

Effect of solvent in the solvothermal synthesis of nickel(II)-terephthalate complex

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Abstract: This research aims to replace the use of dimethylformamide (DMF) with a greener solvent in the solvothermal synthesis of nickel(II)-terephthalate complex. Effect of solvent change on the crystallinity degree, thermal stability, and band gap energy of the synthesized complex are also studied. The synthesis was carried out using solvothermal method at 150 °C for 10 hours with a Ni(II) : terephthalate acid mol ratio of 1:1 in several H₂O:DMF solvent compositions (1:0; 1:1; and 0:1). The precipitated products were characterization using ATR-IR, P-XRD, SEM, TGA, and UV-DRS. Experimental data reveals the formation of the Ni(II)-terephthalate complex from three different solvent compositions (H₂O/DMF = 1:0, 1:1, and 0:1). This result suggests that the complex can be synthesized using more environmentally friendly solvents, potentially reducing or substituting the use of DMF solvent. However, the solvent affects the characteristics of the synthesized complex, in which green block microcrystalline solid was obtained when water solvent was used, meanwhile green aggregates with lower crystallinity degree was yielded when DMF or H₂O-DMF solvents were used. The Ni(II)-terephthalate complexes obtained from the H₂O and H₂O-DMF solvents are different to that of from the DMF solvent, but they both has identical powder diffraction pattern with previously reported [Ni₃(OH)₂(C₈H₄O₄)₂(H₂O)₄].2H₂O compound. Furthermore, the use of water as the solvent increase the crystallinity degree and thermal stability, but lower the band gap energy level of the synthesized Ni(II)-terephthalate complex, compared to that of obtained from the DMF solvents.

Keywords: Green Chemistry, Nickel Complex, Dimethylformamide, Benzenedicarboxylate, Porous Material.

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INTRODUCTION

Indonesia has the highest abundance of nickel in the world, one million tons for nickel production with reserves reaching 21 million tons (US Geological Survey, 2022). Therefore, Indonesia's government pushes the national industry to enhance the nickel processing, including to increase its potency and economical value. Apart from being used as stainless steel material, turbines, and raw materials for electric vehicle batteries [1], an effort can be made to increase the value of this

mineral, which is by converting nickel into functional material, such as coordination polymers for wide range of applications.

Functional coordination polymer can be in the form of metal-organic frameworks (MOF) when the polymeric structure extent into 3D arrays. MOF has open framework with diverse porosity, high crystallinity, and high surface area. In some cases, it has very high thermal stability. Coordination polymers and/or MOF are gaining global interest to be developed as functional materials for gas

adsorption, energy storage, drug delivery, cancer diagnostics, electrochemical sensors, etc. [2], [3].

The use nickel as main ingredient in the functional coordination polymers is also growing, marked by the discovery of many new compounds that have potential applications. The investigated Ni(II)-MOF is a two-dimensional structure formed from Ni(II)-terephthalate through solvothermal synthesis conducted at different temperatures and using various organic or aqueous solvents. The complex has been used as a supercapacitor [4], CO₂ reducing agent [5], electrocatalyst for urea oxidation [6] and oxygen evolution [6], removal contaminants [7], and others.

Meanwhile, terephthalic acid or 1,4-benzene dicarboxylic acid (Figure 1) is being widely used as bridging ligand and commercially available. It is structurally rigid and has good thermal stability. The presence of two carboxylate groups in *para*-position, with benzyl ring in the middle part, makes the ions easily coordinate to the metal ion in several coordination modes (terminal, bridge, and chelate) [8]. Nonetheless, this compound is soluble in organic solvents such as dimethyl sulfoxide (DMSO) or N,N-dimethylformamide (DMF), which is a polar solvent but hazardous to the environment [9]; for example, synthesis of Ni(II)-terephthalate using DMF solvent at 130 °C has been reported by Prananto *et al.*, 2024 [10].

