

Novel Metal Coordination Complexes Based on 4-Aminophenol: Spectroscopic Analysis and Antibacterial Test

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Abstract: The aims of this research are to synthesize and determine the formula, characteristics, and complex structure of Cu(II) and Co(II) with 4-aminophenol and to investigate their antibacterial activity. The complexes were synthesized by refluxing a solution of CuSO₄·5H₂O and CoSO₄·7H₂O, respectively, with 4-aminophenol in methanol for 1 h. The products were characterized using UV-Vis spectroscopy, atomic absorption spectroscopy, thermal analysis, conductivity, FTIR, and magnetic moment. The formation of the complex was indicated by shifting of maximum wavelength of the metal solution toward shorter, i.e., 817 to 421 nm for Cu(II) and 566 to 450 nm for Co(II). From the characterization, the proposed formulas of the complexes are [Cu(4-aminophenol)₄]SO₄ and [Co(4-aminophenol)₄(H₂O)₂]SO₄·5H₂O forming square planar and octahedral geometry, respectively. Both complexes are paramagnetic with negligible antibacterial activity against Staphylococcus aureus, Staphylococcus epidermidis, Escherichia coli, and Pseudomonas aeruginosa.

Keywords: cobalt; copper; complex; 4-aminophenol

■ INTRODUCTION

4-Aminophenol is a derivative of phenol with an amine group in the para position, which is commonly used as antipyretics, analgesic drugs, and synthetic materials in various fields such as petroleum, photography as a redox reagent, rubber, developer, chemical inhibitor, and others [1]. The 4-aminophenol is a strong analgesic and weak anti-inflammatory compound which is very toxic. Reducing toxicity and increasing the activity of the compound is ably done by modifying the molecule as well as forming metal complexes. The 4-aminophenol can be used as ligands because it has amine (NH₂) and hydroxy (OH) groups that can act as electron donors to bond with metals.

Metal complexes are compounds consisting of a central metal ion with a ligand donating its lone pair of electrons to the central metal ion [2]. The central metal ion is surrounded by two or more molecules or ions, called ligands, that form a coordinating covalent bond with the central metal ion. Metal complexes have attracted attention in various applications in inorganic chemistry and have been used in the field of pharmacy, biology, medicine, clinics, industry, and others [3-4]. In addition, transition metal complexes and ligands as active drugs have been widely studied due to the possibility that complex compounds may have different pharmacological activities [5]. In designing effective complex compounds, the choice of metal ion structure and ligand is an important factor [6]. Transition metal

complexes of Cu, Co, Ni, Zn, and Ag with ligands are usually used for pharmaceutical applications as antibacterial, anticancer, and antioxidant [7-8]. Copper is widely used in the synthesis of complex compounds because it is proven to have high antibacterial power and low toxicity, so Cu(II) ions are used as an antibacterial substitute for silver [9]. Another transition metal that has been widely used is Co(II). In the complex compound prepared by Mishra et al. [10], the N and O groups of the ligands bind to metal ions Co(II), Cu(II), Ni(II), Zn(II), and Cd(II). Herrera et al. [11] synthesized a complex of Co(II), Ni(II), and Cr(III) with 2-thiozoline-2-thiol and showed better antibacterial activity. Al-Zaidi et al. [12] synthesized Co(II) with 1-(4-(4(diethylamino)-2-hydroxybenzylidene)amino)phenyl)ethanone oxime ligand and the results showed improved antibacterial properties compared to the ligand and its complex ion. Prajapati et al. [13] synthesized Co(II) with 2-[(E)-(2-hydroxybenzylidene)amino]benzoic acid and showed good antibacterial activity.

Based on the explanation above, 4-aminophenol has the potential to be ligands coordinating with Cu(II) and Co(II). Based on our knowledge, both complexes with identical structure never been synthesized before. Herein, the $[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4\cdot\text{H}_2\text{O}$ and $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4\cdot 5\text{H}_2\text{O}$ complexes have been successfully synthesized and characterized. The complexes were also tested for antibacterial activity against *Staphylococcus aureus*, *Staphylococcus epidermis*, *Escherichia coli*, and *Pseudomonas aeruginosa*.

