Malaysian Journal of Analytical Sciences
(MJAS)
Published by Malaysian Analytical Sciences Society
ANALIS
Persatuan Sains Analisis Malaysia

# STUDY OF SOLVOTHERMAL SYNTHESIS OF MAGNESIUM-BASED METAL-ORGANIC FRAMEWORKS

## (Kajian Sintesis Solvoterma Kerangka Logam-Organik Berasaskan Magnesium)

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Received: 18 April 2023; Accepted: 6 June 2023; Published: 23 June 2023

### Abstract

Metal-organic frameworks (MOFs) are a class of reticular materials consisting of metal ions coordinated to organic ligands. Theoretically, magnesium metal of the s-block has low electronegativity due to their large ionic radii and low ionic charges. The coordination number of magnesium immensely varies depending on the electrostatic interactions with the ligands. Therefore, designing strategic synthesis of Mg-based MOFs becomes a challenge hence its scarcity in literature. This study aims to investigate the different procedure of synthesizing Mg-MOFs using both flexible and rigid organic linkers in organic solvents at high temperature; termed solvothermal method. Magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$) are used as the metal source and mixed with naturally occurring plant acids as the organic linkers; malic acid and tartaric acid. Rigidity was introduced by addition of aromatic organic ligands of benzene-1,4-dicarboxylic acid (BDC) and benzene-1,3,5-tricarboxylic acid (BTC). By varying precursor ratios and organic solvents, we hope to improve the reaction condition for the previously reported synthesis of Mg-MOFs. Single crystal X-ray diffraction (SCXRD) and powder X-ray diffraction (PXRD) analysis showed that the same quality crystals and high crystallinity powder have been produced under improved reaction conditions. The coordination of s-block metal ions has also been found to be most suited in a solvent mixture of $H_2O$ and *N,N*-dimethylformamide (DMF).

**Keywords:** metal-organic framework, nanomaterial, solvothermal synthesis, s-block, green chemistry

### Abstrak

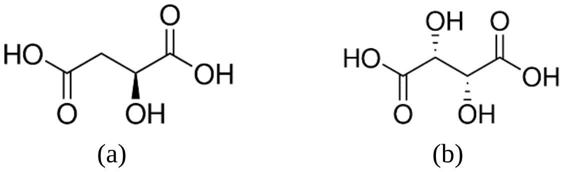
Kerangka logam-organik (MOFs) adalah satu kelas bahan retikulasi yang terbentuk dari ion logam dikoordinasikan ke ligan organik. Secara teori, logam blok-s magnesium mempunyai nilai keelektronegatifan yang rendah kerana radius ion yang besar dan cas ion yang rendah. Nombor koordinatan antara logam magnesium berbeza-beza bergantung kepada interaksi elektrostatik dengan ligan yang berkaitan. Justeru, perancangan sintesis MOF berasaskan magnesium secara strategik adalah satu cabaran berikutan kekurangan perbincangan mengenainya dalam tinjauan literatur. Kajian ini bertujuan untuk meneliti pelbagai prosedur sintesis Mg-MOF menggunakan penghubung organik samada fleksibel mahupun tegar pada suhu yang tinggi; iaitu kaedah solvoterma. Magnesium nitrat heksahidrat ($Mg(NO_3)_2.6H_2O$) digunakan sebagai sumber logam dan dicampurkan dengan asid tumbuh-tumbuhan sebagai ligan organik semula jadi; asid malik dan asid tartarik. Ketegaran dalam kerangka dimasukkan melalui penambahan ligan aromatik organik iaitu asid benzena-1,4-dikarboksilik (BDC) dan asid benzena-1,3,5-trikarboksilik (BTC). Dengan mempelbagaikan nisbah pendahulu dan pelarut organik, kami berharap dapat menambah baik keadaan tindak balas yang telah dilaporkan bagi sintesis Mg-MOF. Analisa pembelauan hablur tunggal sinar-X (SCXRD) dan pembelauan serbuk sinar-X (PXRD) menunjukkan bahawa hablur yang sama kualiti dan serbuk dengan kehabluran yang tinggi telah berjaya disintesis dengan penambahbaikan terhadap keadaan tindak balas. Campuran pelarut $H_2O$ dan *N*,*N*-dimetilformamida (DMF) pula merupakan keadaan yang paling sesuai untuk pengkoordinatan logam blok-s.