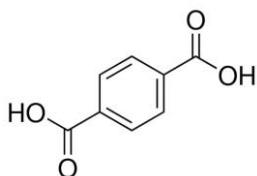


Figure 1. Structure of terephthalic acid (H₂-C₈H₄O₄)

DMF is a polar hydrophilic aprotic solvent. It is frequently used in the solvothermal synthesis of coordination polymers due to its ability to dissolve a wide range of metal salts and organic linkers. However, DMF can coordinate to the metal centre (as terminal ligand) through the oxygen carbonyl group and occupying potential adsorption sites thus may reducing the surface area. Moreover, DMF commonly has a strong odour, particularly due to the presence of dimethylamine impurities, and hazardous for human health and the environment [2], [11].

According to the Chemical Evaluation and Research Institute (CERI) Japan, DMF has dangerous effects on organisms in the environment, such as causing death,

immobilizing, and inhibiting the growth of aquatic organisms. Meanwhile, in humans and animals, DMF can be well absorbed by the skin and can be distributed quickly to various organs, such as the liver, kidneys, brain, and adrenal glands [12].

Therefore, this study aims to produce functional Ni(II)-terephthalate complexes via solvothermal reaction, using greener solvents by adding and/or replacing DMF with water. However, different type of solvent may alter the complex formation equilibrium and thus may resulting in a different product, as in the case of other Ni(II) complex [13]. This paper also presents the effect of solvent on the crystallinity degree, thermal stability, and band gap energy level of the synthesized Ni(II)-terephthalate complex.

MATERIALS AND METHODS

Chemicals and instrumentation

This study used these chemicals as received from Sigma-Aldrich, namely terephthalic acid (H₂-C₈H₄O₄), nickel(II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O), dimethylformamide (C₃H₇NO), demineralized water (H₂O), and ethanol (C₂H₅OH).

Precipitated complexes were characterized using these instrumentations, namely infrared spectroscopy (IR-Spirit T – Shimadzu), powder X-ray diffraction (X'Celerator Scientific – Panalytical), scanning electron microscopy (FEI INSPECT-S50 – Thermo Fisher), differential thermal gravimetry (Simultaneous TG/DTA–DTG 60 – Shimadzu) and ultraviolet-visible diffuse reflectance spectroscopy (SPECORD 200 PLUS).

Synthesis and Characterisation of the Ni(II) Complex

A 2 mmol terephthalic acid was also dissolved with 10 mL DMF. Next, a 2 mmol nickel(II) acetate tetrahydrate was dissolved with 10 mL DMF or H₂O. For H₂O/DMF = 1:0, the terephthalic acid was directly added into the Teflon but the nickel(II) solution was using 20 mL of H₂O. Both solutions were transferred into 50 mL Teflon and placed into an autoclave, tightly closed, and then heated in an oven at 150 °C for 10 hours. After it finished, the oven was cooled down to room temperature (rate = 10 °C/hrs). The solid products in the solution were subsequently separated by filtration using Whatman no. 41 paper, washed multiple times with DMF and ethanol, and then dried at 110 °C for 3 hours.

The dried products were then stored in a desiccator containing silica gel beads.

The dry solid was characterized using: (a) infrared spectroscopy (ATR-IR), at wavelengths of 4000-400 cm^{-1} , (b) powder X-ray Diffraction (p-XRD), at room temperature with 2θ angles of 10-50 $^\circ$ using $\text{Cu K}\alpha_1 =$

1.540598 \AA , (c) scanning electron microscopy (SEM), with a magnification of 5,000 and 20,000x, (d) thermogravimetric analysis (TGA), at 25 – 600 $^\circ\text{C}$ with flow rate of 10 $^\circ\text{C}/\text{minute}$, and (e) Diffusion Reflectance UV-Vis (UV Vis-DRS) at wavelengths of 200-1,100 nm using Tauc plot method.

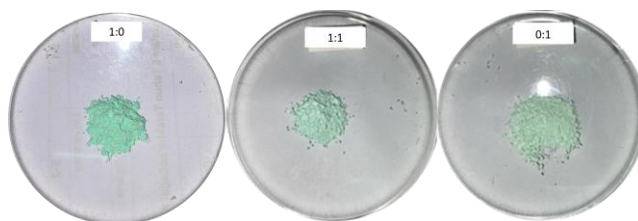


Figure 2. Physical appearance of the Ni(II) complexes ($\text{H}_2\text{O}:\text{DMF} = 1:0; 1:1; \text{ and } 0:1$)

RESULTS AND DISCUSSION

Synthesis of the complex

Three solvothermal reactions were performed and the results are presented in Table 2. The three reactions are differentiated based on solvent composition, namely $\text{H}_2\text{O}:\text{DMF}$ of 1:0, 1:1, and 0:1. All reaction produces green solid with slightly different paleness (Figure 2). Reaction using water solvent produces greener powder than two other reactions. This slight colour difference maybe an indication of different compound or identical compound with different lattice molecules. Moreover, it is observed that the use of pure DMF solvent resulted in much higher yield compared to two other solvents.

