



Synthesis, Spectral, Thermal and Antimicrobial Activities of some new Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of 2- Hydroxy-5-nitrobenzaldehyde and β - diketones (Pentane-2,4-dione, 1-phenylbutane-1,3-dione, 1,3-diphenylpropane-1,3-dione)

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Abstract: Some new mononuclear complexes $[ML_1L_2(NO_3)_2]$ {where $M = [Co(II), Ni(II), Cu(II) \text{ and } Zn(II)]$, $L_1 = 2\text{-Hydroxy-5-nitrobenzaldehyde}$ and $L_2 = \beta\text{-diketones (Pentane-2,4-dione, 1-phenylbutane-1,3-dione, 1,3-diphenylpropane-1,3-dione)}$ }, have been synthesized and were characterized by elemental analysis, molar conductance, FTIR spectra, UV, magnetic moment and thermo gravimetric analysis (TGA). The relative antimicrobial studies of different mixed ligand metal complexes shows that $Cu(II)$ complex is more effective towards gram positive bacteria like *S. aureus*. The octahedral geometry of $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ metal complexes were confirmed by their IR spectra, magnetic properties and electronic spectra. The mixed ligand metal complexes were subjected to thermo gravimetric analysis to study their thermal stability and decomposition mechanism. The molar conductance of metal complexes suggests their non electrolytic nature.

Keywords: Nitrosalicylaldehyde, β -diketones, Transition Metal ions, Thermo gravimetric analysis, ESR, Antimicrobial studies

I. Introduction

A considerable attention has been shown by the scientists to study the potential biological activities of mixed ligand metal complexes of substituted salicylaldehyde and β -diketones [1,2]. A number of mixed ligand complexes of substituted salicylaldehyde with various transition metals ions have been synthesized [3-8]. 1,3-diketones exhibits various biological activities, such as antioxidants, antitumor and antibacterial and are also key intermediates to various heterocyclic compounds[9-12]. Thermal analysis and biochemical activities of $Zn(II)$, $Cd(II)$ and $Hg(II)$ complexes with 2-aminobenzaldehyde phenylhydrazone “nitrin” ligand were reported [13]. Earlier various metal complexes of transition metals with shifts base showing antibacterial and antimicrobial activities have been reported by our research group[14-15].

This significant increment in the activity of the mixed ligand metal complexes can be explained on the basis of chelation theory [16]. It is, however, known that the chelation makes the ligand to act as more powerful and potent bacteriostatic agents that leads to inhibit the growth of bacteria and fungi more than the free ligand [17,18]. This encouraged us to synthesize and investigate the antimicrobial activities of some mixed ligand metal complexes. In this paper, we have also reported the spectral and thermal studies of various transition complexes with mixed ligands.

II. EXPERIMENTAL

Materials and physical measurements

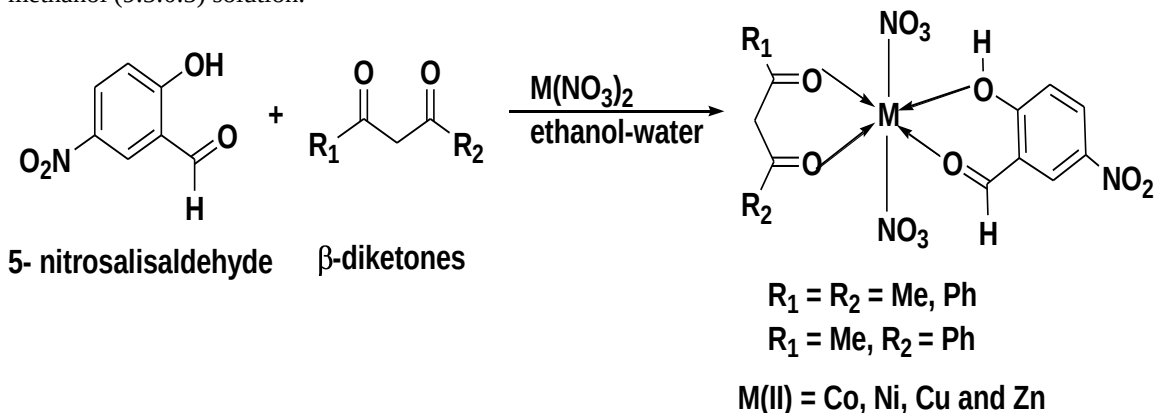
All the chemicals used were of analytical grade and procured from standard firm like Merk and Aldrich. All the solvents used were purified by using standard procedure [19]. Pentane-2,4-dione was purified by double distillation and 1-phenylbutane-1,3-dione, 1,3-diphenylpropane-1,3-dione, pentane-2,4-dione and 5-nitrosalicylaldehyde were purified by recrystallization from ethanol. The metal nitrates were dissolved in double distilled water and standardized [20]. The metal content of the complexes were estimated gravimetrically by reported processes [21].

