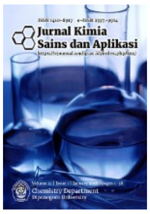
ISSN: 1410-8917
Jurnal Kimia Sains & Aplikasi
e-ISSN: 2597-9914

Jurnal Kimia Sains dan Aplikasi 23 (3) (2020): 75–82

Jurnal Kimia Sains dan Aplikasi
Journal of Scientific and Applied Chemistry

Journal homepage: http://ejournal.undip.ac.id/index.php/ksa



Synthesis of Metal–Curcumin Complex Compounds (M = Na^+, Mg^{2+}, Cu^{2+})

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https://doi.org/10.14710/jksa.23.3.75-82

Article Info

Article history:

Received: 1st December 2019
Revised: 11th March 2020
Accepted: 20th March 2020
Online: 31st March 2020

Keywords:
curcumin; Cu^{2+}–curcumin complex; complex Mg^{2+}–curcumin; Na^+ curcumin complex.

Abstract

Curcumin complex compound, ML_n (L = curcumin; M = Na^+, Mg^{2+}, Cu^{2+}) has been synthesized from the reaction between curcumin and metal precursors (NaCl, $MgSO_4.7H_2O$, $CuCl_2.2H_2O$) in ethanol under reflux conditions. Synthesis takes place through the reaction between the metal ions Na^+, Mg^{2+}, or Cu^{2+} as the central atom and curcumin as the ligand. Curcumin has been consumed after the reaction lasts for four hours, shown by thin-layer chromatography in which a new spot appears at higher Rf as the spot of curcumin disappears in the reaction mixture. Compared with the spectrum of curcumin, the FTIR spectra of the complexes show changes in the absorption bands and shifts of wave numbers particularly in absorption bands of phenolic –OH and C=O enol groups which strongly indicates the coordination of metal ions with the curcumin ligand which is proposed to be in β–1,3 diketone system. Also, the FTIR spectra of the reaction product showed typical absorption bands for the metal-oxygen group, M–O, at 524 cm^{-1}, 670 cm^{-1} and 470 cm^{-1} in Na^+–curcumin, Mg^{2+}–curcumin and Cu^{2+}–curcumin, respectively.

1. Introduction

The search and modification of luminescence-based materials of complex compounds from abundant sources in nature both metals and ligands is still being carried out to provide other alternatives to metal sources that are well known for their properties as electroluminescence materials, but their abundance is small [1]. Phosphorescence materials on the basis of complex compounds of platinum metal group with various ligands such as pyridine derivatives have been developed and used in various applications such as phosphorescence light emitters, as has been reported in various reviews and some examples are referred to in this paper [1, 2, 3, 4, 5, 6, 7]. However, the abundance of platinum is so small on earth that efforts to find and develop sources of metals with greater abundance are increasingly important. Furthermore, the search for potential ligand material that is available in nature [8, 9] and is not toxic is also another point that needs to be addressed by considering the use of environmentally friendly material so that it can enter into the circular economic cycle.

Curcumin (1,7–bis [4–hydroxy–3–methoxy–phenyl] –1,6–heptadiene–3,5–dion) is a compound that has two phenolic groups along with the β–1,3 diketone group which can act as ligands such as acetylacetonato (acac) ligands. Based on its general structure, the 1,3–diketone group in curcumin is capable of forming keto–enol tautomery, so that it can produce stable complex compounds (Figure 1), however, under acidic or neutral conditions, curcumin will be in the keto system while in alkaline conditions will be in the form of enol. Under controlled reduction conditions through an electrochemical approach, the β–1,3 ketone group can be reduced to a COH group that changes the properties of curcumin [10]. The potential of curcumin is well known in the medical and non–medical fields. In the medical field, curcumin is reported to have anti-cancer, anti–Alzheimer's, and antioxidant activity; however, it has limitations in terms of biodispersion or bioavailability. The complexation of curcumin with metals at ligand β–diketone sites has been presented as an innovative and promising approach [11]. The emission properties of curcumin as well as curcumin complexes with various metals such as magnesium, zinc, copper, and manganese have been reported [12], so the development of curcumin–based materials is interesting and promising.

