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Synthesis of Magnesium Dicarboxylate Complex

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Abstrak

Senyawa kompleks magnesium dicarboxylate telah berhasil disintesis dalam berbagai pH di bawah proses hidrotermal atau solvotermal. Terbukti bahwa kondisi sintesis mempengaruhi bentuk senyawa karena proses nukleasi, tetapi tidak berpengaruh pada gugus fungsi senyawa yang disintesis. Senyawa kompleks dikarakterisasi dengan menggunakan spektroskopi resonansi magnetic (NMR), Ionisasi electrospray (ESI-MS), spektroskopi inframerah (FT-IR).

Abstract

The synthesis of magnesium dicarboxylate complex were completed and the coordination chemistry of magnesium dicarboxylate was investigated in the different pH under hydrothermal or solvothermal processes. It was proven that the synthesis conditions affected the shape of the compound due to the nucleation process, but had no effect on the functional groups of the synthesized compounds. Complex compound was characterized by Nuclear Magnetic Resonance (NMR), Electrospray ionization (ESI-MS), and Fourier transform-infrared spectroscopy (FT-IR).

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Introduction

The role of magnesium as a chemical reagent, desulfurization agent, and vital ingredients in fireworks has been investigated. Interaction as a cofactor in biological systems related to proteins makes this element attract the attention of many researchers to develop their applications both in medicine and chemistry (Dudev, *et al.*; 2003, Arijit, *et al.*; 2010]. On the other hand, an understanding of the chemical coordination of magnesium in ligands, for example, oxygen-containing substances such as carboxylic, hydroxyl, and water, is still complicated to explain (Mojumdar, *et al.*; 2001). Naturally, magnesium can bind nucleic acids through water molecules or can directly bind proteins (Sawada, *et al.*; 1993, Black, *et al.*; 1994, Taylor, *et al.*; 1963]. Water molecules play a major role in stabilizing magnesium cations in deep balls, this fact is investigated through ab initio and DFT calculations (Dudev, *et al.*; 1999). They found that the ab initio dielectric and continuum calculations on the model system revealed the importance of the ionization potential of acid ligands in their ability to bind magnesium.

The effect of the carboxylic group bound to metal ions on the acidity of water molecules bound to the same cation has been assessed by Katz and colleagues (Li Hui Jia, *et al.*; 2011). They have shown that the energy needed to deprotonate one of the water molecules bound to magnesium in the $Mg[H_2O]_6^{2+}$ gas phase complex is only about 40% of what is needed to deprotonate isolated water molecules. This fact implies that binding of water molecules with magnesium ions can make the water molecules become active, which impacts on the ease of the deprotonation process.

Among all metalloproteins that naturally occur, which contain Mg(II) appear to be the most numerous and well studied experimentally and theoretically. We have focused on the study of complex crystalline materials from magnesium that are closely related to the understanding of design, synthesis, and material properties. In particular, we have been interested in building a coordination complex to develop an organic-metal framework (MOF) because of the promising prospects offered by open networks to build complexity into molecular gaps where highly fussy and selective chemical transformation can be carried out.

Methods

1. Materials

Anthracene (AR TCI Chemical), Fumaric Acid (AR Fluca Chemie), Maleic Anhydride (AR Fluca Chemie), Magnexium Nitrate Hexahydrate (AR Sigma Aldrich), Dimethyl Formamide (HPLC RCI Labscan), Xylene (AR RCI Labscan), 1,4-Dioxane (HPLC Sigma Aldrich), Sodium Hydroxide (AR RCI Labscan), Sodium Hydrogen Carbonate (AR RCI Labscan), Hydrochloric Acid (AR RCI Labscan), Ethyl Acetate (AR RCI Labscan), DI Water (Siemens Ultra ClearTM TWF EDI, Germany).