Characterization of the complex

The synthesized complexes underwent characterisation using powder-XRD, SEM, and ATR-IR. These three analyses were conducted to confirm whether the synthesized complex was truly Ni(II)-terephthalate complex or not and to identify whether the complexes forms identical compound or not.

Infrared analysis was conducted to identify the functional groups contained in the compounds which were then used as background information on the presence of terephthalate ligand in the complex. Infrared spectra of the complexes and the free ligand as reference are presented in Figure 3.

The typical terephthalate strong absorption bands are observed at wavenumbers around 1600-1400 cm^{-1} , which correspond the symmetric and asymmetric stretch of the carboxylate group. Moreover, the

benzyl ring adsorption was confirmed at around below 1000 cm^{-1} . Infrared spectra of all complexes are similar to that of the free ligand with some shifting observed at around 1750 cm^{-1} to 1650 cm^{-1} due to the coordination bond between the carboxylate group and the nickel(II) centre. This implies the three reactions are producing Ni(II)-terephthalate.

Table 1. Results from each reaction series

$\text{H}_2\text{O}/\text{DMF}$	Solid product	Yield (mg)
1:0	Green powder	195
1:1	Pale green powder	182
0:1	Pale green powder	340

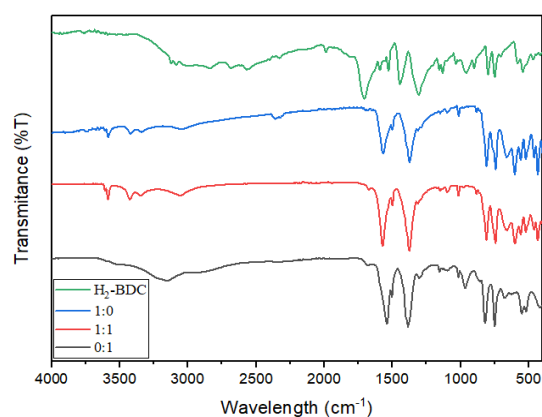


Figure 3. Infrared spectra of terephthalic acid (green spectra) and the synthesized Ni(II)-terephthalate

Infrared spectra of the complex from the H_2O and $\text{H}_2\text{O}:\text{DMF}$ shows similarity with that of Ni(II)-hydroxy-terephthalate complex previously reported by Carton *et al.* (2007). The hydroxy ligand is indicated from the peaks around 3500-3400 cm^{-1} . However, infrared spectra of the complex obtained from DMF

reaction shows some differences with the other two (Figure 3), particularly in the region of 3500-3400, 1000-900, and below 750 cm^{-1} which indicating that there may be different in ligand composition or in ligand coordination motif. Thus, further infrared spectra analysis is also done to predict the coordination motif of the terephthalate ligand.

The distance between asymmetric and symmetric stretch of the carboxylate groups, or delta (Δ), can be used to predict the coordination motif of the ligand to the metal centre. Nakamoto (2009) highlights, with some limitation, that monodentate motif of the carboxylate group is commonly observed when the Δ value of the complex is higher than the Δ value of the corresponding ionic compound. Meanwhile, if the Δ value of the complex is lower than the Δ value of the corresponding ionic compound, then it is predicted that the carboxylate group forms bidentate or chelate motif. In this case, the corresponding ionic compound used is terephthalate ions, with Δ of ~ 130 . Based on the calculation, the carboxylate groups of the complex from the H_2O ($\Delta = 112$) and $\text{H}_2\text{O}:\text{DMF}$ 1:1 ($\Delta = 104$) solvents are predicted to display a bidentate motif, whereas complex from the DMF ($\Delta = 142$) is predicted to form monodentate motif. To support this prediction, powder XRD analyses were done and the data was compared with previously known compound of Ni(II)-terephthalate in the literature [14].