The synthesis of curcumin complex compounds (M = Ni, Mg, Zn, Cu) by exploiting β–1,3 diketone system has been summarized and reported, in various strategies and approaches, including by protecting phenolic groups through modification of – OH group to form either –OR (R = Me, Et, nBu) or –OC(O)Me (–OC(O)OR) [11]. Another approach is to react under alkaline conditions with the β–1,3 diketone system in the form of an enol so that its affinity for metal ions increases [13].

In this paper, we will discuss the synthesis of the curcumin–metal complex (M = Na^+, Mg^{2+}, Cu^{2+}) and characterization using FTIR spectroscopy methods and compared with curcumin spectrum. The reaction of alkali and alkaline earth metal ions with curcumin has been reported and summarized [11], although reports on the complex have only been rarely found. The idea of this research is to make complex compounds from ligands from natural materials with metal ions that are larger in abundances, such as main groups and transition period metals, then investigate the properties and its potential application. We have previously reported the synthesis of chlorophyll–based complexes with metal precursors in methanol and reflux conditions [14].

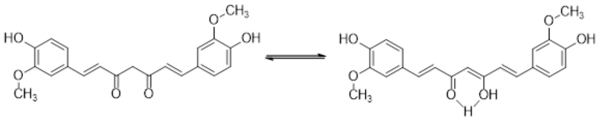

Figure 1. Schematic of the keto-enol group in curcumin taking place in the β–1,3 diketone group [15]

2. Methodology

The methodology is described in the equipment and materials section, followed by the research procedures in the experiments section.

2.1. Equipment and Materials

The materials used in this study were distilled water (H_2O) (Amidis), dichloromethane (CH_2Cl_2) (Merck), ethanol (C_2H_5OH) (Merck), filter paper, curcumin ($C_{21}H_{20}O_6$) (Sigma–Aldrich), methanol (CH_3OH) (Merck), anhydrous magnesium sulfate ($MgSO_4$) (Merck), magnesium sulfate heptahydrate ($MgSO_4.7H_2O$) (Merck), sodium chloride (NaCl) (Merck), thin-layer chromatography (TLC) silica gel 60 F_{254} (Merck), silica gel 60 (230–400 mesh ASTM) (Merck KgaA) and copper (II) chloride dihydrate ($CuCl_2.2H_2O$) (Merck). The instrument used was the FTIR spectrophotometer (Shimadzu) with samples measured in the form of KBr pellets.

2.2. Experiment

The synthesis of the metal–curcumin complex (M = Na^+, Mg^{2+}, Cu^{2+}) was carried out with a metal: curcumin molar ratio of 1: 2 for magnesium (II) and copper (II) metals, whereas for sodium (I) metal, the ratio was 1 : 1. Curcumin was dissolved in ethanol then the solid NaOH was added to the solution. The initial state of the curcumin solution was dark orange. After the addition of the NaOH solid, the color changed to dark red in neutral or basic conditions and was in the form of a keto-enol tautomery (see Figure 1). Furthermore, the metal precursors which had been dissolved in a small amount of ethanol were added into the mixture dropwise while stirring and heated. The mixture was then refluxed in an ethanol solvent for 4 hours. The reaction was followed by thin-layer chromatography (TLC) at 0 minutes, 30 minutes, 1 hour, 2 hours, and 4 hours using dichloromethane/methanol (19: 1) as eluent. The eluent composition is the best in showing the spots of curcumin.