**Kata kunci:** kerangka logam-organik, bahan nano, sintesis solvotermal, blok-s, kimia hijau

## Introduction

Metal-organic frameworks (MOFs) are reticular materials composed of metal ions linked by organic ligands with specific functional groups such as carboxylate that can coordinate to the metal nodes [1]. The most dominant choices for the metals are from the p- and d-block elements due to the pronounced characteristics of transition metals such as visible light absorption, multiple oxidation states and predictable coordination geometries. On the other hand, MOFs based on s-block elements are relatively less studied. One of the main factors for the lack of interest is the unpredictable MOF structure due to having little control over the metals' coordinative behaviour. Large difference in electronegativity between s-block metal and carboxylate oxygen atom leads to a mainly ionic interaction. Thus, the coordinative nature of the metal centre throughout the network is instead determined primarily by the orientation of the functional groups, directly influenced by steric considerations [2]. Despite the setbacks, s-block MOFs can provide distinctive and intriguing properties inherited from their respective s-block elements; inexpensive and non-toxic [3]. The unpredictable coordination behaviour of the ionic metal nodes may result in interesting characteristics such as low density, flexible networks and water-soluble MOFs [4]. Therefore, s-block MOFs have the potential of a wide range of applications. Biocompatible MOFs can be designed from s-block metals such as $Na^+$, $K^+$, $Mg^{2+}$ and $Ca^{2+}$ which are already involved naturally in biological processes. Apart from amino acids which have been extensively studied as linkers, plant acids on the other hand have been largely under the radar and investigating their potential in biocompatible MOFs synthesis will be significant.

It is useful to study the previously reported synthesis as part of the ongoing effort to improve the methodologies of synthesizing s-block metal MOFs. While s-block metals generally have the same behaviour, ions with different properties will contribute to variations in reactivity. $Mg^{2+}$ provides more control to the connections of metal-linker to form the framework. A larger $Ca^{2+}$ ion compared with $Mg^{2+}$ resulted in higher coordination number [2]. Furthermore, since s-block metals ions are hard metals, they preferably form ionic bonds with hard-heteroatom based organic ligands. Carboxylates consequently are the most used linkers. Some reports of using soft bases require modification of the heteroatom onto the organic linkers such as N-based carboxylates to yield a stable structure [5]. For the reaction condition, solvothermal synthesis has been the most widely used method with few variations on the parameters. For example, group 1 metals are best dissolved in polar solvents like ether due to the ability to coordinate to the metals [3]. Therefore, the main objective of this study is to identify the ideal method that has been used to synthesize Mg-based MOFs and make improvements on them.



(a) (b)

Figure 1. The organic linkers used in this study (A) L-(–)-malic acid and (B) L-(+)-tartaric acid

The solvothermal synthesis of Mg-MOF in this study are done with different combination of solvents to achieve condition than the previously reported methods. We utilize aliphatic linkers from naturally occurring plant acids for possible biocompatible applications. Previously it has been reported the pesticide encapsulation by two porous calcium L-lactate MOFs [6]. However, successful synthesis of MOFs with such properties are rare since the framework of s-block metals tend to be flexible and nonporous [2]. Therefore, we also incorporate rigid aromatic linkers that have shown the ability to form porous and more stable MOFs. Herein the s-block metal used is $Mg^{2+}$ ion. The aliphatic linkers used are plant acids of malic acid and tartaric acid while the aromatic dicarboxylic acids are benzene-1,4-dicarboxylic acid (BDC) and benzene-1,3,5-tricarboxylic acid (BTC).