Powder X-rays diffraction analysis was conducted at ambient temperature, and the findings are depicted in Figure 4. The diffraction patterns of samples from the H_2O and $\text{H}_2\text{O}:\text{DMF}$ solvents are nearly identical to each other (only differ in the intensity peaks),

indicating that they both form compound with identical crystal system. However, the diffraction patterns of the complex from the H_2O and the $\text{H}_2\text{O}:\text{DMF}$ solvents are different from those of the DMF solvent. Thus, DMF solvent is likely forms Ni(II)-terephthalate compound with different compositions, coordination motifs, or crystal systems.

When these data were compared to the Cambridge Crystallographic Data Centre (CCDC), powder diffraction pattern of the complexes that obtained from the H_2O and $\text{H}_2\text{O}:\text{DMF}$ solvents is identical to that of $[\text{Ni}_3(\text{OH})_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ complex, with CCDC no. 638866, previously reported by Carton *et al.* (2007), although different synthetic condition was used (72 hrs 150 $^\circ\text{C}$ using Ni(II)-nitrat and disodium terephthalate). This result is also in agreement with the infrared analysis result as discussed above [15].

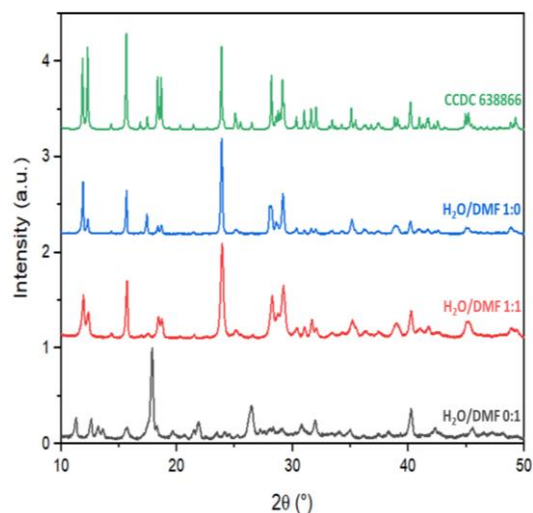


Figure 4. Powder X-ray diffraction patterns of the Ni(II)-terephthalate complexes

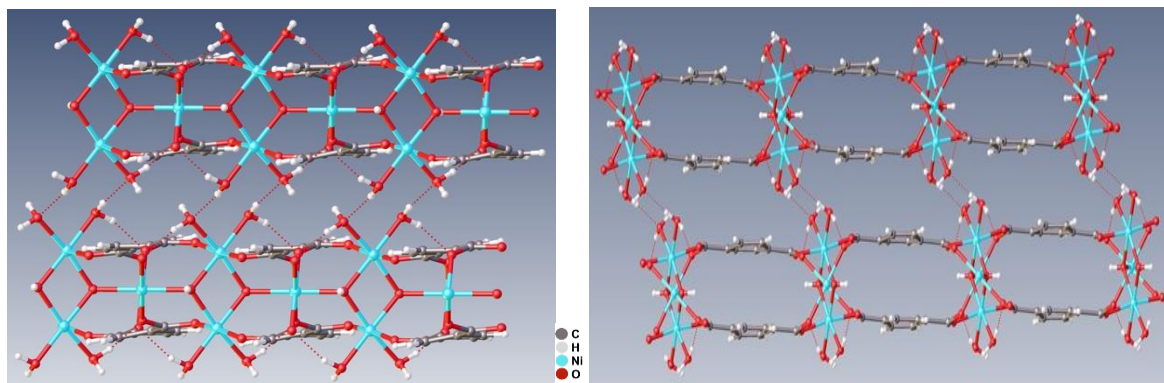


Figure 5. Crystal packing of $[\text{Ni}_3(\text{OH})_2(\text{H}_2\text{O})_4(\text{C}_8\text{H}_4\text{O}_4)_2]_2$, as reported by Carton *et al.* (2007), observed along the a axis (top) and c axis (bottom), with hydrogen bonds represented by red dots

Part of $[\text{Ni}_3(\text{OH})_2(\text{C}_8\text{H}_4\text{O}_4)_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ crystal packing, generated using Olex2 software

(Dolomanov *et al.*, 2009) is shown in Figure 5. Two bridging ligands (hydroxo and dianionic

terephthalate) were observed, in which each hydroxo ligand is bridged to three different nickel centres, whereas each terephthalate ligand is connected to four different nickel centres. The octahedral nickel complex display 2D coordination polymers, which then grew into 3D-hydrogen bonded networks.