2.2.1. Na^+–curcumin complex

Curcumin (252 mg, 0.684 mmol) was dissolved in 30 mL of ethanol mixed with solid NaOH (27 mg, 0.684 mmol) reacted with sodium chloride (NaCl) (20 mg, 0.342 mmol). After the reflux process, the color changes to a deep dark red, which indicates the initial interaction between the Na metal and the curcumin ligand. The solids of the reaction product were then isolated using column chromatography with 60 silica gel stationary phase (230–400 mesh) and dichloromethane mobile phase. In column chromatography, sample preparation was carried out by impregnating the reaction solids in silica gel (using a dry system). The solid reaction product (214 mg) was dissolved in a small amount of dichloromethane (2 mL) and then mixed with silica gel in the same amount as the sample. After mixing evenly, then the solid was dried at room temperature. The next stage was elution of the sample mixture. The results from the column were then followed by analyzing using TLC. The product was in the dichloromethane phase. Then dichloromethane was evaporated using a rotary evaporator producing a reddish dry solid. The solid Na^+–curcumin complex was stored in a sample bottle and put in a desiccator.

2.2.2. Mg^{2+}–curcumin complex

Curcumin (59 mg, 0.162 mmol) was dissolved in 30 mL ethanol, then mixed with solid NaOH (6 mg, 0.162 mmol), and then reacted with magnesium sulfate heptahydrate ($MgSO_4.7H_2O$) (20 mg, 0.081 mmol). The reaction solution was isolated by the solvent extraction method using a dichloromethane/H_2O solvent. The product was in the dichloromethane phase. The product solution was dried using $MgSO_4$ anhydrous. Then dichloromethane was evaporated using a rotary evaporator with nitrogen gas (N_2) flowing to produce a dry reddish Mg^{2+}–curcumin complex solid amount of 48.5 mg.

2.2.3. Cu^{2+}–curcumin complex

Curcumin (86 mg, 0.234 mmol) was dissolved in 30 mL ethanol mixed with solid NaOH (9 mg, 0.234 mmol), then reacted with the metal precursor $CuCl_2.2H_2O$ (20 mg, 0.117 mmol). The solids of the reaction product were purified through separation using column chromatography using 60 silica gel (230–400 mesh) stationary phase and dichloromethane mobile phase. In separation by column chromatography, silica gel was suspended first with dichloromethane eluent, then put into a column which had been clogged with cotton. The preparation of solid samples from the reaction was carried out with a dry system. The solid (43 mg) was dissolved in a small amount of dichloromethane (1 mL) and added with silica gel as much as the number of samples. The mixture was stirred until the solvent evaporated to obtain a sample mixture in a dry state. The sample mixture was transferred over the surface of the stationary phase in the column. Then a mobile phase was added to the sample until the column was ready for use. The results from the column were followed by analyzing using TLC. The product was in the dichloromethane phase. Then dichloromethane was transferred using a rotary evaporator to produce a brownish-red dry solid.

3. Results and Discussion

3.1. Synthesis of M–curcumin Complex (M = Na^+, Mg^{2+}, Cu^{2+})

The M–curcumin complex was synthesized through the reaction between curcumin and metal precursors in ethanol solvent and reflux conditions (T = 80°C). Metal precursors used are sodium chloride (NaCl), magnesium sulfate heptahydrate ($MgSO_4.7H_2O$), and copper(II) chloride dihydrate ($CuCl_2.2H_2O$). In choosing a solvent suitable for complex synthesis, the properties of the solvent need to be known. Ethanol is a solvent that is capable of solvating and has a donor number (DN) of 18.5 kcal mol^{-1} [16] which is smaller than the coordinated ligand on the metal so that the possibility of the position of the ligand to be replaced by a solvent can be avoided [17]. The use of ethanol as a solvent is also because ethanol is a polar organic solvent that can dissolve curcumin well. Curcumin solubility will increase with decreasing the polarity index of a solvent. Ethanol has a polarity index of 5.2 [17], which is between polar and nonpolar, so curcumin dissolves easily in ethanol. Curcumin can act as a bidentate ligand which has a chelating effect of two O donor atoms in the β–1,3 diketone system so that it can bind to the metal Na^+, Mg^{2+} and Cu^{2+} ions which act as central atoms in the M–curcumin complex (Figure 2).