■ EXPERIMENTAL SECTION

Materials

The $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 7\text{H}_2\text{O}$, $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$, 4-aminophenol, and solvent (methanol, DMF, and DMSO) are purchased from Merck. All chemicals were used without treatment.

Instrumentation

The molar absorptivity and electronic transition of both complexes' solutions were estimated using a double-beam UV-Vis spectroscopy (Shimadzu PC 1601). The complex formula was estimated by measuring the metal

content of the complex using an Atomic Absorption Spectrophotometer (AAS, Shimadzu AA-665). The presence or absence of water molecules in the complexes was determined using Thermal Gravimetry Analysis/Differential Scanning Calorimetry instrument (TG/DSC, Shimadzu 50) with a heating rate of 10 °C/min. Electrical conductivity of the Cu(II) and Co(II) complexes and some known metal salts solution in DMF and DMSO, respectively, at 25 °C using a conductivity meter (Jenway CE 4071). Infrared spectra of 4-aminophenol and the complexes were measured as KBr pellets in the frequency range of 4000–450 cm^{-1} using Fourier-transform infrared spectrophotometer (FTIR, Prestige-21 Shimadzu). The magnetic properties of the powder Cu(II) and Co(II) complexes can be determined moment with Magnetic Susceptibility Balance (MSB, Auto Sherwood Scientific 10169) and corrected using Pascal's constant.

Procedure

Synthesis of Co(II) complex

The Co(II) complex was synthesized by dissolving the 4-aminophenol (0.436 g) in 10 mL methanol. The metal $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ (0.281 g) was also dissolved in 10 mL methanol. The ligand solution was heated and stirred with a magnetic stirrer and then added dropwise into the metal solution was put into the ligand. The solution was refluxed for 1 h at 60 °C. The solution is then concentrated until it reaches half of the initial volume. The solution is allowed to stand (crystallize) until a precipitate is formed. The precipitate formed was washed with acetone and dried under a vacuum.

Synthesis of Cu(II) complex

The Cu(II)-4-aminophenol complex was synthesized in a ratio of 1:4 by dissolving $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (0.249 g, 0.1 mmol) in 10 mL and 4-aminophenol (0.436 g, 0.4 mmol) in 10 mL methanol. The 4-aminophenol ligand solution was heated on a hot plate while stirring using a magnetic stirrer then a $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ metal solution was added dropwise into the 4-aminophenol ligand solution. The mixed solution was then refluxed for 1 h at 67 °C. The resulting solution was evaporated and concentrated until a precipitate was

formed. Then the precipitate was filtered using filter paper and then dried.

Antibacterial test

Antibacterial activity of Cu(II), Co(II), 4-aminophenol, Cu(II)-4-aminophenol, and Co(II)-4-aminophenol complex against *S. aureus* ATCC 25923, *S. epidermis* ATCC 12228, *E. coli* ATCC 25922, and *P. aeruginosa* ATCC 27853 was tested using paper disc diffusion method. The inhibition of bacteria was shown as the diameter of the clear zone in the test samples. The three test samples, namely metal $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, ligand 4-aminophenol, Cu(II)-4-aminophenol complex were made with various concentrations (ppm): 125, 250, 500, and 1000. Positive controls used were commercial antibiotics vancomycin, chloramphenicol, and meropenem 30 $\mu\text{g}/\text{disk}$ and the negative control used was DMSO (the solvent).

RESULTS AND DISCUSSION

Indication of the Formation of Metal Complexes

The change in color from brass (4-aminophenol ligand solution in methanol) to blackish brown color (complex solution in methanol) indicated the formation of the cobalt complex. The shift in the absorption of the maximum wavelength of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (566 nm) towards a smaller wavelength (450 nm) can be seen in Fig. 1. The shift of the maximum wavelength indicates the formation of complexes between Co(II) and 4-aminophenol ligands. Water molecules as coordinated ligands on Co(II) being replaced by 4-aminophenol. Similarly, Co(II)-nicotinamide complex that was synthesized by Rahardjo et al. [14] also experienced a shift towards a lower wavelength from 512 nm (cobalt salt solution) to 506 nm (complex solution).