SEM was utilised for morphological analysis of the complex, with the findings depicted in Figure 6. Upon 20,000x magnification, complex that precipitated from the water solvent forms block microcrystalline solid. Meanwhile, when the solvent was changed into partly DMF (1:1) or fully DMF (0:1), the morphology of the complex turns into irregular aggregates with smaller particle size. It indicates that the use of greener solvent (water) lead to the formation of bigger and higher level of crystalline solid of Ni(II)-terephthalate complex.

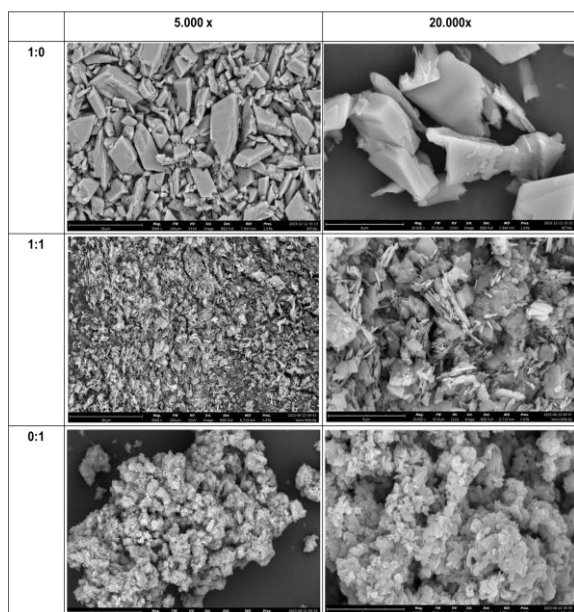


Figure 6. SEM images of Ni(II)-terephthalate complex, obtained from the H₂O-DMF ratios of 1:0 (top), 1:1 (middle), and 0:1 (bottom).

Effect of solvent on the crystallinity degree, thermal stability, and band gap energy level of the synthesized complex

According to the powder XRD data (Figure 4) and through deconvolution analysis, employing water as a solvent resulted in the formation of a complex with increased crystallinity. This result is also in agreement with the morphology assessment by SEM (Figure 6). The degree of crystallinity of the complexes obtained from the H₂O:DMF = 1:0, 1:1, and 0:1 are 85.98%, 78.64%, and 68.90%, respectively. This result suggests that not only

the change of solvent can alter the product composition, but also can increase the crystallinity degree of the product. Water as solvent seems to have a role in the growth rate during the crystallisation process which predicted to happen during the slow cooling of the reaction from 150 °C to room temperature. When pure DMF was used as solvent, this growth rate is much higher and thus resulted in less crystalline complex or even amorphous product.

Thermogravimetric analysis was conducted to study the thermal stability of the synthesized complex, from room temperature to 600°C, and the results are presented in Figure 7. In general, complex obtained from the H₂O solvents shows better thermal stability compared to that of the DMF solvent.

As also observed in the infrared spectroscopy and powder-XRD analyses mentioned above, complex from the DMF solvent shows different thermogravimetric profile than complexes from the two other solvents. From 50 °C, the sample already undergo gradual mass loss of 15% up to around 200 °C, which probably due to the loss of lattice solvent, such as water or DMF, followed by steady decline with only 5% mass loss up to 400 °C. The sample was then decomposed at around 450 °C with the final product expected to be nickel(II) oxide.