As in acetylacetone ligand, the β–1,3 diketone system in the structure of curcumin is a potential donor atom (ligand). Also, in the right conditions, it is responsible for coordinating with metal ions. When viewed from its structure, there are three potential positions that can play a role in the formation of complexes, namely the two ring groups containing the methoxy and hydroxyl groups at both ends of the curcumin structure, and the ketone system in the middle. The reaction in neutral or basic conditions causes the ketone system to be in the form of an enol, thereby increasing the potential for coordination in the system rather than on the phenolic ring. The ratio of curcumin moles to metal ions is made 2: 1 to accommodate the formation of complexes with central atomic coordination numbers of four from 2 bidentate ligands. This situation will be very likely to occur in copper (II) metals and may be formed in magnesium (II) ions. Nevertheless, in the sodium metal ion (I), the coordination number of the ion is uncertain. When considering the charge, a curcumin molecule in the form of an enol will likely be countered by a sodium ion, which might form an O–Na–O chelate with a mole ratio of 1: 1 (Figure 2).

The reaction is carried out under neutral conditions to facilitate coordination with the ligand, in this case, the oxygen atom as a donor atom. Furthermore, each metal precursor of NaCl, $MgSO_4.7H_2O$, and $CuCl_2.2H_2O$, which has been dissolved in a small amount of ethanol (1 mL), is added to the curcumin solution drop by drop while stirring and heating. The mixture is then reacted by the reflux method. Reflux is a method of extraction with the aid of heating. The heating process in the reflux method can increase the ability of ethanol solvents to dissolve metals that do not dissolve entirely at room temperature. The principle of the reflux method is that the solvent used evaporates at high temperatures, then cooled by the condenser. The vaporized solvent condenses and drops back into the reaction container so that the amount of the solvent does not change during the reaction.

The steric and electronic effects of curcumin ligands affect the synthesis and stability of the M–curcumin complex, in which case the steric effect can dominate. There are three oxygen atom positions in the curcumin ligand that are likely to coordinate with metals, namely the first and second positions in the aromatic ring at the two ends of the chemical structure chain and the third position in the carbonyl group (C=O) of the aliphatic hydrocarbon chain, and these three positions can chelate coordinate with metals. The existence of steric repulsion in oxygen atoms (ortho position) can reduce the interaction of metal bonds at that position, making it easier for metals to coordinate on the carbonyl group (C=O) with the oxygen atom as the electron donor atom. The interaction between metals and curcumin is thought to occur through bonding with carbonyl groups (C=O), which is one of the chromophores in the electronic transition in the conjugation system of curcumin compounds. Besides, the addition of base NaOH causes O atoms in the –OH (enol) group to be more ionic due to the deprotonation of H atoms so that it can strengthen the assumption that the metal tends to bind to the O atoms in the –OH (enol) group. Figure 2 shows the prediction of the reaction of metal precursors with curcumin.

