ stretching in methyl group. Further, the weak and intense absorption peaks are observed in the region 1650 - 1300 cm^{-1} which could be due to asymmetric and symmetric stretching modes at 1625 cm^{-1} and 1506 cm^{-1} are

correspond of C=O of the 1,4-benzenedicarboxylic acid. Aromatic ring can also show the peaks in this region corresponding particularly at $1600\text{ cm}^{-1}(\nu)$, $1580\text{ cm}^{-1}(\nu)$, 1440 cm^{-1} due to C=C stretching and C-H bending vibrations. The absorption peaks in the region $1300 - 1200\text{ cm}^{-1}$ are due to C-N stretching and C-H bending in the plane. The region showing absorption bands in the range $1100- 1060\text{ cm}^{-1}$ indicates the aromatic 1,4 substitution. In the same region, C=C and C=N stretchings can show the absorption peaks. The peaks in the region, $930 - 880\text{ cm}^{-1}$ correspond to C-N-C bending in the plane. The region from $780 - 850\text{ cm}^{-1}$ can attributed to the deformation of carbonyl substituent out of the plane. This FTIR pattern is almost similar to the pattern (b), which corresponds to the MOF synthesized by conventional heating. However, it differs from pattern (b) with respect to intensity. The peak intensities are more in pattern (a) when compared to that of pattern (b). Elemental analysis, % obs. (calc. for $[\text{Zn}(\text{bdc})_2(1\text{-MI})]$), C: 30.9, H: 1.14, N: 8.011. Found C: 32.02, H: 2.20, N: 10.66 and C: 31.9, H: 1.98, N: 9.94 for the complex synthesized at room temperature and by conventional heating route respectively. Results are infer that the synthesis of similar MOF by applying both routes with high purity.

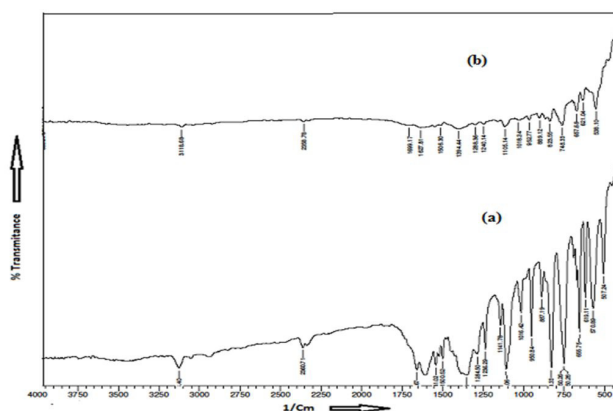


Figure 2. FTIR spectra for the MOFs (a) synthesized at Room-temperature by stirring (b) synthesized by conventional heating at elevated temperature.

Table 1. FTIR spectral data of the as synthesized MOF.

Wave Number (cm^{-1})	Assignment
3116	C-H stretching of benzene ring
2358	C-H stretching in methyl group
1615,1450,1430,	Aromatic skeleton peaks
1288	C-N stretching
1105, 1018	Peaks indicate the aromatic substitution pattern and 1,4- substitution
	C-N (1)-C
952,889	C-H bending out of the plane
808	Associated with the out of plane deformation of the two carbonyl substituents.
748	

Powder X-ray diffraction (PXRD) studies were employed to characterize the MOFs as it is a very informative tool to investigate crystalline properties of a synthesized material. The XRD patterns for zinc MOFs are presented in Figures 3. In the figure, pattern (a) and (b) correspond to the MOFs synthesized at room temperature and conventional heating route respectively. The PXRD data was collected with the monochromatic high-intensity $\text{CuK}\alpha$ radiation at $\lambda = 0.1541874\text{ nm}$. The solid crystals obtained in the synthesis were used directly without any modifications. High intensity Bragg diffraction peaks are observed at 2θ values, 10.6 and 17.2 in pattern (b). The

same peaks are also present in pattern (a), but the relatively intensities are significantly less. The broader Bragg diffraction peaks in pattern (a) in comparison with pattern (b) indicate the presence of smaller crystallites.

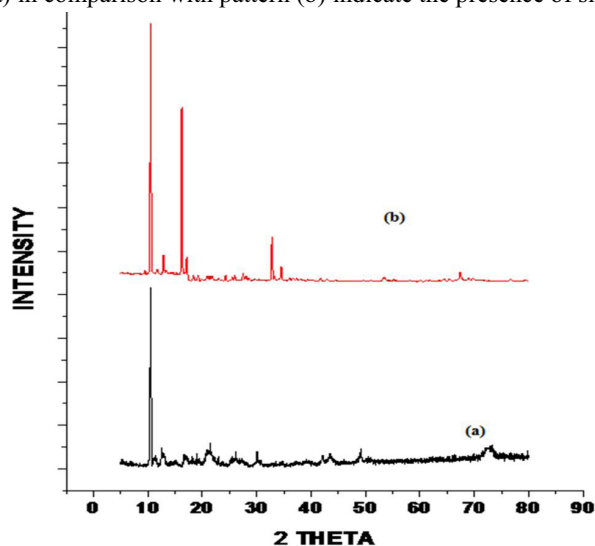


Figure 3. PXRD patterns of the MOFs: (a) synthesized at Room-temperature (b) synthesized by conventional heating at elevated temperature.