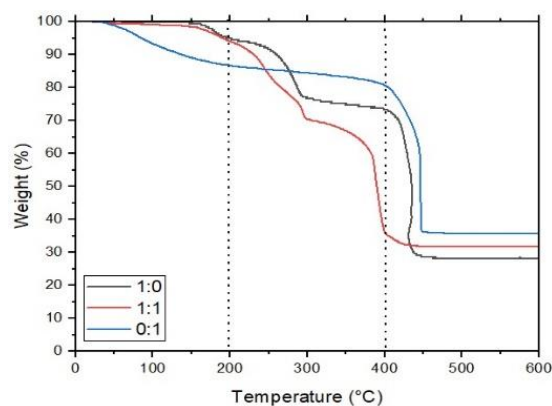


Figure 7. Thermogravimetric graph of the synthesized Ni(II)-terephthalate complexes

Complex from the H₂O solvents show a clear three-stage of decomposition profile, namely 150-200 °C (around 6-7% mass loss) due to the release of lattice water, 250-290 °C (around 20% mass loss) which correspond to the elimination of water and hydroxo ligands, and 400-450 °C (around 48% mass loss) due to decomposition of the complex into nickel(II) oxide. Meanwhile in the complex from the H₂O-DMF (1:1) solvent, the three-

decomposition stage was not as clear as in that of the H₂O-DMF (1:0) complex. Particularly, the decomposition in the last two stages was occurred at lower temperature, which probably due to the bulky sample may be mixed with amorphous complex (Figure 6) that also generated from the DMF solvent.

The band gap energy level of the complexes was determined through UV-Vis Diffuse Reflectance Spectroscopy (DRS) analysis. This analysis involved plotting the photon energy $(\alpha h\nu)^2$, resulting in linear relationships in each domain. Extrapolation of the linear line to the x axis produces the band gap energy (E_g) values, as presented in Figure 8. The band gap energy indicates that the active site of the analysed compound can be activated when irradiated by light with a certain wavelength, thus the compound can be used as photocatalyst when higher energy or a longer irradiation time is given.

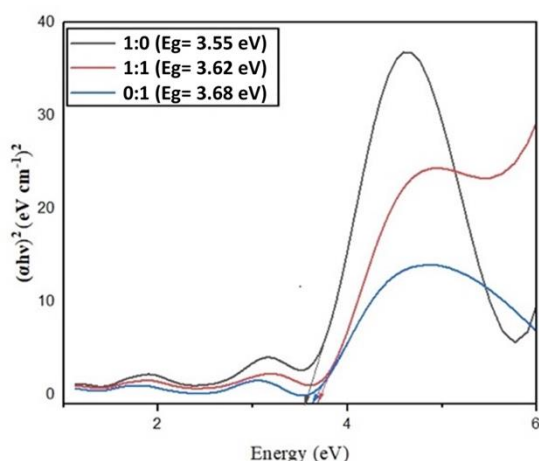


Figure 8. UV-Vis DRS spectra and bandgap energy (top right) of the Ni(II)-terephthalate complexes.

The three synthesized complexes can absorb UV light at a wavelength of 200-350 nm. The band gap energy level of the complex from the pure water solvent is lower and it getting higher with the uses of DMF solvent. Complex from the 1:0 variation produces a band gap energy of 3.55 eV, while the 1:1 produces 3.62 eV, and the 0:1 produces 3.68 eV. These values indicates that the synthesized Ni(II)-terephthalate complex has potential to be used as photocatalyst.

CONCLUSION

The Ni(II)-terephthalate complexes were synthesised using three different solvent compositions (H₂O/DMF = 1:0, 1:1, and 0:1), demonstrating the potential of utilising greener

solvents by minimising or substituting DMF with water. The solvent composition alter the characteristics of the synthesised Ni(II)-terephthalate, in which when water was used as the solvent, block microcrystal solid were produced, whereas when DMF or H₂O/DMF solvents were used, irregular and smaller size of aggregate were obtained. The synthesized complex from H₂O and H₂O/DMF solvents are identical to previously known compound of [Ni₃(OH)₂(C₈H₄O₄)₂(H₂O)₄].2H₂O, but differs to that of from the DMF solvents. The use of water as the solvothermal solvent reduces the band gap energy level, but increase the crystallinity degree and thermal stability of the synthesized Ni(II)-terephthalate complex, compared to complexes that synthesised from the DMF or H₂O/DMF solvents.

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