In this study, we hope to study the pattern in which s-block MOFs are synthesized and improve the established methods that has been used to synthesize Mg-MOFs. The effect of varying the synthesis parameters; solvents, temperature and time are studied. Improvements in term of less use of organic solvents, milder reaction conditions and shorter reaction time are preferred. The resulting compounds were then characterized by powder X-ray diffraction (PXRD) and, when possible, single crystal X-ray diffraction (SCXRD) [1]. Based on the findings, we outline few suggestions in approaching the synthesis of s-block MOFs using various biocompatible linkers.

## Materials and Methods

### Materials

All reagents and solvents were commercially purchased and used without further purification.

### Synthesis of MOFs

All of the reagents were mixed in 6 ml solvents at molar ratio outlined in Table 1 & 2. A molar ratio of 1 equates to 0.4 mmol. The solvents used are *N*,*N*-dimethylformamide (DMF), deionized water ($H_2O$), ethanol (EtOH), dimethylacetamide (DMA) and tetrahydrofuran (THF). Unless stated, the ratio of solvents used in a mixed system are of equal parts except for triethylamine (TEA) where only 2 drops are added into the glass vial. The solutions were made to reach homogeneity by sonication, before being put into the oven at 120°C until the product is formed. The metal source used are magnesium nitrate hexahydrate ($Mg(NO_3)_2.6H_2O$). The organic ligands used as plant acids used are L-(–)-malic acid (Mal), $(CH_2CHOH)(CO_2H)_2$ and L-(+)-tartaric acid (Tar), $(CHOH)_2(CO_2H)_2$. The aromatic linkers are $H_2BDC$ (benzene-1,4-dicarboxylic acid) and $H_3BTC$ (benzene-1,3,5-tricarboxylic acid).

### Characterization

Single crystal X-ray diffraction (SCXRD) are collected by a Gemini E Oxford Diffraction diffractometer with monochromatized Cu Kα radiation. Powder X-ray diffraction (PXRD) data are recorded at ambient temperature on a Shimadzu-600 diffractometer with Cu Kα radiation ($\lambda$=15406Å, 30kV, and 40 mA) with a scan speed of 2° $min^{-1}$ and a step size of 0.02° in 2$\theta$. The simulated PXRD patterns and unit cells database are obtained from the Cambridge Crystallographic Data Centre (CCDC). Both methods are used to identify the resulting solids by comparing the unit cells of the crystals with existing data and the X-ray diffraction patterns of the powders with existing spectra of their respective reagents.

## Results and Discussion

The reaction conditions are chosen from methods that have been previously used to successfully synthesize MOFs across the periodic table. Polar solvents such as DMF and EtOH are some of the common solvents [7] while addition of $H_2O$ into the mixture has been proven to yield Mg-based MOFs [2]. Where possible, SCXRD has been used to identify the resulting crystals while PXRD was used for the obtained powder.

Table 1. Parameters used for Mg-MOF reactions varying the solvent ratio

| **Precursors** | | **Molar Ratio of M:L** | **Sample Code** | **Solvent Ratio** | | | **Observation** |
|---|---|---|---|---|---|---|---|
| **Metal** | **Linker** | | | $H_2O$ | DMF | EtOH | |
| $Mg^{2+}$ | L1: Tartaric acid<br>L2: BDC | 2:1:1 | 1 | 1 | - | - | No solid |
| | | | 2 | - | 1 | - | No solid |
| | | | 3 | - | - | 1 | No solid |
| | | | **4** | 1 | 1 | - | Crystal |
| | | | 5 | 1 | - | 1 | No solid |
| | L1: Tartaric acid<br>L2: BTC | 1:3:2 | 6 | 1 | - | - | No solid |
| | | | 7 | - | 1 | - | No solid |
| | | | 8 | - | - | 1 | No solid |
| | | | **9** | 1 | 1 | - | Crystal |
| | | | 10 | 1 | - | 1 | No solid |
| | | | 11 | - | 1 | 1 | No solid |
| | | | 12 | 1 | 1 | 1 | No solid |

