

Synthesis and Thermal Characterization of *p*-Coumaric Acid Complexes of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} Metal Cations and Biological Applications

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ABSTRACT

The phenolic compound used in this study is *p*-coumaric acid, which is the derivative of phenolic acid playing a role in giving color, odor and taste to the plants. The *p*-coumaric acid is an organic compound derived from cinnamic acid. There are three isomers of this structure as ortho-, meta- and para- depending on the location of the hydroxyl group within the structure. In this study, metal complexes of *p*-coumaric acid ligand with the transition metal cations (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) were synthesized. The structure of the synthesized complexes was studied via elemental analysis, infrared and ultraviolet-visible spectroscopy, magnetic measurements, melting point and thermal analysis. Furthermore the biological properties of these new molecules were studied.

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Key Words:

p-coumaric Acid; Metal Complexes; Thermal Analysis; Spectroscopy; Biological Activity.

INTRODUCTION

Phenolic compounds or polyphenols are the chemical compounds with the hydroxyl bounded benzene ring, which exist in large amounts in plants, give color to fruits and flowers and provide protection against environmental stress [1-3]

Phenolic substances constitute the most important group of natural antioxidants. These substances are common in plant foods such as fruits, vegetables, spices, cereals and drinks. In addition, they are also known as free radical scavenger and chain breakers [4,5].

The antioxidant effects of the phenolic compounds comes from the resonance stability of phenol radical and from features such as scavenging free-radicals, forming compounds with metal ions (metal chelating) and preventing or reducing the formation of singlet (radical) oxygen. These compounds are capable of releasing hydrogen of hydroxyl groups in the aromatic rings present in the structure to prevent the oxidation of lipids and other

biomolecules (e.g. proteins, carbohydrates, nucleic acids) by free radicals [6-8]. Antioxidants convert chain-forming radicals into less reactive species by acting as a hydrogen atom transmitter. The antioxidant radical formed in this way is stabilized by displacing the oxygen atom with unpaired electrons on the aromatic ring. Therefore, the molecules with the antioxidant feature often carry a functional phenolic group in the structure [9-12].

These compounds are also called flavonoids. They have positive effects on nutrition physiology, regulate the permeability of the capillary circulatory system and lower blood pressure [13].

The subject in this study was *p*-coumaric acid within the group of phenolic acids giving color, odor and taste to the plants. The *p*-coumaric acid is a phenolic compound derived from cinnamic acid has three isomers depending on the bonding position of the hydroxyl group in the structure as ortho-, para- and meta- has the molecular formula of C₉H₈O₃ and

the molecular weight of 164.15 g.mol⁻¹, has melting point of 210-213°C. Exists much in orange [14], cherry, coffee, chocolate and wine [15]. The ability to kill tumor cells, the oxidative damage of p-coumaric acid on DNA was reported. It shows the toxic effects when taken in high amounts [16]. It is also known that the p-coumaric acid is particularly effective against gastric cancer [17].

P-coumaric acid has the capability to fight against antibacteria, antifungal and also parasites [18]. The p-coumaric acid the most important derivatives of the cinnamic acid is among the notable pharmaceuticals with the properties such as reducing high blood pressure, preventing stroke (antiaggregant) and being an anti-tumor agent [19].

The structural characterization of p-coumaric acid complexes with transition metals such as lanthanum [20], europium [21], cerium [22], zinc [23], manganese [24],

(Cu(NO₃)₂·3H₂O), zinc (II) nitrate heptahydrate (ZnSO₄·7H₂O), sodium bicarbonate (NaHCO₃) and p-coumaric acid, all bought from Sigma-Aldrich, were used.

As the first step in the synthesis of the complexes, p-coumaric acid and sodium bicarbonate, 0.02 moles each, were dissolved separately in the medium of 50:50 (v/v) EtOH:H₂O and reacted with each other. The reaction medium was stirred continuously up to all carbon dioxide formed during the reaction fully removed from the environment. Related metal salts were added on the sodium p-coumarate salt remaining purely in the solution media in the ratio of 1:2 mole (metal: ligand) and stirred on a hot plate at 60°C to obtain clear solution. The solution obtained at the end of the process was kept at reflux for about a day at 75°C. The samples were allowed to crystallize at room temperature for 3 to 6 weeks, and filtered after crystallization to dry at the same condition.