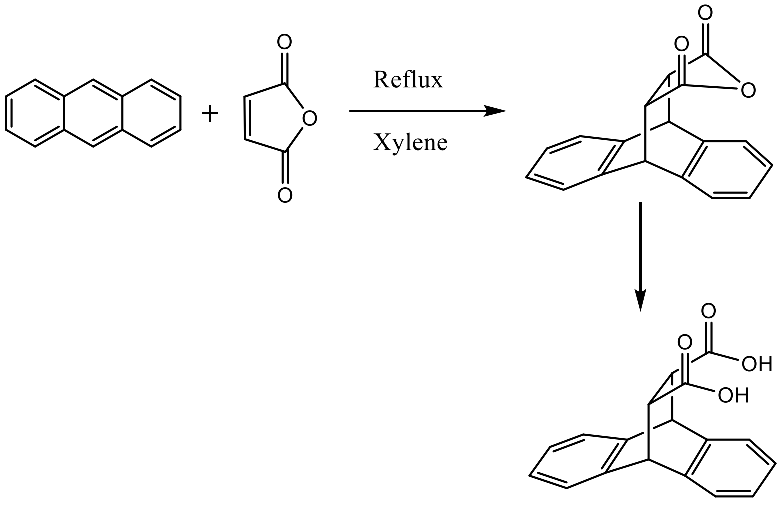
2. Instrumentation

The 1H- and 13C-NMR spectra of cis-adduct and trans-adduct compound in acetone-d_6 were collected on a 400-MHz Bruker Avance NMR Spectrometer. The morphology, structure and elemental analyses of catalysts were utilized by Field-Emission Scanning Electron Microscopy (FE-SEM, Hitachi SU8010) which has SE resolution 1.3 nm and field emission tip as the filament source. The micrographs were taken in various magnifications at electron acceleration voltage of 4.0 kV. By using the same instrument, the analysis by Energy Dispersive X-ray Spectroscopy (EDX) was conducted at electron acceleration voltage of 15 kV. Fourier transform-infrared spectroscopy (FT-IR) was performed using Bruker Hong Kong Limited model ALPHA. Thermo Gravimetric Analysis - Differential Scanning Calorimetry (TGA-DSC) was performed using a TA instruments SDT2960 simultaneous at the heating rate of 20 °C per minute in the range from room temperature to 800 °C under nitrogen gas. Electrospray ionization (ESI) mass spectrometry was carried out using a microTOF and in the positive mode ion. Gas chromatography with mass spectrometry (GC-MS) spectra were obtained by Agilent 7890 (GC) and Agilent 5975 (MS) with an HP-5 capillary column.

3. Procedure

   Synthesis of cis-form and trans-form dicarboxylic acid

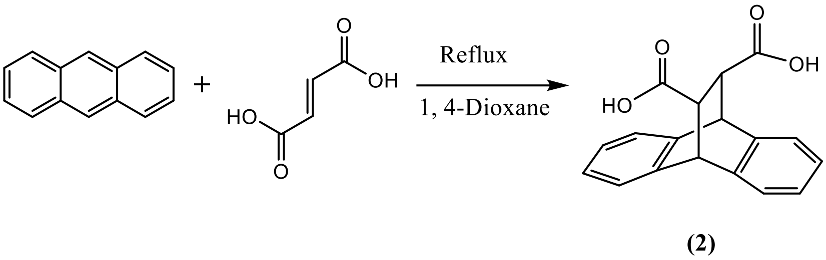
   a. Synthesis of cis-(9,10)-dihydro-(9,10)-ethanoanthracene dicarboxylic acid



(1)

Anthracene (2.00 g, 11.22 mmol) and maleic anhydride (1.09 g, 11.22 mmol) were dissolved in xylene (25 mL) in a 100 mL round-bottom flask, and refluxed at the temperature of 146 °C for 6 hours, whereby the solution turned yellow. The solution was dried in vacuo, yielding a pale yellowish. Powdery solid which was subsequently dissolved in hot base condition after stirring for 24 hours (50 mL, 60 °C), forming a clear yellow solution. The basicity of solution was adjusted by 1 M of NaOH until pH 10. The addition of 1 M of HCl until pH 1. The resulting solution was allowed to cool to room temperature, yielding a white powder of **1**. Solid cis-decca was recrystallized from hot ethyl acetate. Colorless prismatic crystals formed upon cooling the ethyl acetate solution. Yield in 81 % yield, mp = 260 – 263 °C

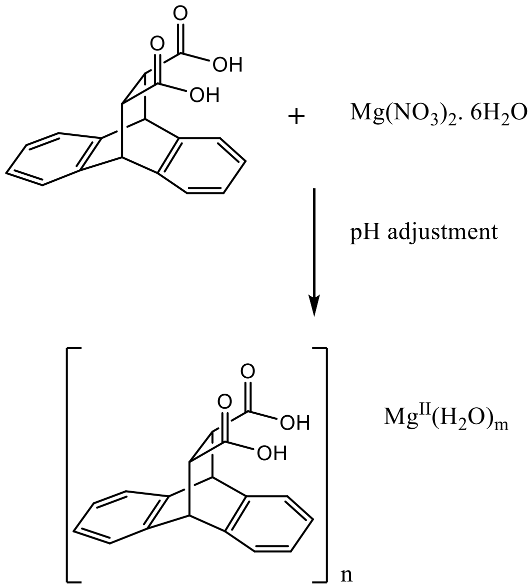
   b. Synthesis of trans-(9,10)-dihydro-(9,10)-ethanoanthracene dicarboxylic acid



(2)

Anthracene (3.00 g, 17 mmol) and fumaric acid (0.645 g, 5.6 mmol) were dissolved in 1, 4-dioxane (25 mL) in a 100 mL round-bottom flask, and refluxed at the temperature of 106 °C for 72 hours, whereby the solution turned light brown. The solution was dried in vacuo, yielding a pale brown. A saturated solution (100 mL) of unsaturated Na_2CO_3 was added, and the mixture was stirred for a day at room temperature. The mixture was filtered (in order to remove the unreacted anthracene), and concentrated HCl was added to the clear solution until pH = 1. The solid product of **2** was recovered by filtration. Yield = 1.62 g (98 %). Mp = 251 – 252 °C.