The molar conductivities in DMSO ($10^{-3}M$) at room temperature were measured using an Equiptronics digital conductivity meter. The magnetic susceptibility measurements of the complexes were made on Goy balance using $Hg[Co(SCN)_4]$ as standard. Electronic spectra of complexes were recorded on Elico SL-171 spectrophotometer at 25°C using ethanol/acetone as solvent. Thermo gravimetric analysis of mixed ligand metal complexes were done at a constant heating rate of 10°C /min up to 1000°C temperature on a TGA instrument

model Perkins Elmer (Pyris Diamond) and FTIR spectra of metal complexes were recorded on Perkin Elmer-842 spectrophotometer.

Synthesis of Mixed Ligand Complexes of Co(II), Ni(II), Cu(II) and Zn(II)

Metal complexes were prepared by refluxing the equimolar solutions of 5-nitrosalicylaldehyde, β -diketones and metal nitrate solutions at 50-60°C for 3hrs. The pH of the reaction mixture was maintained between 6.5 to 7.0. The colored precipitates obtained were filtered washed several times with hot water followed by ethanol to remove the soluble impurities. The washed colored solids were dried in an oven at 100 °C for 1hr and finally kept in desiccators over anhydrous CaCl_2 . The dried solid were recrystallized with benzene : methanol (9.5:0.5) solution.



Scheme 1

Pharmacological Evaluation of Antimicrobial Activity

All the newly synthesized metal complexes were screened for their antibacterial and antifungal activities. In preliminary screening, the antimicrobial tests were carried out by both the disc-diffusion method [22-24] and the serial dilution method [25], using Mueller-Hinton agar (MHA) medium and Sabouraud's dextrose agar (SDA) medium, for bacteria and fungi respectively. The discs (6mm in diameter), impregnated with the test compounds (25 $\mu\text{g}/\text{ml}/\text{disc}$ for bacteria and 1000 $\mu\text{g}/\text{ml}/\text{disc}$ for fungi). Negative controls were prepared using the DMSO solvent, to dissolve the test compounds. Ofloxacin (25 $\mu\text{mg}/\text{ml}/\text{disc}$) and Clotrimazole (1000 $\mu\text{g}/\text{disc}$) were used as positive reference standards for determining the sensitivity of each microbial species tested [24]. The inoculated plates were incubated at 37°C for 24 hrs and 27°C for 72 hrs for bacterial and fungal strains respectively. Antimicrobial activity was evaluated by measuring the diameter of zone of inhibition against test organisms. The antibacterial and antifungal activities of mixed ligand metal complexes were screened *in vitro* against different bacteria (*Bacillus subtilis*, *Staphylococcus aureus*, *Escherichia coli* and *Salmonella typhi*) and fungi (*Aspergillus flavous*, *Aspergillus niger*, *Puccinia triticina* and *Fusarium species*).

The percentage of growth of inhibition was calculated by measuring the diameter of the microbial colony in the control and test plates by the following expression

$$\% \text{ inhibition} = (\text{C}-\text{T}) / \text{C} \times 100$$

Where C = diameter of microbial colony in millimeter in control plate.

T = diameter of microbial colony in test plate.

II. RESULTS AND DISCUSSION

The coloured microcrystalline mixed ligand metal complexes were found to be stable at room temperature. The complexes were soluble in methanol and DMSO but insoluble in water, carbon tetrachloride and chloroform. On elemental analyses and mass estimation by Fenger's method [26], it was concluded that in mixed ligand metal complexes, ligands and metal are in 1:1:1 molar ratio possessing general formula $[\text{ML}_1\text{L}_2(\text{NO}_3)_2]$ [where M = Co(II), Ni(II), Cu(II) and Zn(II), L_1 = 2-Hydroxy-5- nitrobenzaldehyde and L_2 = β - diketones (pentane-2,4-dione, 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione)]. The low molar conductance values (11.30-21.6 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) of complexes shows their nonelectrolytic nature. All analytical and physical data of mixed ligand metal complexes were shown in **Table-1**.