Table 2. Parameters used for Mg-MOF reactions varying the molar ratio of precursors

| **Sample Code** | **Solvent** | **Molar Ratio of Precursors** | | | | | **Observation** |
|---|---|---|---|---|---|---|---|
| | | $\mathbf{Mg^{2+}}$ | **BDC** | **BTC** | **Tar** | **Mal** | |
| 13 | DMF:$H_2O$ | 2 | 1 | - | 2 | - | No solid |
| 14 | DMF:$H_2O$ | 3 | - | 1 | 2 | - | No solid |
| 15 | DMF:$H_2O$ | 2 | 1 | - | - | 2 | No solid |
| 16 | DMF:$H_2O$ | 3 | - | 1 | - | 2 | No solid |
| 17 | DMA | 2 | - | - | 8 | - | No solid |
| 18 | DMA | 2 | 1 | - | - | - | No solid |
| 19 | DMA | 2 | - | 1 | - | - | No solid |
| 20 | EtOH | 2 | - | - | 8 | - | No solid |
| **21** | EtOH | 2 | 1 | - | - | - | Powder |
| **22** | EtOH | 2 | - | 1 | - | - | Powder |
| 23 | DMF:$H_2O$:TEA | 2 | 1 | - | 8 | - | No solid |
| **24** | DMF:$H_2O$:THF | 2 | 1 | - | 8 | - | Crystal |
| 25 | DMF:$H_2O$:THF:TEA | 2 | 1 | - | 8 | - | No solid |

### Mg-MOF crystals

The method used for crystal **4** yields Mg(Tar)($H_2O$), a rectangular MOF crystal (Figure 2A) with refcode CELJOU (Table 3). The MOF was previously synthesized by a better method in terms of solvent and reaction condition. As opposed to solvothermal synthesis with DMF:$H_2O$ solvent at 120°C (Table 1), the original method uses only water as the medium with warming in silicone oil bath at 60°C for 5 min before being left to sit for 16 hrs. While the original method is the preferred green synthesis route, the method for crystal **4** establishes that the solvothermal synthesis with DMF as its base can act as a universal template capable to synthesize a myriad of MOF crystals. This is also observed by others whereby the decomposition of DMF to its respective formic acid and dimethylamine (base) provides the desired linker deprotonation rate capable of slowly forming high quality crystals of a lot of MOFs [7].