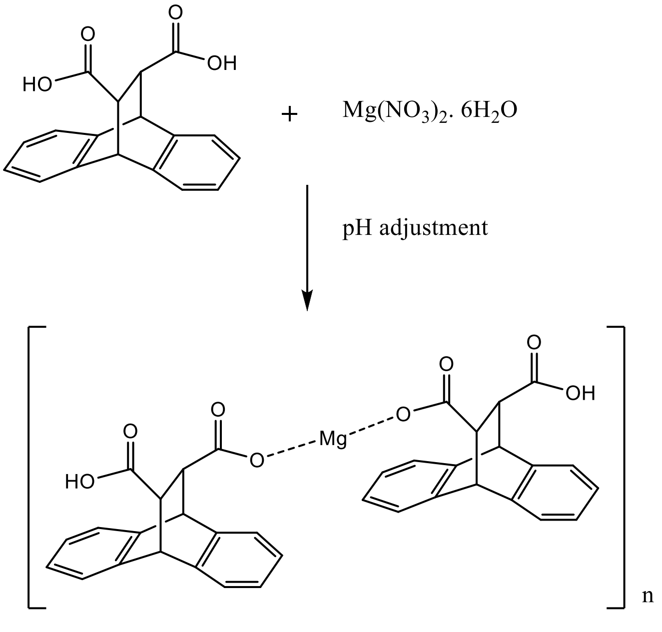
c. Synthesis of cis-magnesium complex



(3)

The synthesis of magnesium dicarboxylate complexes is carrying out in a autoclave reactor under hydrothermal reaction. Cis-adduct (0.5 g, 1 mmol) was added to the distilled water (10 cm^3) and stirred for a while under heating. Then, adjust pH to 7 and 10 by using 20% w/v of NaOH, respectively. $Mg(NO_3)_2.6H_2O$ (0.256 g, 1 mmol) was added to the mixture. Placed the mixture to the Teflon autoclave for 24 hours under air at 180 °C and resulting product **3**.

d. Synthesis of trans-magnesium complex



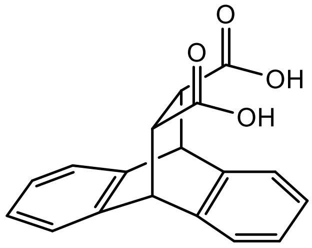
(4)

The synthesis of magnesium dicarboxylate complexes is carrying out in a autoclave reactor under hydrothermal reaction. Trans-adduct (0.5 g, 1 mmol) was added to the distilled water (10 cm^3) and stirred for a while under heating. Then, adjust pH to 7 and 10 by using 20% w/v of NaOH, respectively. $Mg(NO_3)_2.6H_2O$ (0.256 g, 1 mmol) was added to the mixture. Placed the mixture to the Teflon autoclave for 24 hours under air at 180 °C and resulting product **4**.

Results and Discussion

1. Synthesis of cis-(9,10)-dihydro-(9,10)-ethano anthracene dicarboxylic acid (1)

The initial material for the synthesis of metal complexes is cis-(9,10)-dihydro-(9,10)-ethanoanthracene dicarboxylic acid (1). This is prepared with reasonable results from anthracene and maleic anhydride in 1 : 1 for molar rations, in the presence of xylene.



(1)

Figure 1. Chemical structure of cis-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (cis-decca)

The treatment is then followed by reacting with sodium hydroxide. The anhydride obtained in the hydrolyzed addition reaction was easily converted to salt from the appropriate dicarboxylic acid, this free acid was obtained by acid treatment. In a number of cases, it was found that dicarboxylic acids are easily converted to anhydrides; thus, recrystallization of cis-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (cis-decca) from hot ethyl acetate is sufficient to produce acid anhydride.

The ESI-MS data shows the pure cis-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (cis-decca) was obtained after 6 hours reaction under reflux system in 81 % yield, mp = 260 – 263 °C. The purity was confirmed by NMR spectra. ^{1}H NMR (400 MHz, $(CD)_2CO-d_6$ δH : 3.75 (s, 2H) CH, 4.92 (s, 2H) CH, 7.22-7.52 (m, 8H) CH aromatic.

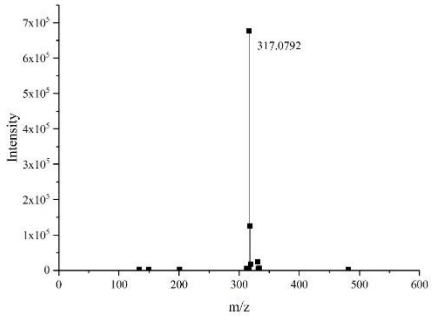


Figure 2. ESI-MS spectra of cis-9,10 dihydroanthracene-9,10-α,β-succinic acid anhydride (cis-decca)

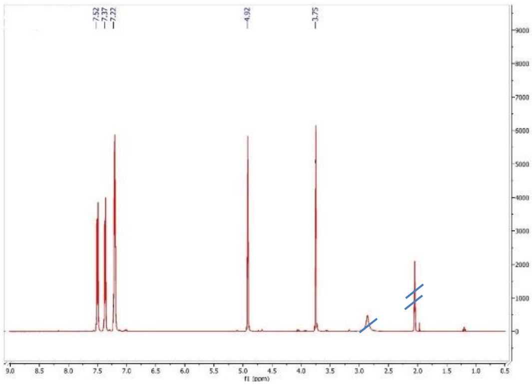


Figure 3. NMR spectra of cis-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (cis-decca).