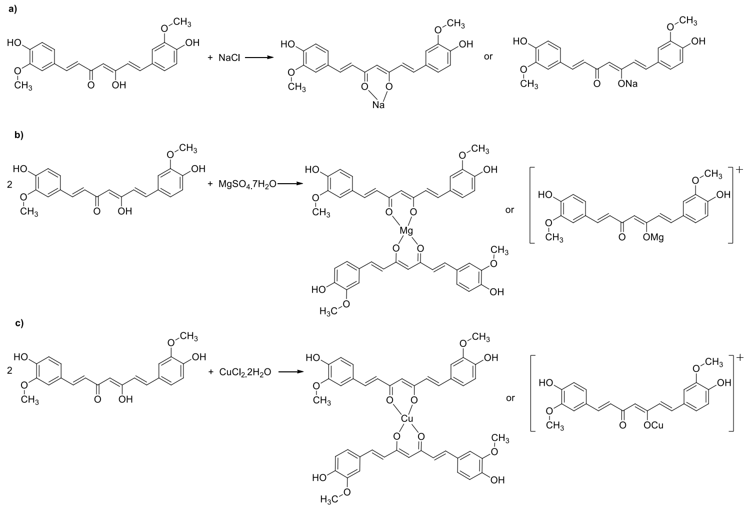

Figure 2. Schematic prediction of the reaction of metal precursors with curcumin

Figure 3. Thin-layer chromatography under a 254 nm UV lamp for (a) curcumin along with an isolated reaction product, (b) Na^+–curcumin; (c) Mg^{2+}–curcumin and (d) Cu^{2+}–curcumin

The reaction of the formation of the M–curcumin complex was followed using thin-layer chromatography (TLC) at 0 minutes, 30 minutes, 1 hour, 2 hours, and 4 hours. Thin-layer chromatography (TLC) is an absorption chromatography in which the stationary phase is a solid substance called an adsorbent (silica gel) and a mobile phase in the form of a developing solvent (eluent). The principle of TLC is that the chemical component moves up to follow a more polar eluent, because the adsorbent absorption (silica gel) of the chemical composition is not the same so that the component moves at different speeds based on its polarity level, causing separation. Before development, the development vessel is saturated with mobile phase vapor first. It is intended that the separation of chemical components can be optimal and to accelerate elution.

The TLC stage is the first step in finding suitable eluents for use in column chromatography separations, in this case, dichloromethane/methanol eluents with a volume ratio of 19: 1. The mobile phase was chosen because of the ability of methanol to increase the dichloromethane polarity so that an eluent system is formed that can separate chemical components well based on the value of the retardation factor (Rf). The stationary phase also determines the Rf value of a component. The stationary phase used in TLC is silica gel 60 F_{254}. Silica gel is a polar compound, and the number 254 is the wavelength of UV light it can absorb. The TLC results were then observed using a UV lamp with a wavelength of 254 nm and calculated the Rf value of each spot. Figure 3 shows the profile of the results of TLC curcumin and the L–curcumin complex, while the Rf value of curcumin and M–curcumin complex is presented in Table 1.

Table 1. Rf values of thin-layer chromatography of curcumin and M–curcumin complex

Eluent	Rf values			
	Curcumin	Na^+–curcumin	Mg^{2+}–curcumin	Cu^{2+}–curcumin
dichloromethane: methanol (19:1)	0.81	0.91	0.86	0.88

TLC analysis can indicate the number of components contained in the curcumin compound and the L–curcumin complex, which can be identified by the appearance of spots. TLC analysis results showed only one spot both in curcumin and in the reaction mixture, also the difference in Rf between curcumin with the L–curcumin complex, where curcumin has a Rf value of 0.81. It has been reported that the value of Rf curcumin using dichloromethane/methanol (19: 1) eluent is 0.8 [18]. The spots of the Na^+–curcumin, Mg^{2+}–curcumin, and Cu^{2+}–curcumin complexes are yellow that appear under UV light 254 nm with Rf values of 0.91, 0.86 and 0.88, respectively, slightly higher than Rf curcumin in the same eluent. This difference in Rf is contributed by the metal content in curcumin, where the alkali metal sodium causes the most apparent shift.

Purification of Na^+–curcumin and Cu^{2+}–curcumin complexes is carried out through a column chromatography method with a stationary phase in the form of silica gel 60 and the mobile phase used for elution is dichloromethane. In the preparation stage of column chromatography, a cotton swab is inserted into the column to prevent silica gel from leaving the column. This causes silica gel to interact well with the solids resulted from the reaction. The developed silica gel is poured into the column. The pouring of silica gel and dichloromethane eluent should be evenly distributed and through the column wall so that it is homogeneous, and the position of the column must be perpendicular so that separation can be optimal. The tap in the column must keep flowing so that the eluate is good and gives the silica gel a chance to absorb the sample.