Meanwhile, the formation of the copper complex was indicated by a color change from brown (4-aminophenol solution) to black solution. The synthesis product was black precipitates (0.396 g; 64.39%). Fig. 2 shows a shift in the maximum wavelength absorption (λ_{max}) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (817 nm) towards a lower wavelength in the Cu(II)-4-aminophenol complex (421 nm). The shift in wavelength indicates the formation of Cu(II)-4-aminophenol complex. It also proves that 4-aminophenol

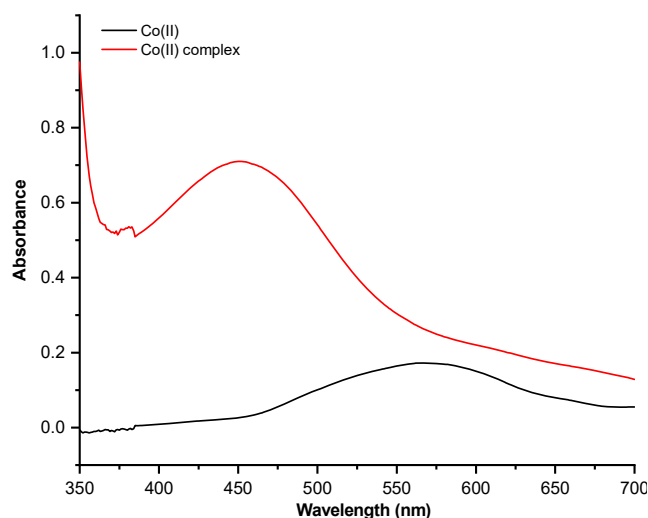


Fig 1. UV-vis spectra of Co(II) and its complex in methanol

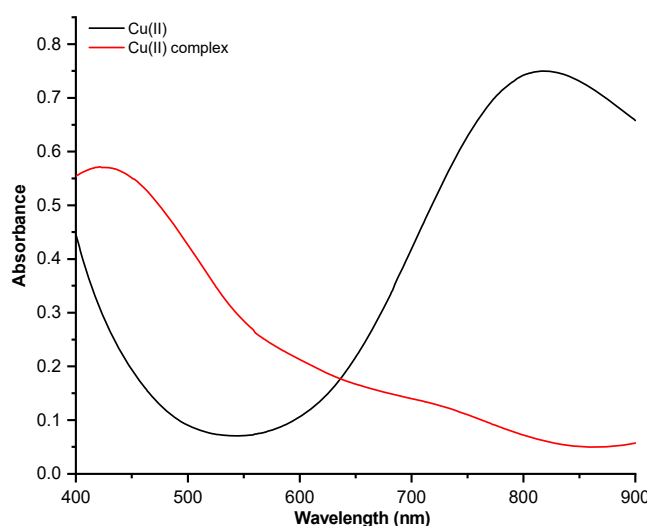


Fig 2. UV-vis spectra of Cu(II) and its complex in methanol

has a stronger ligand field energy than H_2O so that it is able to substitute H_2O positions. Other syntheses of copper complexes also experienced a maximum wavelength shift, as in the $\text{Na}_2[\text{Cu}((E)\text{-}2\text{-}(2\text{-hydroxy-}3\text{-methoxybenzylimidazolium) acetic acid})_2]$ complex a shift occurred from 700 nm to 380 nm [15] and the $\text{Cu}(\text{Indal-4-aminoantipyrine})\text{Cl}_2$ from 850 nm to 380 nm [16].

Atomic Absorption Spectrophotometer (AAS)

The results of the measurement of copper and cobalt content experimentally with AAS in Cu(II)-4-

aminophenol were $10.59 \pm 0.22\%$ and $8.62 \pm 0.20\%$, respectively (Table 1). The results of the measurement of copper and cobalt content are compared with theoretical Cu levels in various possible complex formulas as shown in Table 1, it can be estimated that the complex compound formula Cu(II)-(4-aminophenol) is Cu(4-aminophenol)₄SO₄(H₂O)_n (n = 0, 1, or 2) and Co(4-aminophenol)₄SO₄(H₂O)_n (n = 5, 6, or 7).