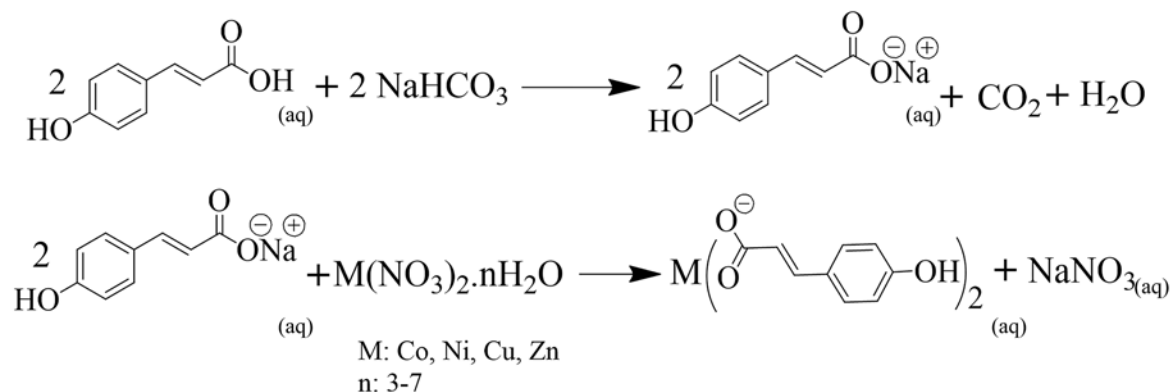


Figure 1. Synthesis reaction.

copper [24] and cadmium [24,25] and various chemical and physicochemical properties with alkali metals (Li, Na, K, Rb) [26] were studied in the literature.

In this study, metal complexes of p-coumaric acid ligand with the transition metal cations (CoII, NiII, CuII, ZnII) were synthesized. The structure of the synthesized complexes was studied via elemental analysis, infrared and ultraviolet-visible spectroscopy, magnetic measurements, melting point and thermal analysis. Furthermore the biological properties of these new molecules were studied.

MATERIAL AND METHOD

Synthesis

In the synthesis of complexes, cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), nickel (II) nitrate hexahydrate (NiSO₄·6H₂O), copper (II) nitrate trihydrate

Synthesis reaction was shown in Figure 1.

Determination of Antimicrobial and Total Antioxidant Capacity

Escherichia coli (ATCC 25922), *Staphylococcus aureus* (ATCC 25923), *Enterococcus faecalis* (ATCC 29212), *Pseudomonas aeruginosa* (ATCC 27853), *Candida albicans* (ATCC 10231) were used as test microorganisms. All strains were obtained from the culture collection at Hitit University, Faculty of Science and Arts, Department of Molecular Biology and Genetics, Molecular Microbiology and Biotechnology Research Laboratory. The antimicrobial activities were evaluated by disc-diffusion method. The total antioxidant capacity (TAC) was determined using an automated colorimetric measurement method.

RESULTS AND DISCUSSION

In this study, metal complexes of p-coumaric acid ligand

Table 1. The elemental analysis data of complexes.

Complex	MW g/mol	Yield	Contents % Found (calc.)		Color	d.p. °C	μ_{eff} BM
			C	H			
$[\text{Co}(\text{C}_9\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ $\text{C}_{20}\text{H}_{20}\text{CoO}_9$	439.28	91	49,84 (49,22)	5,32 (4,59)	pink	186	3,77
$[\text{Ni}(\text{C}_9\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$ $\text{C}_{24}\text{H}_{24}\text{NiO}_{10}$	457.05	87	48,11 (47,30)	4,17 (4,85)	green	191 decomp	2,65
$[\text{Cu}(\text{C}_9\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_2]$ $\text{C}_{18}\text{H}_{18}\text{CuO}_8$	425,88	93	51,63 (50,76)	4,57 (4,26)	blue	189	1,62
$[\text{Zn}(\text{C}_9\text{H}_7\text{O}_2)_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ $\text{C}_{20}\text{H}_{20}\text{ZnO}_9$	445.73	81	49,13 (48,50)	3,97 (4,52)	white	186	Dia.

with the transition metal cations (Co^{II} , Ni^{II} , Cu^{II} , Zn^{II}) were synthesized. The structure of the complexes synthesized was studied via the elemental analysis, infrared and ultraviolet-visible spectroscopy, magnetic measurements, melting point and thermal analysis. Theoretical and experimental results summarized in Table 1 showing chemical composition analysis are consistent with each other. Magnetic susceptibilities of complexes in terms of the Bohr Magneton are also consistent with octahedral structures [27].