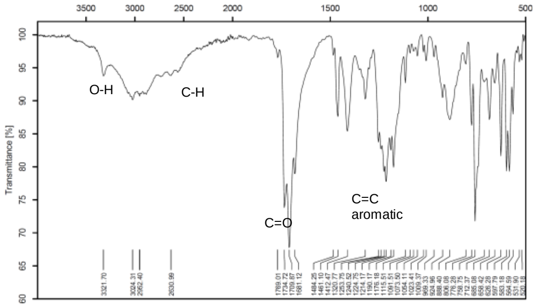
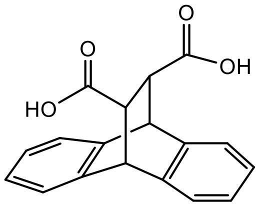


Figure 4. FTIR spectra of cis-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride (cis-decca).

2. Synthesis of trans-(9,10)-dihydro-(9,10)-ethanoanthracene dicarboxylic acid (2)

The Diels-Alder reaction shows real stereochemical selectivity. In the reaction involving the addition of dienophile to diene it will produce additional compounds in the cis position. The relative position of the substituents in dienophils will be maintained in the adduct. As we mentioned in the previous chapter, maleic anhydride reacts with anthracene to produce an addition of cis-anhydride, while fumaric acid produces an adduct of trans-carboxylic acid.



(2)

Figure 5. Chemical structure of trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (trans-deccaH_2)

The high purity of trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (trans-deccaH_2) has been successfully produced after 72 hours in a reflux system with 1,4-dioxane as a solvent in 98 % yield, mp = 251 – 252 °C, confirmed by ESI-MS data. The purity was also confirmed by NMR spectra. 1H NMR (400 MHz, $(CD)_2CO$-d_6 δH: 3.38 (s, 2H) CH, 4.84 (s, 2H) CH, 7.13-7.44 (M, 8H) CH aromatic

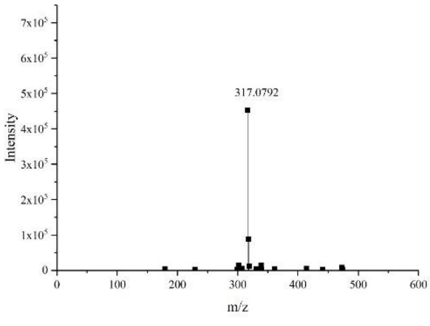


Figure 6. ESI-MS spectra of trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (trans-deccaH_2)

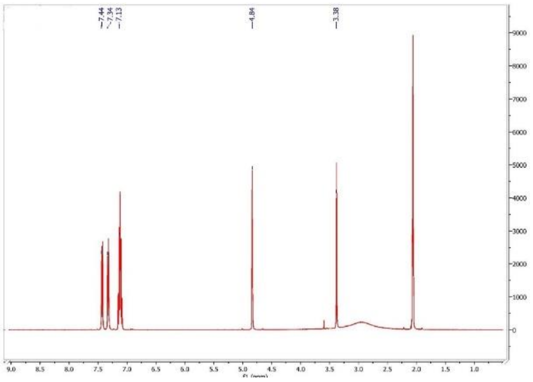


Figure 7. NMR spectra of trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (trans-deccaH$_2$)

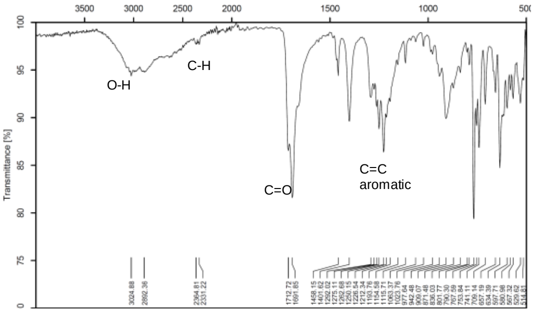


Figure 8. FTIR spectra of trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (trans-deccaH$_2$)

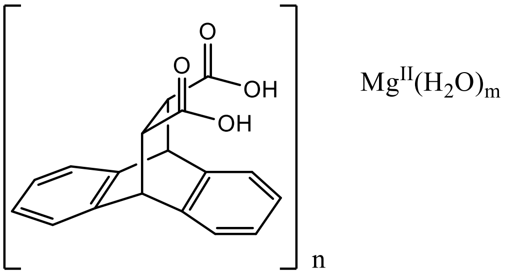
3. pH-dependent structures of magnesium dicarboxylate study under hydrothermal process

The coordination complex with a backbone built from metal ions as a connector and ligand as a link has been studied intensively. Apart from a variety of research-oriented application of metal complex compounds, great attention has also been devoted to their structures which have proven to change widely from simple discrete species to complex supramolecular networks depending on the nature of metal ions, ligand substituents, stoichiometry, and the presence of additional components such as donor or crystallization solvent.