Thermal Analysis

The thermogram of the Cu(II)-4-aminophenol complex in Fig. 3 shows the occurrence of a mass shift of the complex as much as 3.12% at a temperature of 30–155 °C equivalent to the release of one H₂O molecule (theoretical calculation: 2.93%). Therefore, the empirical formula of Cu(II) complex is Cu(4-aminophenol)₄(SO₄)(H₂O). For Co(II) complex, the thermogram shows a twofold decrease in mass (Fig. 4). The first decrease occurred at a temperature of 40–135 °C and the second decrease occurred at a temperature of 135–185 °C. At a temperature of 40–135 °C there is a decrease in mass of 13.90% which is equivalent to five H₂O molecules (theoretical calculation: 13.205%). The second decrease was reduced by 6.06% equivalent to the release of two H₂O molecules (theoretical calculation: 5.74%). According to Himawati et al. [17], the decrease at a temperature of 30–130 °C water molecules as crystal water, not as a ligand, whereas according to Prajapti et al. [13], reducing mass at a temperature of 150–250 °C is water coordinated with metals. The empirical formula of cobalt complex with 4-aminophenol is Co(4-aminophenol)₄(SO₄)(H₂O)₇.

Molar Conductivity

The molar conductivity of the standard solution in Table 2 shows that the more ions produced in the solution, the greater the value of molar conductivity.

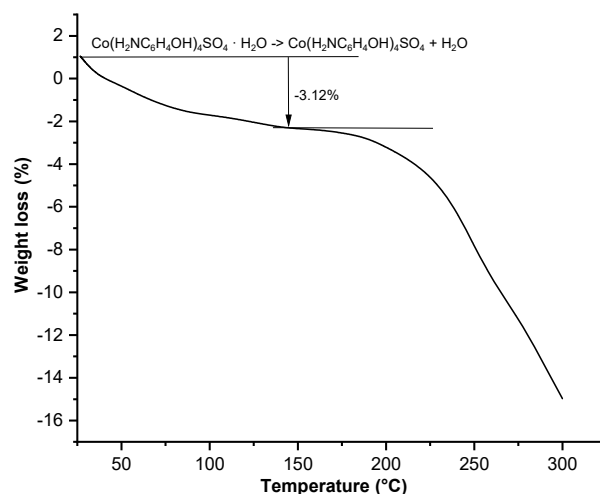


Fig 3. Thermogram of Cu(II) complex

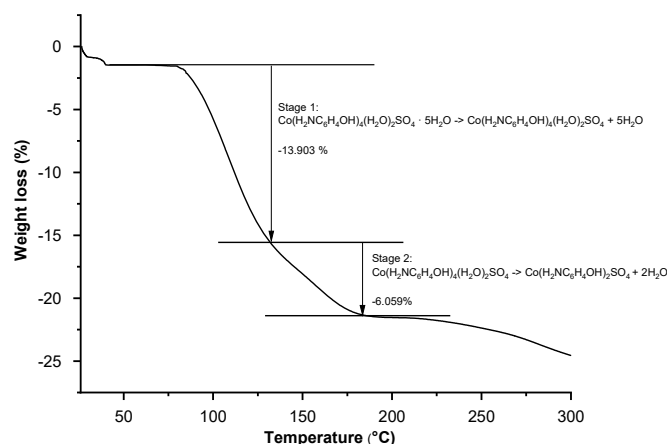


Fig 4. Thermogram of Co(II) complex

Table 1. Proposed formula of the complex based on AAS result

Proposed Empirical Formula	Theoretical metal content (%Cu or %Co)	AAS Result (%)
Cu(4-aminophenol) ₄ SO ₄	10.73	
Cu(4-aminophenol) ₄ (SO ₄)(H ₂ O)	10.41	10.59
Cu(4-aminophenol) ₄ (SO ₄)(H ₂ O) ₂	10.11	
Co(4-aminophenol) ₄ (SO ₄)(H ₂ O) ₅	8.66	
Co(4-aminophenol) ₄ (SO ₄)(H ₂ O) ₆	8.42	8.62
Co(4-aminophenol) ₄ (SO ₄)(H ₂ O) ₇	8.22	