Infrared Spectroscopy

The infrared spectra of complexes recorded at 450-4000 cm^{-1} is given in Figure 2. For *p*-coumaric acid, the strong and broadband at 3000-2900 cm^{-1} corresponds to -OH group, in the same way the other spectra data obtained can be given as; C=O group originating from carboxylic acid at 1688 cm^{-1} , supportive C-O peaks at 1260-1100 cm^{-1} and the aromatic C-H stretching at 2879 cm^{-1} . In addition, the peak at 973 cm^{-1} refers to the -OH substituent at the para position. The strong and the broad band obtained at 3600-3000 cm^{-1} for the complexes obtained is originating from -OH group of water included in the structure. In our complex, there are stretching vibrations at 2590 and 2860 cm^{-1} corresponding aromatic C-H bands. The C=O group originating from carboxylic acid in Co^{II} , Ni^{II} , Cu^{II} and Zn^{II} metal complexes gives valence vibrations at 1635, 1632, 1613 and 1638 cm^{-1} , respectively. The asymmetric and symmetric absorption bands of COO^- in carboxylic acid correspond to stretching vibration at 1505-1515 cm^{-1} and 1385-1398 cm^{-1} . The absorption bands corresponding to the M-O bindings underlying the complex have stretching vibrations at 510 and 531 cm^{-1} for Co^{II} complex; at 514 and 535 cm^{-1} for Ni^{II} complex; at 499 and 571 cm^{-1} for Cu^{II} complex; at 515 and 533 cm^{-1} for Zn^{II} complex. Some stretching and bending vibrations of the complexes are summarized in Table 2.

Thermal Analysis

It can be determined from the differential thermogravimetric (DTG) analysis of the complexes between Co^{II} and *p*-coumaric acid ligand that

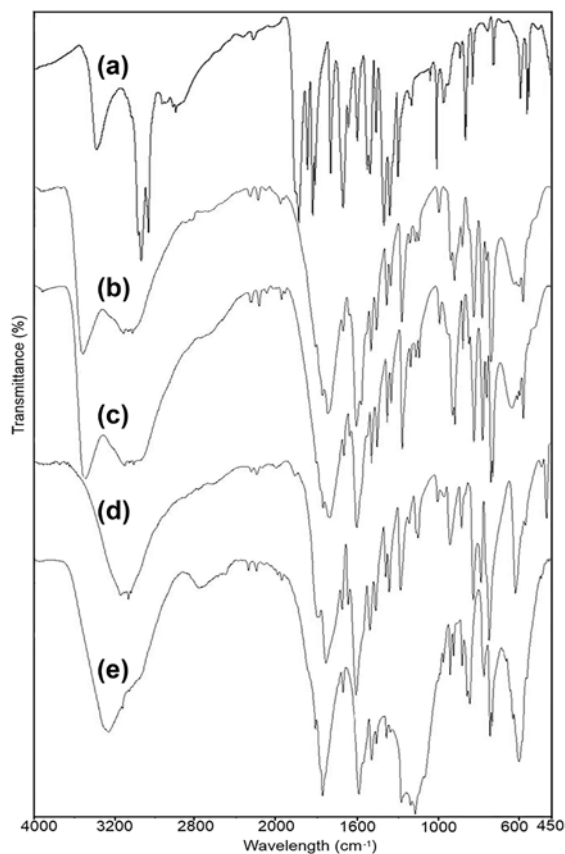
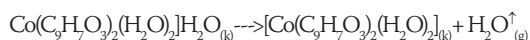


Figure 2. The infrared spectra of *p*-coumaric acid (a) and Co^{II} (b), Ni^{II} (c), Cu^{II} (d) ve Zn^{II} (e) complexes.

it decomposes at four stages corresponding to maximum temperatures of 58, 84, 228, 314°C. The first decomposition step is the removal of 1 mole of crystal water from the structure.



It is the complete removal of 2 moles of water molecules of ligand within the coordination sphere from the structure at the decomposition step of 84°C within the temperature range of 79-152°C.

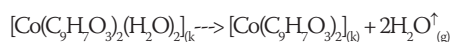


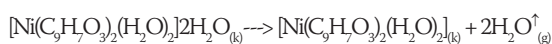
Table 2. The infrared spectra peaks of complexes containing *p*-coumaric acid.