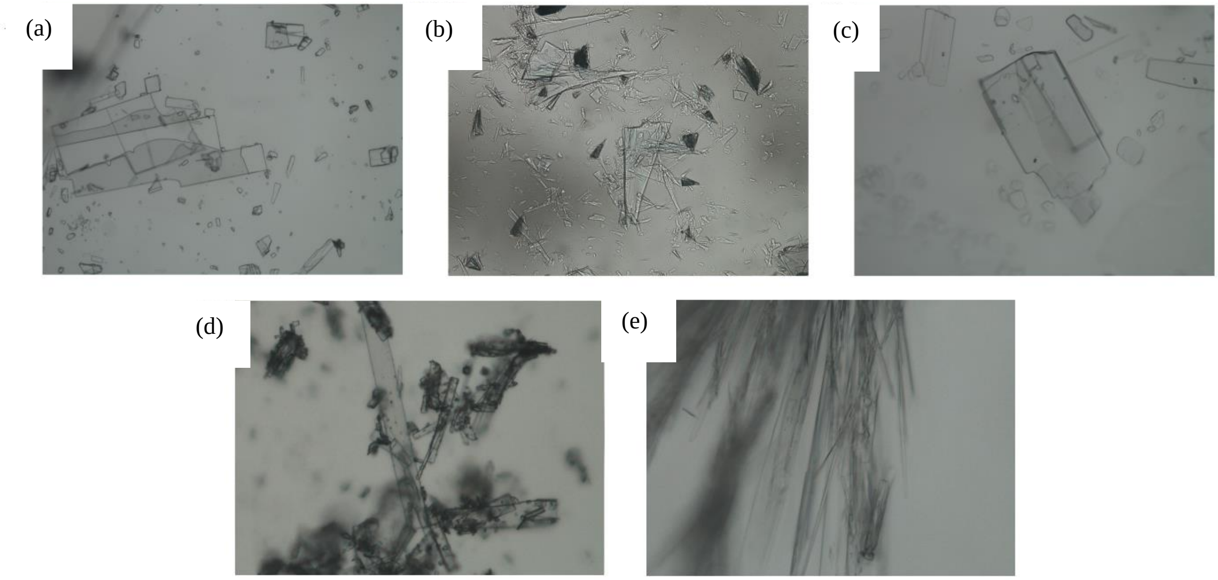


Figure 2. Microscopic view at ×20 magnification for crystals of (a) **4**; (b) **9**; (c) **24**; ×40 magnification for microcrystalline powder of (d) **21**; (e) **22**

The method used for crystal **24** synthesized Mg(Tar)($H_2O$) MOF with refcode JIFXIG (Table 3) having similar morphology (Figure 2B) to crystal **4**. The original reported method uses PTFE lined autoclave at 100°C while the crystal **24** can be obtained in a normal glass vial at 120°C (Table 2). This allows for bulk synthesis to be possible since pressure resistance autoclave synthesis can only be done in small batches. Similar to the method used for crystal **4**, the use of DMF increases the control on the reaction. The deprotonation rate is highly tuneable by controlling the amount of formic acid or dimethylamine by adding them manually before the solvothermal reaction begins.

Table 3. Unit cell parameters of Mg-MOF crystals

| **Crystal** | **CCDC Refcode** | **Space Group** | ***a* / Å** | ***b* / Å** | ***c* / Å** | ***α* / °** | ***β* / °** | ***γ* / °** | **V / Å³** |
|---|---|---|---|---|---|---|---|---|---|
| **4** | CELJOU [8] | $P2_12_12_1$ | 7.904 | 11.119 | 18.213 | 90.0 | 90.0 | 90.0 | 1601 |
| **9** | JIFXIG [9] | $P2_12_12_1$ | 7.878 | 11.100 | 18.157 | 90.0 | 90.0 | 90.0 | 1587 |
| **24** | DOHDOU [10] | $R\bar{3}c$ | 8.148 | 8.148 | 22.788 | 90.0 | 90.0 | 120.0 | 1310 |

The method used for crystal **9** produces plate-like Mg($OOCH)_2$(HOOCH) MOF crystal (Figure 2C) with refcode DOHDOU (Table 3). The solvent used for crystal **9** is an equal mixture of DMF:$H_2O$ (Table 1), while the reported previous method is DMF:EtOH:$H_2O$ with ratio 10:0.5:0.5. This means the amount of DMF has been reduced significantly. Moreover, the previous method requires an addition of 0.1 ml of formic acid. The successful synthesis of crystal **9** shows that enough formic acid can be obtained from the disintegration of DMF at high temperature. In addition, the temperature and reaction vessel needed is also not as demanding. While the previous method is carried out in a Teflon lined autoclave at a temperature of 140°C, crystal **9** can be synthesised in a glass vial at 120°C. It is important to note that for the original method, substituting the metal precursor for other metal salts such as $Mg(ClO_4)\cdot 6H_2O$ gives the same result. Thus, it can be inferred that the same observation is true for crystal **9**.

### Mg-MOF powder

There are two powder MOFs identified by their PXRD in comparison with the simulated pattern from the database. Powder **21** (Figure 2D) is the $Mg_3(BDC)_3(EtOH)_2$ MOF (Figure 3) with refcode KIFKAM [11] incorporating the BDC linker and the solvent EtOH in the framework. The reaction condition of this MOF is the same as the original reported method, except for the solvent. The use of fully EtOH instead of EtOH:$H_2O$ mixture may be the reason for the formation of powder **21**. It has been understood that water is ineffective in synthesizing some MOFs [12], making it a suitable modulator in MOF synthesis. Thus, modulated-solvent mixture is ideal in controlling the crystallization rate [13], resulting in the preferred crystal size compared to the fast, uncontrolled synthesis of the powder. On the other hand, lowering the temperature or reducing the reaction time does not produce any crystals.