Table 2. Average molar conductivity of the complexes and metal salts

Solvent	Compounds	Average molar conductivity (S cm ² /mol)	Number of ions	Average molar conductivity of the complex
DMF	CoSO ₄ ·7H ₂ O	10	2	[Cu(4-aminophenol) ₄]SO ₄ ·H ₂ O = 16 S cm ² /mol
	CuSO ₄ ·5H ₂ O	16	2	
	CuCl ₂ ·2H ₂ O	28	3	
DMSO	FeSO ₄ ·7H ₂ O	6	2	[Co(4-aminophenol) ₄ (H ₂ O) ₂]SO ₄ ·5H ₂ O = 10 S cm ² /mol
	CoSO ₄ ·7H ₂ O	10	2	
	CuCl ₂ ·2H ₂ O	32	2	
	CoCl ₂ ·6H ₂ O	86	3	

By comparing the value of the molar conductivity of the complex sample solution with the molar conductivity of the standard solution, it can be seen the number of ions produced in the sample solution. The molar conductivity of Cu(II)-4-aminophenol complex solution in DMF measured by electrical conductivity is close to the value of the electrical conductivity of the CuSO₄·5H₂O solution, which indicates the number of ions in the complex is 2. This indicates that the complex solution is an electrolyte with a ratio of cation and anion charges. in a 1:1 ratio. Thus, the sulfate in the complex does not act as a ligand but as a counter ion. Therefore, the possible complex formula for Cu(II)-4-aminophenol is [Cu(4-aminophenol)₄]SO₄·H₂O.

The molar conductivity of the Co(II)-4-aminophenol complex solution in DMSO is similar to the value of the molar conductivity of the CoSO₄·7H₂O solution, which both have a value of 10. This indicates that the number of ions contained by the Co(II)-4-aminophenol complex is two ions. This shows that the ratio of the total charge of cations and anions in the Co(II)-4-aminophenol complex is 1:1, so the formula for the Co(II)-4-aminophenol complex is [Co-(4-aminophenol)₄(H₂O)₂]SO₄·5H₂O with SO₄²⁻ as the counter ion.

FTIR

The functional groups that bind to metal central ions can be estimated through FTIR absorption. OH-phenol is at an absorption range of 3531–3640 cm⁻¹, H₂O is at 3200–3570 cm⁻¹ (broad) [18], and the shift of C–N absorption from 1612 to 1607 cm⁻¹, as seen in Fig. 5,

indicating the formation of Cu(II) complex [19]. This also occurred in the Cu(II) with 1,3,4-thiadiazolethiosemicarbazone, which showed a shift in NH₂ absorption from 3264 to 3246 cm⁻¹ and from 3152 to 3134 cm⁻¹ and C–N absorption from 1605 to 1599 cm⁻¹ [20]. Cu(II) complex with Schiff based-on glycine also showed a shift in C–N absorption from 1641 to 1600 cm⁻¹, which indicates the coordination of nitrogen atom to copper [21]. In this research, NH₂ absorption in the ligand and [Cu(4-aminophenol)₄]SO₄ shifts in a smaller absorption value from 3352 and 3287 cm⁻¹, respectively. This indicates the coordination of the nitrogen atom of the –NH₂ in 4-aminophenol on the Cu(II). The hydroxyl (O–H) group does not appear in the spectra, it is probably due to overlapping with the NH₂ group. This also is supported by the appearance of

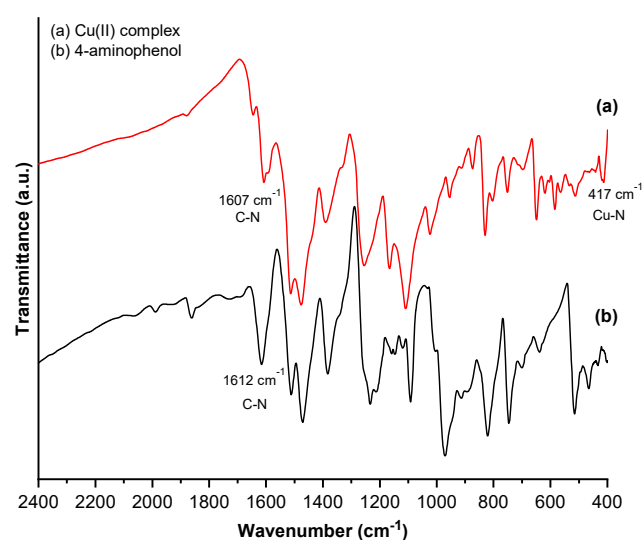


Fig 5. FTIR spectra of 4-aminophenol and Cu(II) complex

Cu–N absorption at 417 cm^{-1} . A new absorption at 414 cm^{-1} indicates the presence of metal bonds with the NH_2 (Cu–N) also happened at Batool et al. [22].