Groups	<i>p</i> -coumaric acid	Co ^{II}	Ni ^{II}	Cu ^{II}	Zn ^{II}
$\nu(-OH)_{H_2O}$	-	3600-3000	3600-3000	3600-3000	3600-2900
$\nu(-OH)_{carboxyl}$	3000-2900	-	-	-	-
$\nu(CH_2)$	2879,2685	2830,2665	2812,2611	2860,2591	2808,2698
$\nu(C=O)_{carboxyl}$	1688	1635	1632	1613	1638
$\nu(COO)_{asym.}$	-	1513	1515	1505	1511
$\nu(COO)_{sym.}$	-	1385	1396	1398	1385
$\Delta\nu_{asym-sym}$	-	128	119	107	126
$\nu(C-C)_{ring}$	1597,1478	1562,1437	1552,1444	1577,1475	1545,1450
$\nu(C-O)_{carboxyl}$	1260-1100	1244-936	1247-953	1261-947	1246-940
$\delta(-OH)_{carboxyl}$	973	-	-	-	-
$\nu(M-O)_{carboxyl}$	-	510,531	514,535	499,571	515,533

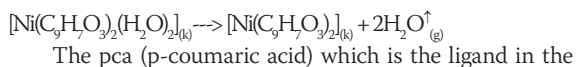
The pca (*p*-coumaric acid) which is the ligand in the complex was removed from the medium by decomposing at the temperature range of 155-385°C. The black colored compound of CoO was remained as the decomposition products.



It can be determined from the DTG curve of the complexes between Ni^{II} and *p*-coumaric acid ligand that it decomposes at four stages corresponding to maximum temperatures of 76, 139, 219 and 398; 775°C. The first decomposition step is the removal of 2 moles of crystal water from the structure.



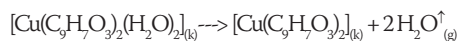
It is the complete removal of 2 moles of aqua ligand within the coordination sphere from the structure at the decomposition step of 139°C within the temperature range of 130-162°C.



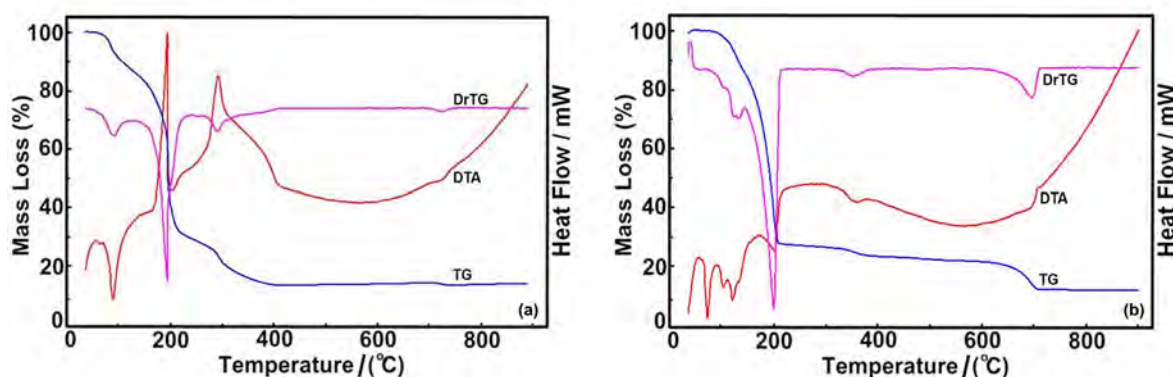
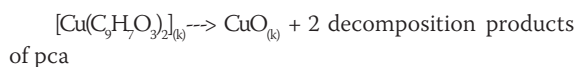
complex was removed from the medium by decomposing at the temperature range of 164-790°C. The black colored compound of NiO was remained as the decomposition products.



It can be determined from the DTG curve of the (VII) complexes between Cu^{II} and *p*-coumaric acid ligand that it decomposes at three stages corresponding to maximum temperatures of 83, 223; 260, 856°C. The first decomposition step is the removal of 2 moles of ligand water from the structure.



The pca (*p*-coumaric acid) which is the ligand in the complex was removed from the medium by decomposing at the temperature range of 138-871°C. The black colored compound of CuO was remained as the decomposition products.