Therefore, investigating a hydrothermal reaction or solvothermal reaction is the first step to synthesizing novel material. In addition, we need to consider crystal-matched reactions and growth when the crystallization process is involved in the synthesis process. We are developing the trend of hydrothermal or solvothermal synthesis towards complex compounds that are in accordance with the liquid nucleation mechanism of hydrothermal or solvothermal processes, different from the mechanism of taming solid-state reactions. This method can facilitate and accelerate the reaction among the reactants, promote hydrolysis, followed by crystal growth resulting in self-assembly of complexes in the solution. Another feature that distinguishes polycarboxylic ligands from aromatic nitrogen-donor ligands is the number of factors that influence the level of protonation and deprotonation. Protonation and deprotonation are not only affected by the ligand's coordination ability but also the charge of the ligand, the metal-to-ligand ratio and, finally, the topology produced.

Various aspects of the structural chemistry of polycarboxylic aromatic ligands are very sensitive to the conditions of synthesis which require systematic thorough study of the effect of each individual factor, such as pH, temperature, and solvent, in coordination mode and the state of protonation of these ligands. This information is very valuable because once conditions for the formation of certain building blocks can be identified, it becomes possible for researchers to expand the structure while maintaining the framework topology by increasing ligand length and in the future can produce compounds with much larger pores.

4. Crystallization of magnesium-cis-9,10-dihydro-(9,10)-ethano-anthracene dicarboxylic acid at pH 7



(3)

Figure 9. Chemical structure of Magnesium-cis-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (trans-deccaH2)

Crystals obtained in the form of irregular fibrous lamellar, and appear in light brown color. Mg(II) cation is attacked to two monoprotonated dicarboxylates for charge balance. This structure mostly stabilized by network of hydrogen bonds and Van der Waals interaction in which Mg(II) cation is bound to six water molecules at the inner coordination and four water molecules at the outer coordination.

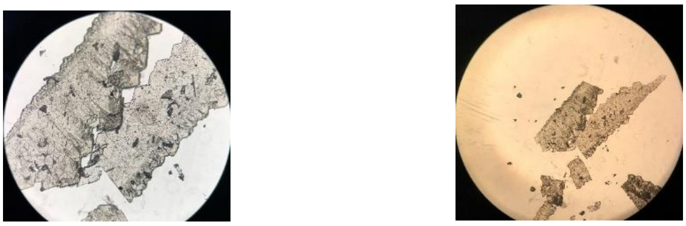


Figure 10. Microscope of magnesium-cis- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7 under hydrothermal.

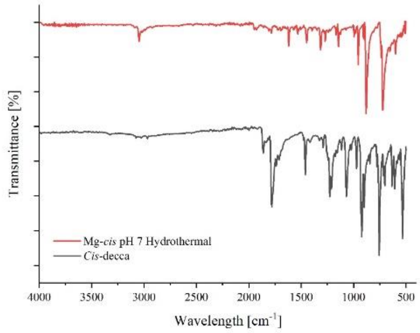
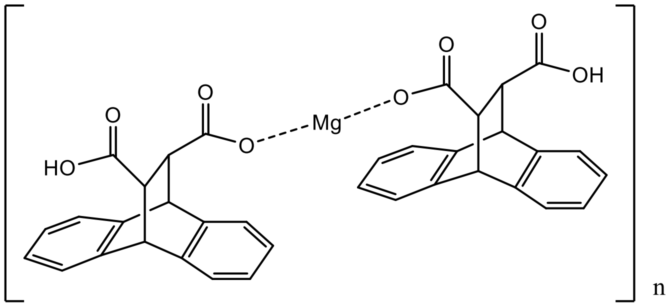


Figure 11. FTIR spectra of magnesium-cis- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7 under hydrothermal

Crystallization of magnesium-cis-9,10-dihydro-(9,10)-ethano-anthracene dicarboxylic acid at pH 10

The result of hydrothermal process in this condition remain in slurry. The nucleation to cis-9,10-dihydroanthracene-9,10-α,β-succinic acid anhydride with magnesium (II) might be incompleted. This shows that at this condition, pH 10, the cis-adduct is not deprotonated and it does not form a complex with magnesium complex. Many factors behind the formation of slurry, instead of crystals. One of them is the temperature gradient that is not enough for the growth of the crystal seed. Furthermore, the isomerization from cis to trans-dicarboxylic acid is probably due to the catalytic activity of magnesium ion in the crystallization step.