In Co(II) complex, NH_2 and C–N absorption shifted toward smaller from 3342 (4-aminophenol) to 3282 cm^{-1} (complex) and 1385 to 1384 cm^{-1} (Fig. 6). A similar case also happened to $[\text{Co}(\text{Phen})_2(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$, C–N absorption shift from 328 to 1314 cm^{-1} [23]. Absorption of water molecules does not appear. However, the presence of absorption at 524 cm^{-1} indicates the presence of Co–N bonds. This shows that in the complex $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$, the cobalt ion binds to the nitrogen atom of NH_2 and the oxygen atom of H_2O .

UV-Vis

$[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ showed an absorption at 417 nm (23981 cm^{-1}), as revealed in Fig. 1. Copper complexes that have electronic absorption in the region of 20366 and 20202 cm^{-1} have ${}^2\text{B}_{1g} \rightarrow {}^2\text{E}_{1g}$ transitions and have a square planar geometry [24]. Thus the complex of $[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ is estimated to have square planar geometry. The Co(II) complex, $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ showed one absorption peak at a wavelength of 450 nm ($22,222\text{ cm}^{-1}$). Co(II) complex with Schiff base salicylidenic ligand at a maximum wavelength of 470 nm ($21,276\text{ cm}^{-1}$) has an electronic transition of ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ and has octahedral geometry [25]. Thus, $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ is also estimated to have octahedral geometry. Electronic spectral data of $[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ are shown in Table 3.

Magnetism

The results of the measurement of the effective magnetic moment (μ_{eff}) of $[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ is 1.79 and 5.30 BM , respectively. $[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ has similar magnetic properties to other Cu(II) complexes in the range $1.70\text{--}2.0\text{ BM}$, which show paramagnetic characteristics with one unpaired electron [19,26–28]. The result of $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ is similar to the effective magnetic moment value of the copper complex according to $[\text{Co}(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]\text{Cl}_2$, which was reported by Rahardjo et al. [14] was 5.3 BM and Obaid et al. [29] was 5.25 . The high spin octahedral Co(II) geometry has an effective magnetic moment value of $4.7\text{--}5.3\text{ BM}$ [24]. The significantly higher moment magnetic of octahedral Co(II) complexes than that of spin-only value (μ_{s} , 3.87 BM) for three unpaired electrons is due to the orbital contribution to the magnetic moment [30–31]. The proposed structures of the Cu(II) and Co(II) complexes are shown in Fig. 7.

$[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ is 1.79 and 5.30 BM , respectively. $[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ has similar magnetic properties to other Cu(II) complexes in the range $1.70\text{--}2.0\text{ BM}$, which show paramagnetic characteristics with one unpaired electron [19,26–28]. The result of $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$ is similar to the effective magnetic moment value of the copper complex according to $[\text{Co}(\text{Nicotinamide})_2(\text{H}_2\text{O})_2]\text{Cl}_2$, which was reported by Rahardjo et al. [14] was 5.3 BM and Obaid et al. [29] was 5.25 . The high spin octahedral Co(II) geometry has an effective magnetic moment value of $4.7\text{--}5.3\text{ BM}$ [24]. The significantly higher moment magnetic of octahedral Co(II) complexes than that of spin-only value (μ_{s} , 3.87 BM) for three unpaired electrons is due to the orbital contribution to the magnetic moment [30–31]. The proposed structures of the Cu(II) and Co(II) complexes are shown in Fig. 7.