The morphologies of the sample MOFs were further investigated by Scanning electron spectroscopy. In the Figure 4, the images (a) and (b) correspond to the MOF synthesized at room temperature, images (c) and (d) correspond to the MOF synthesized by conventional heating route. SEM images by both the synthesis routes are almost similar. In all images particles are aggregated among themselves to form clusters. The particles are distributed in MOFs as clusters of irregular shaped flakes. Similar morphologies for both samples proving that we are able to synthesize desired MOF under room temperature conditions.

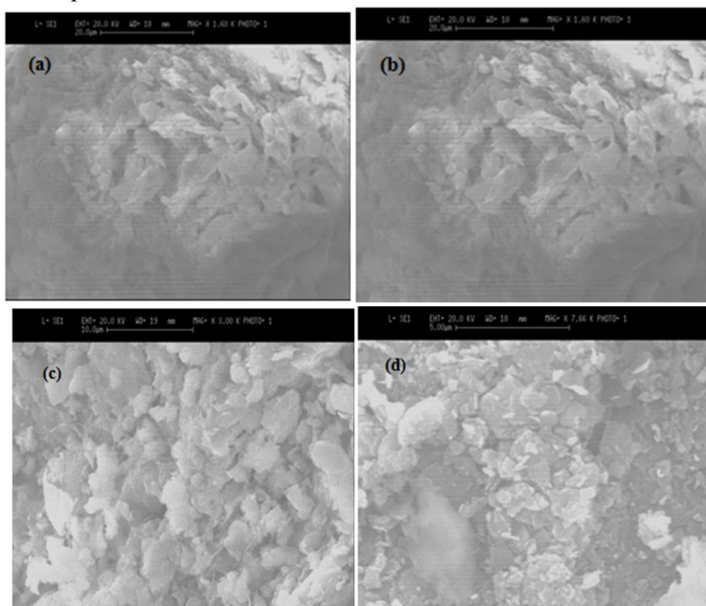


Figure 4. SEM images for the MOF samples. (a) and (b) correspond to the MOF synthesized room temperature and (c) and (d) correspond to MOF synthesized by conventional heating at elevated temperature.

The thermal stability of the as synthesized MOFs was studied using thermogravimetric analysis (TGA) under N_2 atmosphere at a heating rate of $20\text{ }^\circ\text{C}/\text{min}$ without any pre-treatment (Figure 5). Almost similar results were observed for The MOFs obtained by both solvothermal and room temperature. The thermograms show two major weight losses. The first weight loss has been observed in the temperature range of $300\text{ }^\circ\text{C}$ to $400\text{ }^\circ\text{C}$ and the second weight loss has been observed in the range $460\text{ }^\circ\text{C}$ - $540\text{ }^\circ\text{C}$. The first weight loss in about 27 % occurred could be due to the loss of free and lattice water molecules and also DMF molecules. The second weight loss in about 37% can be attributed to removal of phenyl ring and carboxylate group. Once all the solvent molecules were evaporated, the framework starts to collapse and finally results in the formation of amorphous solid. The TGA curve of the compounds indicate two points: (i) the possibility of removal of H_2bdc molecules in the temperature range of $460\text{--}540\text{ }^\circ\text{C}$ (ii) the frame work stability in the temperature range of $460\text{--}540\text{ }^\circ\text{C}$.

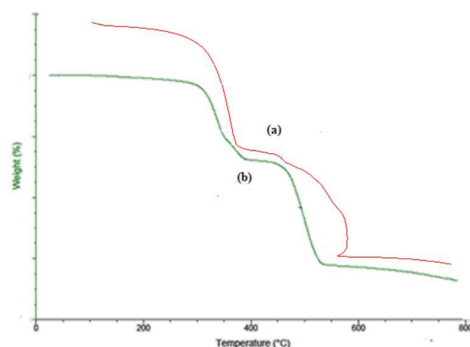


Figure 5. TGA curves of the MOFs synthesized (a) Room-temperature stirring and (b) conventional heating at elevated temperature.