5. Crystallization of magnesium-trans-9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7



(4)

Figure 12. Chemical structure of Magnesium-trans-9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylic acid (trans-deccaH$_2$)

The dicarboxylic acid is totally deprotonated as a dianion. The complex between magnesium and the dicarboxylic acid was formed with 1:1 of molar ratio. The crystal structure of trans-magnesium dicarboxylic acid was obtained as coordination polymers. The Mg(II) cation is bound to four water molecules and two carboxylates at the inner sphere and one water molecule at the outer sphere. The coordination binding mode of this complex was found to be the anti-conformation. The crystal structure was stabilized by hydrogen bonds, electrostatic and Van der Waals interactions.

Figure 13. Microscope of magnesium-trans- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7 under hydrothermal

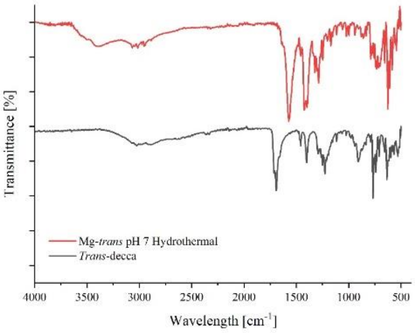


Figure 14. FTIR spectra of magnesium-trans- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7 under hydrothermal

6. Crystallization of magnesium- trans-9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 10

As the pH of the solution increases by 10, the shape of the crystal changes to ordinary cubic morphology with colorless transparent color. Another phenomenon that occurs is a change in the complex magnesium-trans mixture that turns transparent when pH is raised to a higher level. Appearance of turbidity will appear at a certain pH, and run in a transparent direction with increased basicity of the mixture.

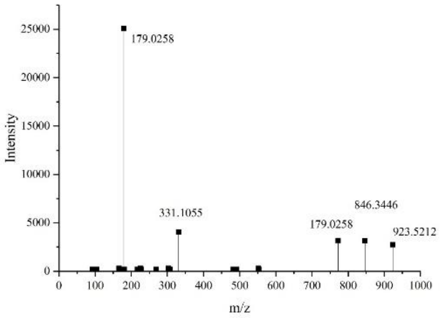


Figure 15. ESI-MS spectra of magnesium-trans- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 10 under hydrothermal

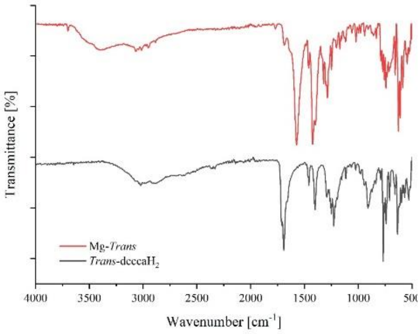


Figure 16. FTIR spectra of magnesium-trans- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 10 under hydrothermal

The FT-IR spectra of Magnesium (II) dicarboxylate with trans-adduct ligands show a strong absorption band occurred in the range 3300 - 3500 cm^{-1} due to the v(O-H) vibrations originating from both lattice and coordinate water molecules. This broad band also indicates the presence of strong hydrogen bonding. The sharp absorption bands at 1573 cm^{-1}, characterize C=O (stretching). The very sharp band observed at 1424 cm^{-1} are attributed to the aromatic C=C (bending).

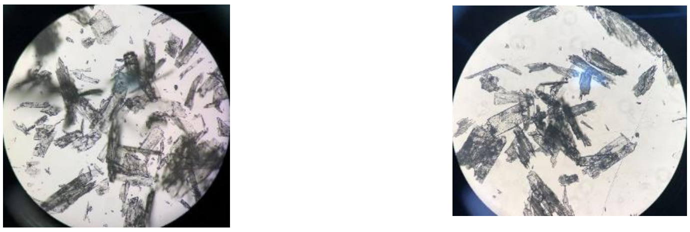


Figure 17. Microscope of magnesium-trans- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 10 under hydrothermal

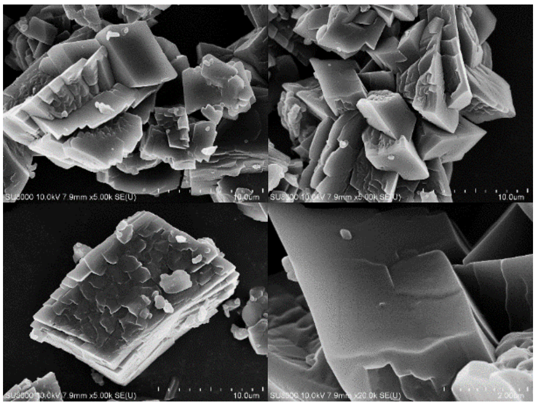


Figure 18. FE-SEM of magnesium-trans- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 10 under hydrothermal

7. Comparison of the structure of magnesium dicarboxylate at pH 7 in varying solvent

In this liquid phase synthesis method, the reaction is carried out at a higher temperature (temperature higher than 100 °C) for several days with the support of closed vessel. Reactants in high boiling polar solvents such as DMF and H2O are taken. The polarity of the solution will also be adjusted in order to dissolve the reactants that play a role and lead to increased crystal growth. The main advantage of this method is that it offers high precursor solubility and the formation of good quality complex crystals that are suitable for structural characterization (Qi Bing, *et al.*; 2015, Debraj, *et al.*; 2014).