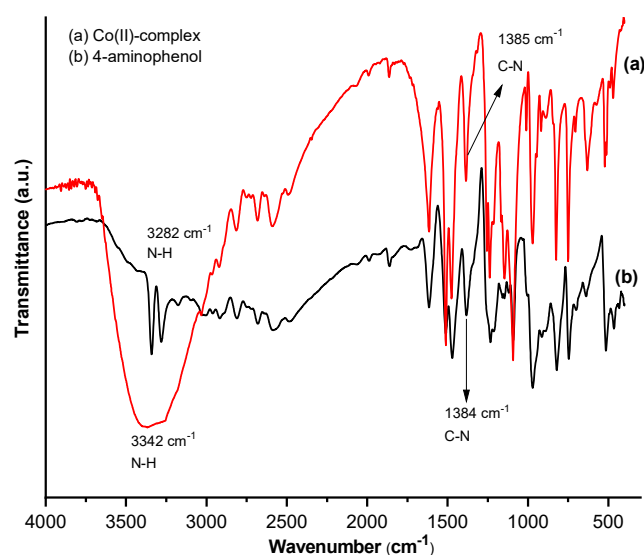


Fig 6. FTIR spectra of 4-aminophenol and Co(II) complex

Table 3. Electronic spectral data of $[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$ and $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$

Compounds	λ_{max} (nm)	Absorbance	ν (cm^{-1})	ϵ ($\text{L mol}^{-1}\text{ cm}^{-1}$)
$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	794	0.146	12595	91.074
$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	566	0.170	12592	35.000
$[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$	417	0.777	23981	795.350
$[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4 \cdot 5\text{H}_2\text{O}$	450	0.710	22222	830.000

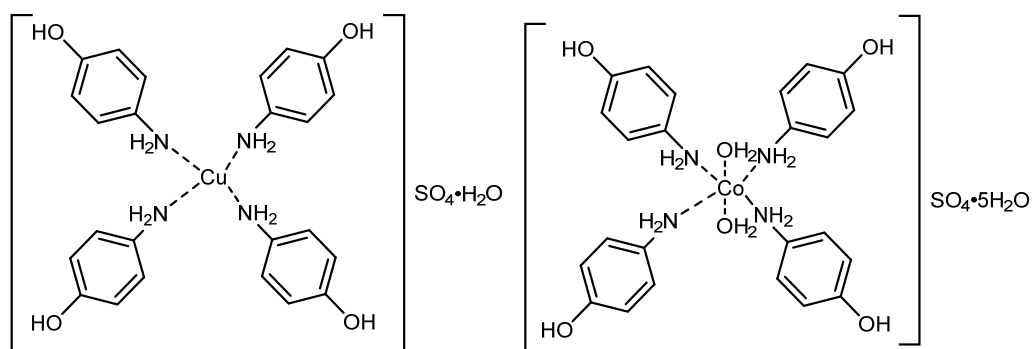


Fig 7. Proposed structures of Cu(II) and Co(II) complexes

Antibacterial Test

$[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4\cdot\text{H}_2\text{O}$ and $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4\cdot 5\text{H}_2\text{O}$ do not show antibacterial activity against *S. aureus* ATCC 25923, *S. epidermis* ATCC 12228, *E. coli* ATCC 25922 and *P. aeruginosa* ATCC 27853.

CONCLUSION

Copper and cobalt complexes are successfully synthesized with estimated formulas $[\text{Cu}(4\text{-aminophenol})_4]\text{SO}_4\cdot\text{H}_2\text{O}$ and $[\text{Co}(4\text{-aminophenol})_4(\text{H}_2\text{O})_2]\text{SO}_4\cdot 5\text{H}_2\text{O}$. Both complexes are paramagnetic and estimated to form square planar and octahedral geometry, respectively. No antibacterial activity was observed against *S. aureus*, *S. epidermis*, *E. coli*, and *P. aeruginosa*.

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AUTHOR CONTRIBUTIONS

Husna Syaima, Sentot Budi Rahardjo, Anisa Nurul Hanifa, and Ariffah Ana Fathonah conceived and planned the experiment. Anisa Nurul Hanifa and Ariffah Ana Fathonah contributed to sample preparation and conducted the experiment. Husna Syaima, Sentot Budi Rahardjo, Anisa Nurul Hanifa, and Ariffah Ana Fathonah contributed to the interpretation of the results of characterization of complexes. Ratna Setyaningsih supervised and analyzed the result of antibacterial activity. Husna Syaima and Sentot Budi Rahardjo took the

lead in writing the manuscript. All authors agreed to the final version of this manuscript.

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