**Figure 3.** The thermal analysis curves for the complexes of (a) Co^{II} and (b) Ni^{II}.

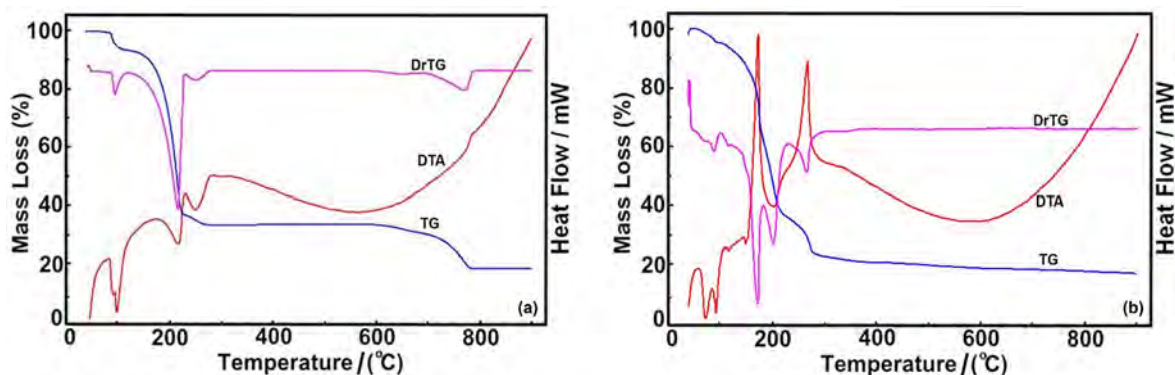
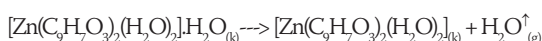
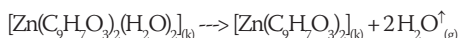


Figure 4. The thermal analysis curves for the complexes of (a) Cu^{II} and (b) Zn^{II}.

It can be determined from the DTG curve of the (VIII) complexes between Zn^{II} and p-coumaric acid ligand that it decomposes at four stages corresponding to maximum temperatures of 62; 86, 113; 150, 178, 285°C. The first decomposition step is the removal of 1 mole of crystal water from the structure.



It is the complete removal of 2 moles of aqua ligand within the coordination sphere from the structure at the decomposition step of 113; 150°C within the temperature range of 91-152°C.



The pca (p-coumaric acid) which is the ligand in the complex was removed from the medium by decomposing at the temperature range of 153-442°C. The grey colored compound of ZnO was remained as the decomposition products.



Complex decomposition steps and decomposition products are summarized in detail in Table 3.

Solid-State UV-vis Spectroscopy

The electronic transition values of complexes obtained according to the visible region spectroscopy (UV-vis)

Table 3. The thermal analysis data for complexes with the ligand of p-coumaric acid.

Complex	Temp. Range(°C)	DTA _{max} (°C)	Leaving Group	Mass Loss(%)		Remnant(%)		Decomp. Prod.	Color
				Exp.	Theoretical	Exp.	Theoretical		
<i>[Co(C₉H₇O₃)₂(H₂O)₂].H₂O</i>									
439,28 g/mole	1	47-78	58	H ₂ O _(hydrate)	4.09	4.20			Pink
	2	79-152	84	2H ₂ O _(crystal)	8.41	8.40			
	3	155-262	228	2C ₈ H ₈ O	55.12	54.22			
	4	265-385	314	2CO	11.82	12.76	16.33	15.74	
<i>[Ni(C₉H₇O₃)₂(H₂O)₂].2H₂O</i>									
457,05 g/mole	1	55-127	76	2H ₂ O _(hydrate)	6.93	7.88			Green
	2	130-162	139	2H ₂ O _(crystal)	8.26	7.88			
	3	164-253	219	2C ₈ H ₈ O	53.63	52.08			
	4	331-790	398;775	2CO	12.63	12.25	16.97	16.35	
<i>[Cu(C₉H₇O₃)₂(H₂O)₂]</i>									
425,88 g/mole	1	70-136	83	2H ₂ O _(hydrate)	4.62	4.23			Blue
	2	138-290	223;260	2C ₈ H ₈ O	57.31	56.33			
	3	660-871	856	2CO	12.98	13.15	19.12	18.66	
<i>[Zn(C₉H₇O₃)₂(H₂O)₂].H₂O</i>									
445,73 g/mole	1	52-90	62;86	H ₂ O _(hydrate)	4.32	4.22			White
	2	91-152	113;150	2H ₂ O _(crystal)	8.51	8.41			
	3	153-255	178	2C ₈ H ₈ O	54.12	55.61			
	4	256-442	285	2CO	12.50	13.01	20.12	19.02	

Table 4. The *in vitro* antimicrobial activity of complexes synthesized.