There are some generally accepted opinions about the main function of solvents: the deprotonation function in carboxylic acid ligands, the promotion of reactions that are difficult to process in aqueous solutions due to the ability to dissolve the reactants, obtaining better crystalline materials, and in the case of metal-organic framework (MOF) synthesis, it is important to choose solvents that are conducive to forming porous structures in the framework as templates.

Although the causes behind the choice of solvents for each synthesis still leave a question mark, from a number of examples of complex synthesis shows that each solvent system has a role in regulating the formation of different coordination environments. In addition to participating in coordination with metal ions, the solvents used in the assembly process also act as guest molecules in the last lattice structure (Andrey, *et al.;* 2014, Kamran, *et al.*; 2011).

Mostly, solvents cannot be incorporated into complex as-synthesized frameworks, they act as structural directing agents or media for the crystal growth process, which means that the deprotonation rate of organic carboxylic ligands can be managed by selecting suitable solvents such as DMF or by adjusting the environmental basis. These solvents can be converted to corresponding amines at higher temperatures and thus cause deprotonation of carboxylates.

The structures of magnesium-cis-9,10-dihydro-(9,10)-ethano-anthracene dicarboxylic acid have been found to depend on different solvents used in the reaction mixture. Changes in structure may be due to different levels of deprotonation of carboxylic acid ligands under different solvents. According to the data, we found that the dimensions of these two magnesium-based coordination complexes were determined by the relative coordination ability of the solvent with the metal. H_2O is found to have high affinity for coordination with metal centers. DMF solvents have a lower affinity for Mg when compared to H_2O. Templates of various solvents can affect the novel structure generated. This structure has different pore size, shape and connectivity because these solvent guest molecules behave like structural directing agents during the self-assembly process.

8. Comparison of the structure of magnesium dicarboxylate containing maleic-anthracene in cis-adduct in pH 7 under hydro-solvothermal

The complex between magnesium and cis- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid was formed at pH 7. As mentioned before, pH is one of the parameters that plays a profound effect on the structural chemistry of ligands and the process of assembling ligands with metal centers that lead to products with diverse structures.

The key influence in the crystal growth mechanism is believed due to be the presence of the carboxylate, which is likely to act as a mono dentate ligand to form a complex with Mg2+ cations, thereafter controlling the nucleation and growth of the crystal. The ligand coordination to metal atoms, preserving the non-ionized carboxyl group and thus creating conditions for intermolecular hydrogen bonding. Hereafter, the stability of such a complex is expected to decrease as temperature and pressure are increased, coordinating the OH− groups present in the solution to the complex and causing the condensation has happened.

In this work, at first we conduct the reaction under hydrothermal processes at 160 °C for 3 days. The crystal that we got is light brown crystal, and followed by the solvothermal processes with DMF as the solvent at 180 °C for 4 days. Unpredictable, we got the clear brownless hexagonal crystal, confirmed by microscope.

Figure 19. Microscope of magnesium-cis- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7 under hydro-solvothermal.

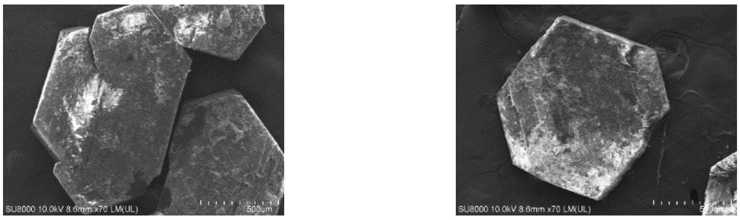


Figure 20. FE-SEM of magnesium-cis- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7 under hydro-solvothermal

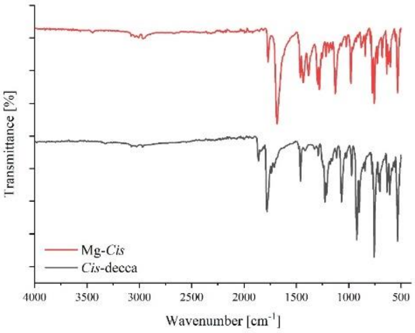


Figure 21. FTIR spectra of magnesium-cis- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7 under hydro-solvothermal

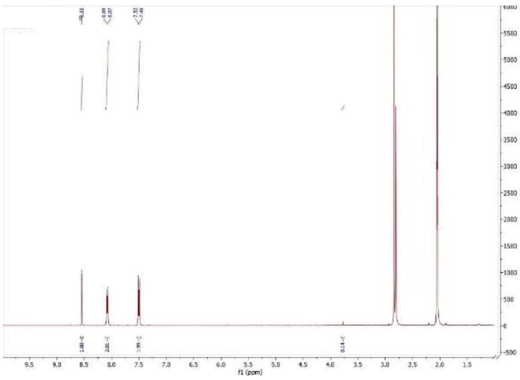


Figure 22. NMR spectra of magnesium-cis- 9,10-dihydroanthracene-9,10-ethanoanthracene-11,12-dicarboxylic acid at pH 7 under hydro-solvothermal

Conclusion

As a result, the method of synthesis of magnesium dicarboxylic compounds, which includes molar ratio, pH, and thermal treatment, by using hydrothermal or solvothermal methods, has shown results in the right direction. This coordination complex compound can be a good start and promises to be a building block as an organic-metal framework.