Table 1. Analytical & physical data of Mixed Ligand Complexes

S.No.	Mixed ligand Complexes	Mol. wt.	Yield %	Molar Conductivity $\Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$	Elemental analysis (Cal.)/Found %			
					C	H	N	M
1.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Co}[\text{C}_5\text{H}_8\text{O}_2](\text{NO}_3)_2$	449.93	82	9.3	31.64 (32.00)	2.34 (2.89)	8.82 (9.33)	12.56 (13.09)
2.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Co}[\text{C}_{10}\text{H}_{10}\text{O}_2](\text{NO}_3)_2$	511.93	79	9.9	38.98 (39.85)	2.32 (2.93)	7.79 (8.20)	10.43 (11.51)
3.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Co}[\text{C}_{15}\text{H}_{12}\text{O}_2](\text{NO}_3)_2$	573.93	81	10.7	44.79 (45.99)	2.37 (2.96)	7.04 (7.32)	9.85 (10.27)
4.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Ni}[\text{C}_5\text{H}_8\text{O}_2](\text{NO}_3)_2$	449.69	79	23.6	30.98 (32.02)	1.59 (2.89)	8.87 (9.33)	12.68 (13.05)
5.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Ni}[\text{C}_{10}\text{H}_{10}\text{O}_2](\text{NO}_3)_2$	511.69	72	15.3	39.68 (39.86)	2.87 (2.93)	7.66 (8.20)	10.87 (11.47)
6.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Ni}[\text{C}_{15}\text{H}_{12}\text{O}_2](\text{NO}_3)_2$	573.99	76	12.7	45.87 (46.01)	2.78 (2.96)	6.59 (7.32)	9.87 (10.23)
7.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Cu}[\text{C}_5\text{H}_8\text{O}_2](\text{NO}_3)_2$	454.54	82	23.3	31.09 (31.68)	2.59 (2.86)	8.76 (9.24)	13.01 (13.97)
8.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Cu}[\text{C}_{10}\text{H}_{10}\text{O}_2](\text{NO}_3)_2$	516.54	82	20.7	39.21 (39.49)	2.79 (2.90)	7.97 (8.13)	11.87 (12.30)
9.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Cu}[\text{C}_{15}\text{H}_{12}\text{O}_2](\text{NO}_3)_2$	578.54	78	22.4	45.07 (45.63)	2.84 (2.93)	6.83 (7.26)	10.31 (10.97)
10.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Zn}[\text{C}_5\text{H}_8\text{O}_2](\text{NO}_3)_2$	456.38	80	13.3	30.92 (31.55)	2.61 (2.85)	8.81 (9.20)	13.17 (14.32)
11.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Zn}[\text{C}_{10}\text{H}_{10}\text{O}_2](\text{NO}_3)_2$	518.38	76	15.62	39.15 (39.35)	2.55 (2.89)	7.69 (8.10)	11.81 (12.61)
12.	$[\text{C}_7\text{H}_5\text{O}_4\text{N}]\text{Zn}[\text{C}_{15}\text{H}_{12}\text{O}_2](\text{NO}_3)_2$	580.38	89	19.7	44.89 (45.48)	2.38 (2.93)	7.01 (7.23)	10.84 (11.26)