Complexes	Strains (Inhibition zones \pm SD)				
	<i>S. aureus</i> ATCC 25923	<i>E. faecalis</i> ATCC 29212	<i>E. coli</i> ATCC 25922	<i>P. aeruginosa</i> ATCC 27853	<i>C. albicans</i> ATCC 10231
<i>p</i> -coumaric acid					
+Co	-	-	-	-	9,0 \pm 1,0
+Ni	-	-	-	-	11,5 \pm 0,5
+Cu	-	-	7,5 \pm 0,5	8,0 \pm 2,0	10,0 \pm 0,1
+Zn	-	-	11,0 \pm 1,0	10,5 \pm 1,5	11,5 \pm 0,5

(*: no inhibition, the amount of complex used: 25 μ L)

of compounds recorded in the interval of 900-200 nm were deduced from the spectral pattern (Figures 4.23 - 4.26). According to these data; d-d transitions could be related to the Co^{II} (V) complexes that were observed at the wavelength of 564.12 nm (⁴T_{1g} → ⁴T_{2g}) (F) and 509.61 nm (⁴T_{1g} → ⁴T_{1g}) (P) (Figure 4.23). The three spin-allowed *d-d* transition belonging to the Ni^{II} (VI) complex were corresponded to the wavelengths of 836.35 nm (³A_{2g} → ³T_{1g}) (P), 641.24 nm (³A_{2g} → ³T_{1g}) (F) and 397.72 nm (³A_{2g} → ³T_{2g}) (F). Therefore, these transition bands confirmed the splitting of *d* orbitals of Ni²⁺ metal cation supporting the octahedral (Figure 4.24). The multiple absorption bands of Cu^{II} (VII) are formed by overlapping peaks and had a broaden shape in a wide range corresponding to the interval of 837.95 - 527.37 nm (Figure 4.25). In the light of these spectral data, it can be thought that Cu²⁺ metal cation confirms “pseudo-octahedral” structure under the influence of the Jahn-Teller effect. The maximum adsorption band of broaden spectrum owned by Cu^{II} (VII) complex corresponded to the wavelength of approximately 677.49 nm (²E_g → ²T_{2g}) [28,29]. There was no any *d-d* electronic transition for an octahedral splitting possible to occur because fully occupied *d* orbitals in the last orbit of Zn^{II} (VIII) complex with the diamagnetic feature as seen from the magnetic susceptibility data (Figure 5) [30-32].

Biologic Applications

The antimicrobial activity and the total antioxidant activity (TAA) of the complexes synthesized are given in Table 4 and 5 respectively.

The antioxidant activity of metal complexes were shown in Table 5. Although the antioxidant values were found to very close to each other, Co^{II} containing molecule has the lowest and the Zn^{II} containing molecules had the highest value. In the case of evaluation of the antimicrobial activities of the complexes (Table 4), it was determined that the most effective metal is zinc. In addition, the metal complexes were found to be effective especially on yeasts and gram negative bacteria according to the inhibition zones obtained for the complexes between transition metal cations (Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) and *p*-coumaric acid, especially

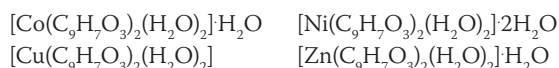
Table 5. The total antioxidant activity results of complexes synthesized.

Metal Complexes	Total Antioxidant Values (mmol Trolox Eq./L)
Co ^{II} (V) complex	0,79
Ni ^{II} (VI) complex	0,84
Cu ^{II} (VII) complex	0,81
Zn ^{II} (VIII) complex	0,89

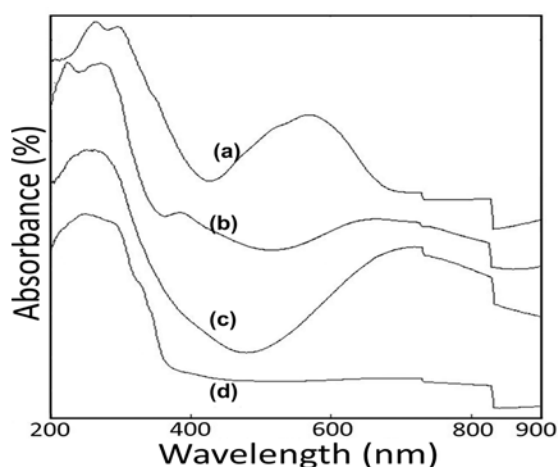
yeasts and gram-negative bacteria appears to be effective.