To study the porosity of the MOF samples, nitrogen gas sorption isotherms were measured at 77K . Prior to gas sorption measurements both the samples were degassed at $150\text{ }^\circ\text{C}$ under vacuum for 2 h. Nitrogen physisorption isotherm is of the type II as expected for the activated samples with diameter more than microporous (Fig. 6). The adsorption and desorption curves trace almost the same isotherm, indicating the retention of the framework during this process. The specific surface area calculated is $140.42\text{ m}^2/\text{g}$ for MOF synthesized at room temperature and the specific pore volume is 0.0347 cc/g . The surface area of MOF synthesized by conventional heating route was almost close to the above value. The pore size distributions for both the MOFs displayed in Fig. 7. In figure plot (a) corresponds to MOF synthesized at room temperature and plot (b) correspond to the MOF synthesized by conventional heating at elevated temperature.

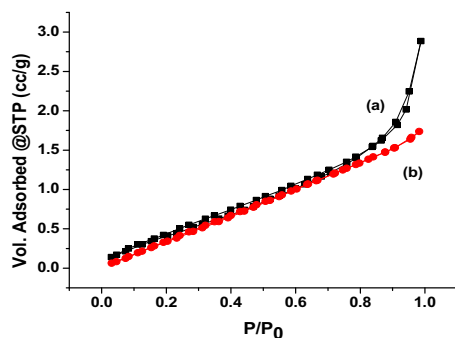


Figure 6. N_2 adsorption / desorption isotherm for as synthesized MOF samples (a) at room temperature (b) by conventional heating at the elevated temperature.

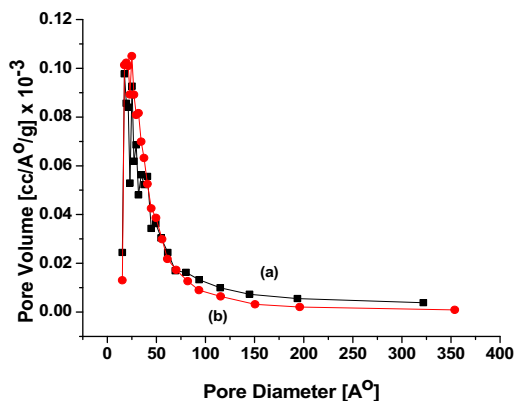


Figure 7. The pore size distribution for as synthesized MOF samples (a) at room temperature (b) by conventional heating at the elevated temperature.

By comparing the complex formed at room temperature with the complex formed by conventional heating route, we had predicted the crystal structure of the complex formed at room temperature (Figure 8). Here, each Zn (II) exhibit square pyramidal coordination environment formed by four oxygen atoms from four bdc ligands. Another oxygen atom from each bdc ligands behaves as a bridging carboxylate for another Zn (II) and one individual 1-MI ligand occupies the axial sites as illustrated in figure. The Zn cation is coordinated by four monodentate carboxylate groups (via oxygen atoms, O1, O2, O3 and O4) from four different bdc anions. Also by one imidazole nitrogen atom (N1) from one 1-methyleimidazole molecules with Zn1 –N distance of 2.001 Å and four O atoms (O1, O2, O3 and O4) from four distinct 1,4- bdc with Zn1-O bond length 2.072 Å, 2.093 Å, 2.058 Å and 2.050 Å respectively. Weak H- bonding provides stability to the framework.

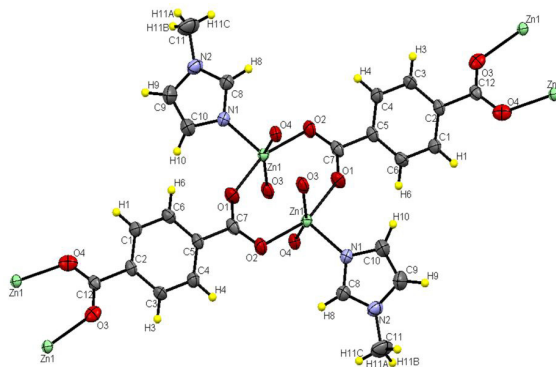


Figure 8. Crystal structure of MOF. Coordination environment around a Zn center. Atomic labelling is given for atoms in the asymmetric unit. Color code: zinc, green; carbon, black; nitrogen, blue; oxygen, red; hydrogen, yellow.

Conclusion

A comparative study of the synthesis of Zinc metal-organic framework by a convenient and cost effective at room temperature under normal atmospheric pressure has been investigated. We have successfully synthesized MOF at room temperature without addition of any additional reactant to enhance the reaction rate. The physicochemical and texture properties were found to be similar for the MOFs synthesized by both conventional and solvothermal route. A comparative study can help one to predict the structure of the complex with two Zn centre and each of which has five coordinated square pyramidal geometry. This method has been proved as a viable alternative to the conventional heating solvothermal route. This method is even safer when compared to the microwave-assisted

solvothermal synthesis, it does not imply the heating of a closed reactor containing nitrates and volatile solvents.

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