Sample preparation is carried out by impregnation of the reaction solids (Na^+–curcumin and Cu^{2+}–curcumin complex) using 230–400 mesh silica gel. Then elution is carried out on the sample mixture. The sample is put into a column when the dichloromethane eluent is approaching silica gel. As soon as the sample is inserted into the column, the dichloromethane eluent is evenly fed into the column wall so that the sample does not stick to the column wall. Samples are distributed regularly through the surface of the silica gel. The process that occurs is the absorption of a substance on the surface of other substances. Then, the eluent can carry the sample, which is not absorbed by silica gel and is eluted out of the column. The results from the column give two layers, the upper layer is red, and the lower layer is yellow, which is then followed by TLC, producing three spots for the upper layer and one spot for the lower layer. The curcumin complex is in the dichloromethane solution phase, and the evaporation of the solvent produces the Na^+–curcumin complex in the form of reddish dry solids and the Cu^{2+}–curcumin complex in the form of brownish-red dry solids.

The Mg^{2+}–curcumin complex was isolated through a solvent extraction method using a mixture of solvents with different polarity levels, dichloromethane/H_2O. The result of extraction forms two layers of liquid phase which do not mix. The top layer is the aqueous fraction in red, while the lower layer is the dichloromethane fraction, which is yellow. Washing with a mixture of dichloromethane and H_2O aims to remove residual metal ions Mg^{2+} and curcumin ligands. Curcumin and M–curcumin complex are then characterized using FTIR spectrophotometer to identify the presence of functional groups.

3.2. FTIR spectra of Curcumin and the L–curcumin Complex (M= Na^+, Mg^{2+}, Cu^{2+})

The peaks of functional groups vibration absorption in FTIR spectrum of curcumin are presented in Figure 4 and compiled in Table 2 along with their interpretations, referring to FTIR spectra in theory and experiment reported by Kolev *et al.* [19]. A sharp peak with moderate intensity at 3510 cm^{-1} is a stretching vibration (υ) of the phenolic –OH group whose value is smaller than the phenolic peak, which is generally observed at 3595 cm^{-1}. This is due to the presence of intramolecular and intermolecular hydrogen bonds between the –OH and –OCH_3 groups in curcumin [19]. The –OH (enol) group stretch vibration theoretically appears at 2979 cm^{-1}, but experimentally this peak does not appear, which is in line with what has been reported [19]. However, bending vibrations (δ) of the COH (enol) group appeared at 1373 cm^{-1} and 1230 cm^{-1} according to calculations, and experimental results reported [19]. In the curcumin spectrum analyzed in the form of KBr pellets, a wide absorption band at 3387 cm^{-1} appears. This is consistent with what was reported by Kolev *et al.* [19]. However, this peak does not appear when FTIR curcumin spectra are recorded from a solution of carbon tetrachloride, chloroform, or acetonitrile. The aromatic vibration of the C–H group from curcumin, in theory, appears in the range of 3200–27700 cm^{-1}, whereas the aliphatic C–H at 3097–3000 cm^{-1} [19]. The curcumin spectrum showed absorption bands at 3070 cm^{-1} from aromatic CH stretching vibrations, whereas at 2939 and 2846 cm^{-1} derived from CH stretching vibrations from the methyl group. The carbonyl functional group, C=O keto compound, is expected to appear in the range 1800 – 1650 cm^{-1}, but the curcumin spectrum does not show any absorption in that range, thus indicating that curcumin is in the form of an enol [19, 20]. In the FTIR curcumin spectrum, vibrations of the C=O group are seen in the absorption band at 1627 cm^{-1}. Kolev *et al.* [19] also reported that the absorption band of the C=O stretch vibration only appears when curcumin is in a non–polar CCl_4 solution, which indicates the presence of a 1,3-diketone in the system. However, this was not observed in either solids or solutions with chloroform and acetonitrile solvents. The FTIR curcumin spectrum also showed absorption bands at 1373 and 1230 cm^{-1}, both of which originated from in-phase bending vibrations (δ) of the COH enol group. This observation is following the results of calculations and experiments that have been reported [19].