CONCLUSION

It was determined as a result of the elemental analysis of the complexes synthesized that the metal: ligand ratio was 1:2 for single ligand and 1:2:2 for multi ligand complexes. According to the elemental analysis results (Table 1), the formula of the complexes were determined to be as follows.



It is estimated that the complexes have metal cation coordination sphere in the shape of octahedral geometry. The complexes obtained from transition metal cations of Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} synthesized have the infrared spectrum (Table

**Figure 5.** The UV-vis spectrum of [Zn(C₉H₇O₃)₂(H₂O)₂] \cdot H₂O complex.

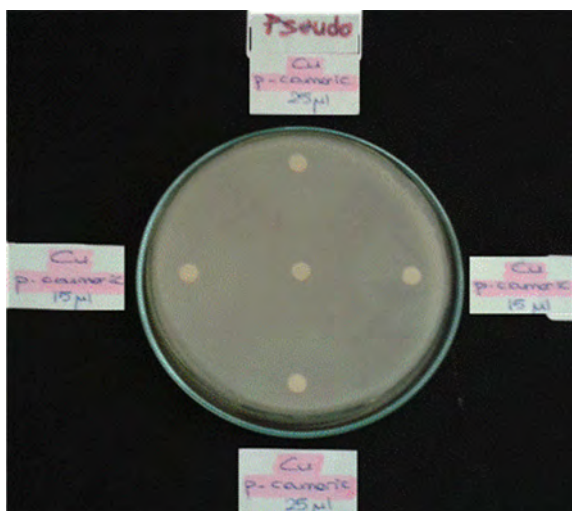


Figure 6. The effect of the Cu^{II} (VII) complex on some microorganisms.

2) in concordance with the binding model proposed in this study. It was determined from symmetric and asymmetric stretching vibrations of carboxylic acid that the binding of p-coumaric acid providing the charge balance of complexes is monoanionic bidentate binding [29,33]. The differences between the symmetric and asymmetric stretching vibrations of the COO⁻ group were obtained as 128 cm⁻¹ for Co^{II}, 119 cm⁻¹ for Ni^{II}, 107 cm⁻¹ for Cu^{II} and 128 cm⁻¹ for Zn^{II} complexes. The differences between symmetric and asymmetric stretching vibrations belonging to the COO⁻ group of p-coumaric acid sodium salt is 145 cm⁻¹ and thus the binding is monoanionic bidentate for the p-coumaric acid containing transition metal complexes.

The estimated structural formula of the complexes, with respect to the results of analysis and similar metal complexes stated previously in the literature [11,29] was proposed as follows:

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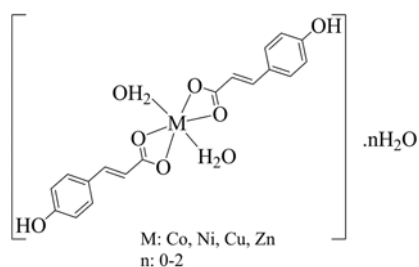


Figure 8. The expected structural formula of complexes.

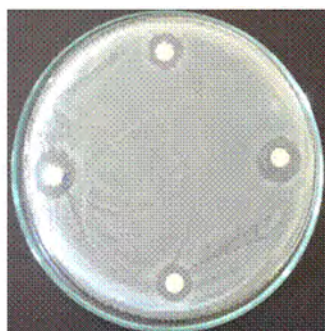
this study. This research was supported by the Science Research Department of Hitit University (Project no: FEF.19004.13.002).

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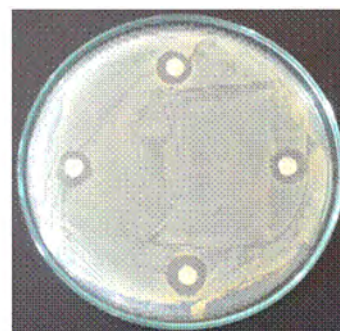
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Candida albicans



P.aeruginosa



S.aureus

Figure 7. The effect of the Zn^{II} (IV) complex on some microorganisms

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