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Conflict of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

Dudev, T., & Lim, C. (2003). Principles Governing Mg, Ca, and Zn Binding and Selectivity in Proteins. *Chemical Reviews*, 103(3), 773-788. doi:10.1021/ cr020467n

Arijit Mallick, Subhadeep Saha, Pradip Pachfule, Sudip Roy and Rahul Banerjee. Selective CO_2 and H_2 Adsorption in a Chiral Magnesium-Based Metal Organic Framework (Mg-MOF) with open metal sites. *J. Mater. Chem.*, 2010, 20, 9073–9080

C. Mojumdar, S. (2001). Thermoanalytical and IR-Spectral Investigation of Mg(II) Complexes with Heterocyclic Ligands. *Journal of Thermal Analysis and Calorimetry*, 64(2001), 629–636

Rodriguez-Blanco, J. D., Shaw, S., Bots, P., Roncal-Herrero, T., & Benning, L. G. (2012). The Role of pH and Mg on The Stability and Crystallization of Amorphous Calcium Carbonate. *Journal of Alloys and Compounds*, 536, S477-S479. doi:https: //doi.org/10.1016/j.jallcom.2011.11.057

Sawada, K., Kanda, T., Naganuma, Y., & Suzuki, T. (1993). Formation and Protonation of Aminopolyphosphonate Complexes of Alkaline-Earth and Divalent Transition-Metal Ions in Aqueous Solution. *Journal of the Chemical Society, Dalton Transactions*, 1993(17), 2557-2562. doi:10.1039/DT9930002557

Black, C. B., Huang, H. W., & Cowan, J. A. (1994). Biological Coordination Chemistry of Magnesium, Sodium, and Potassium Ions. Protein and Nucleotide Binding Sites. *Coordination Chemistry Reviews*, 135-136, 165-202. doi:https://doi.org/10.1016/0010-8545(94)80068-5

Taylor, A. W., Frazier, A. W., Gurney, E. L., & Smith, J. P. (1963). Solubility Products of Di- and Trimagnesium Phosphates and The Dissociation of Magnesium Phosphate Solutions. *Transactions of the Faraday Society,* 59(0), 1585-1589. doi:10.1039/TF9635901585

Dudev, T., Cowan, J. A., & Lim, C. (1999). Competitive Binding in Magnesium Coordination Chemistry: Water versus Ligands of Biological Interest. *Journal of the American Chemical Society*, 121(33), 7665-7673. doi:10.1021/ja984470t

Li-Hui Jia,†,‡ Ru-Yin Li,§ Zhi-Ming Duan,† Shang-Da Jiang,† Bing-Wu Wang,*,† Zhe-Ming Wang,† and Song Gao. Hydrothermal Synthesis, Structures and Magnetic Studies of Transition Metal Sulfates Containing Hydrazine. *Inorg. Chem*. 2011, 50, 144–154

Qi-Bing Bo, Juan-Juan Pang, Hong-Yan Wang, Chun-Hua Fan, Zhen-Wei Zhang Hydrothermal Synthesis, Characterization And Photoluminescent Properties of The Microporous Metal Organic Frameworks with 1,3-propanediaminetetraacetate Ligand and Its Auxiliary Ligand. *Inorganica Chimica Acta 428* (2015) 170–175

Debraj Saha, Tanmoy Maity and Subratanath Koner. Alkaline Earth Metal-Based Metal–Organic Framework: Hydrothermal Synthesis, X-Ray Structure and Heterogeneously Catalyzed Claisen Schmidt rReaction . *Dalton Trans*., 2014, 43, 13006

Andrey A. Yakovenko,*,†,‡ Zhangwen Wei,† Mario Wriedt,†,§ Jian-Rong Li,∥ Gregory J. Halder,‡ and Hong-Cai Zhou . Study of Guest Molecules in Metal−Organic Frameworks by Powder X-ray Diffraction: Analysis of Difference Envelope Density. *Cryst. Growth Des*. 2014, 14, 5397−5407

Kamran Akhbari a & Ali Morsali . Effect of The Guest Solvent Molecules on Preparation of Different Morphologies of ZnO Nanomaterials from the [Zn_2(1,4-bdc)$_2$(dabco)] Mmetalorganic Framework. *Journal of Coordination Chemistry* Vol. 64, No. 20, 20 October 2011, 3521–3530