Table 2. Interpretations of FTIR spectra of curcumin

ν (cm^{-1})	Peak shape	Intensity	Functional groups
3510	sharp	medium	phenol -OH
3070	sharp	very weak	aromatic C-H
2939	sharp	very weak	aliphatic C-H
2846			
1627	sharp	strong	C=O (enol)
1512	sharp	strong	aliphatic C=C
1589	sharp	medium	aromatic C=C
1458			
1427			
1373	sharp	medium	bending COH (enol) (δ)
1234		weak	
1280	sharp	strong	bending C=CH (δ)
1157	sharp	strong	bending CCH (δ)
1026			
964	sharp	strong	in-phase aromatic bending -C=CH- (δ)
817	sharp	strong	out of phase aromatic bending -C=CH- (γ)
725			

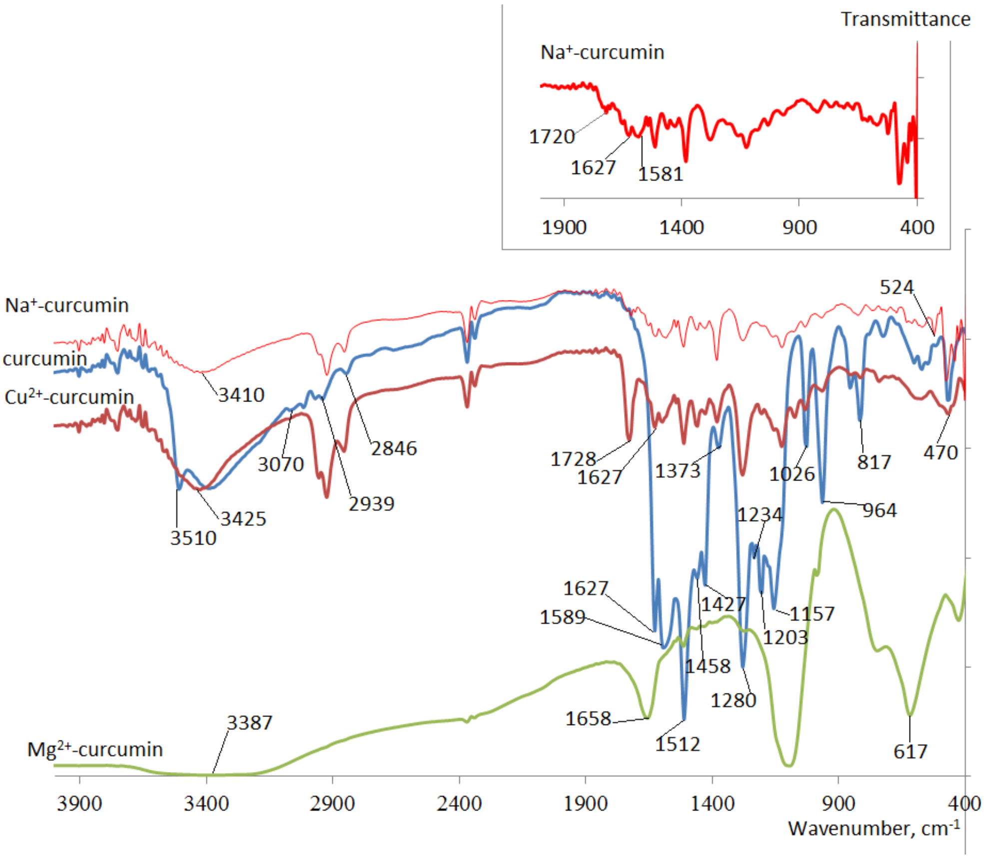

Figure 4. FTIR spectra of curcumin; Na$^+$–curcumin; Cu^{2+}–curcumin, and Mg^{2+}–curcumin. Pieces of Na$^+$–curcumin spectra were added separately to make them clearer.