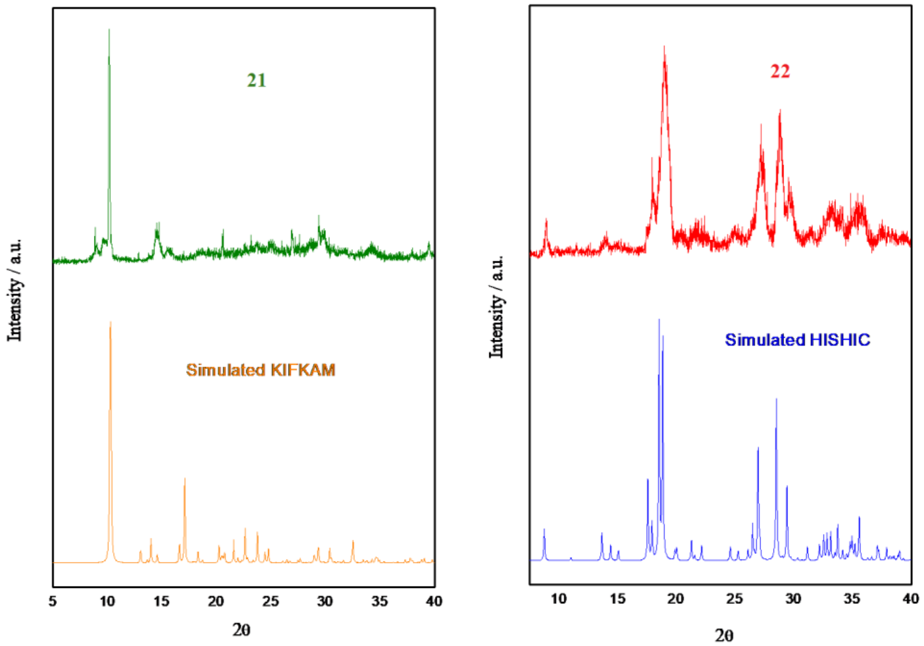


Figure 3. PXRD spectrum of powder **21** and **22** showing high crystallinity of the products. The characteristic peaks of the powder **21** and **22** match with the simulated peaks of an Mg-MOF with refcode KIFKAM and HISHAC respectively

Powder **22** (Figure 2E) is a MOF (Figure 3) with composition $Mg_3(BTC)_2(H_2O)_{12}$ with the refcode HISHIC [14]. The BTC linker and $H_2O$ solvent are incorporated into the framework. Like powder **21**, the original method used the solvent mixture EtOH:$H_2O$ to synthesize the crystals (Table 2). Using only the EtOH produces powder. However, the reaction condition in this case utilises a much lower temperature of 120°C compared to the original optimum temperature of 150°C for the same period of 24 hours. The lowering of the optimum temperature can be used in the bulk synthesis of powder MOF for uses in various applications, where good quality crystals are not necessarily required. For example, the encapsulation of pesticide *cis*-1,3-dichloropropene into a Ca-based MOF-1201 that has been done in its powder form [6].

## Conclusion

In this study, we have explored different approaches in solvothermal synthesis of Mg-MOFs. Characterization from SCXRD and PXRD have been used to identify the synthesized compounds. Improvements have been made to certain aspects of the reaction. Lower temperature, shorter time and less use of organic solvents have been utilised. A solvent system of $H_2O$:DMF shows to be effective in promoting coordination of $Mg^{2+}$ metal ions to the linkers. However, no MOF consisting of both the plant acids and rigid linkers simultaneously were obtained. Understanding the required parameters and conditions for mixed-linker synthesis are crucial. Further studies can be done to investigate the mechanisms of incorporating mixed-linker into s-block frameworks.

## Acknowledgement

The authors gratefully acknowledge the Putra Grant (UPM/700-2/1/GP-IPB/2017/9581000) from Universiti Putra Malaysia (UPM).

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