The curcumin complex spectrum, as shown in Figure 4, shows the changes in the vibrational absorption wavenumbers, peak shape, and peak intensity, compared to the curcumin spectra. The stretching vibration absorption band of the phenolic -OH group becomes wide and shifts to smaller wavenumbers, becoming 3410 cm^{-1} in Na$^+$–curcumin, 3387 cm^{-1} in Mg^{2+}-curcumin, and 3425 cm^{-1} in Cu^{2+}-curcumin. This phenomenon has been discussed in theory, and it was reported that the shape of the phenolic -OH stretch band in compounds containing enol groups in the β-diketone system depends on intramolecular and intermolecular hydrogen bonds, where the stronger the bond, the band shape becomes wider and the intensity decreases [21]. The –OH stretching vibration absorption band observed in curcumin complex spectra might demonstrate that curcumin complexation increases the strength of the intra- and intermolecular hydrogen bonds between the -OH and -OCH$_3$ groups in curcumin. The same observation has also been reported in the Zn-curcumin complex [20]. The vibration absorption band of C-H groups, both aromatic and aliphatic, remains the same as curcumin, but the bending vibration absorption band of -COH (enol) at 1234 cm^{-1} is not visible or is very weak in the curcumin complex spectra.

The C=O enol stretching vibration absorption band also changes, wherein the Cu^{2+}–curcumin complex, a sharp and strong absorption peak appears at 1728 cm^{-1}, which is the C=O uptake of a strong ketone which strongly suspects a strong curcumin complexation at β– 1,3 diketone system. The new absorption band at 1720 cm^{-1}, which is thought to originate from the C=O stretching vibration, was also seen in the Na$^+$–curcumin complex spectra but was weak, whereas in the Mg^{2+}–curcumin complex there was a shift in the absorption band towards greater that is 1658 cm^{-1}. The suggestion that the metal coordination in the β-1,3 diketone system based on shifting the C=O stretching vibration band towards the higher direction was also reported by Moussawi and Patra [20] in the synthesis of the Zn-curcumin complex. Finally, the FTIR spectra of the curcumin-metal complexes show the vibration absorption band of the metal group, M–O, 524 cm^{-1} in Na$^+$-curcumin, 670 cm^{-1} in Mg^{2+}-curcumin and 470 cm^{-1} in Cu^{2+}-curcumin. The difference in wavenumbers is seen between the sodium and magnesium metal complexes with the copper metal, which may be related to the properties of the main metal versus the transition metal. Alkali metal compounds, alkaline earth in this complex, may also play a tendency to bond ionically to produce a more substantial M–O bond with a higher wavenumber than Cu–O. In comparison, M-O vibrations have been reported in the metal-curcumin derivative complex, i.e., at 466, 469, 484, and 463 cm^{-1}, in Mg-O, Zn-O, Cu-O, and Mn-O, respectively [12].

4. Conclusion

The curcumin complex with metals (M= Na$^+$, Mg^{2+}, Cu^{2+}) is strongly suspected of having been successfully synthesized from the reaction between curcumin and related metal precursors in ethanol under reflux conditions. This is confirmed by FTIR spectra where vibrational changes occur mainly in the phenolic -OH group and C=O enol group compared to the curcumin spectrum and the appearance of M-O vibrations in the complex spectra. However, the characterization of complex compounds using other instruments such as elemental analysis, mass spectroscopy, and proton and carbon NMR with various techniques that can ensure the reaction product is still needed.

Acknowledgment

Peni expressed her gratitude to the Director-General of Higher Education Learning and Student Affairs, who sponsored a portion of this research through the 2018 Research Student Creativity Program.

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