Infrared Spectra

The FTIR spectra of mixed ligand metal complexes were compared with that of free ligands to determine the changes that might have taken place during complexation. The $\nu \text{C=O}$ frequencies of the all mixed ligand metal complexes were in the lower region as compared to those of the free ligands. Earlier IR spectra of β -diketones and their metal complexes have been reported by Bellamy and Beecher[27]. For 2,4-pentanedione ligand the bands at 1724 cm^{-1} and 1608 cm^{-1} have been assigned to $\nu \text{C=O}$ and $\nu \text{C-O}$ respectively. In 1-phenyl-1,3-butanedione bands due to $\nu \text{C=O}$ and $\nu \text{C-O}$ have been reported at 1724 cm^{-1} and 1600 cm^{-1} respectively and in case of 1,3-diphenylpropane-1,3-dione $\nu \text{C-O}$ band appears at 1600 cm^{-1} . While in case of Cu(II) complexes, bands at 1580 cm^{-1} , 1550 cm^{-1} and 1524 cm^{-1} have been assigned to $\nu \text{C=O}$ frequencies and those at 1389 cm^{-1} , 1386 cm^{-1} and 1391 cm^{-1} have been assigned to $\nu \text{C-O}$ frequencies of pentane-2,4-dione, 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione ligand moieties respectively. However, Bellamy and Branch[28] observed $\nu \text{C=O}$ absorption bands at 1524 cm^{-1} and 1552 cm^{-1} in Cu(II) complexes of 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione respectively. The substitution of methyl group by a phenyl group affects the perturbed $\nu \text{C=O}$ bands. Holtzclaw and Collman[29] suggested that a phenyl group attached to a carbonyl group in the ligand might set up an interfering conjugation through a quinoid like structure decreasing the double bond character of the adjacent carbonyl group. In some cases nitrate ions worked as counter-anions in the supramolecular network while in others they acted as coordinated ligands. Both mode I (monodentate coordination) and mode II (bidentate coordination) were the most common observed coordination mode in which nitrate ions acted as blocking ligands that made appropriate coordination sites available for other ligands[30-32]. The presence of new weak bands around the region at 568 cm^{-1} and 497 cm^{-1} in all the complexes were attributed to $\nu (\text{M-O})$ linkage [33,34]. While strong bands around 1360 cm^{-1} and 860 cm^{-1} suggested monodentate coordination of $-\text{NO}_3$ group in all the complexes [35].

Electronic Spectra and Magnetic Properties

1. $[\text{CoL}_1\text{L}_2(\text{NO}_3)_2]$ The electronic spectra of Co(II) complex displayed three bands at 8260, 15650 and 19680 cm^{-1} corresponding to the transitions ${}^4\text{T}_{1g} - {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g} - {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g} - {}^4\text{T}_{1g}(\text{P})$ respectively[36]. These transitions as well as the measured value of magnetic moment 4.92 BM suggested the octahedral geometry for these complexes.

2. $[\text{NiL}_1\text{L}_2(\text{NO}_3)_2]$ The electronic spectra of Ni(II) complex exhibited three bands at 10810, 16710 and 25680 cm^{-1} corresponding to the transitions ${}^3\text{A}_{2g} - {}^3\text{T}_{2g}$, ${}^3\text{A}_{2g} - {}^3\text{T}_{1g}$ and ${}^4\text{A}_{2g} - {}^3\text{T}_{1g}(\text{P})$ respectively for octahedral geometry[36]. The magnetic moment value of Ni (II) complexes were found around 3.26 BM which was very close to the value of octahedral environment.

3. [CuL₁L₂(NO₃)₂] The electronic spectra of Cu(II) complex displayed three bands at 12010, 16510 and 20010 cm⁻¹ due to ²B_{1g} - ²B_{2g}(F), ²B_{1g} - ²A_{2g} and ²B_{1g} - ²E_{1g} transitions respectively. Which suggest that Cu(II) have distorted octahedral geometry[37]. The magnetic moment of Cu(II) were found 1.94 BM confirming the octahedral geometry.

4. [ZnL₁L₂(NO₃)₂] In case of Zn(II) complexes no significant absorption band in their electrons were obtained due to diamagnetic nature of zinc.

All the magnetic and UV visible spectral data and remarks are depicted in **Table- 2**. Electronic spectra and magnetic properties confirm that Co(II), Ni(II) Cu(II) and Zn(II) metal complexes shows octahedral geometry.

Table 2. UV-Visible spectra(10⁻³M in DMSO) and magnetic studies of mixed ligand metal complexes

Complexes	λ_{max} , nm	Wavenumber (cm ⁻¹)	ϵ_{max} l.mol ⁻¹ cm ⁻¹	Assignment	β_{eff}	
					Found	Calculated
[CoL ₁ L ₂ (NO ₃) ₂]	262, 418, 526, 789, 978	37640, 23462, 18788, 12412, 10164	1068, 4, 17, 1, 9	⁴ A _{2(g)} - ⁴ T _{1(g)} (v ₃) ⁴ A _{2(g)} - ⁴ T _{1(g)} (v ₂) ⁴ A _{2(g)} - ⁴ T _{2(g)} (v ₁)	3.428	3.968
[NiL ₁ L ₂ (NO ₃) ₂]	265, 342, 401, 998	37168, 28800, 24675, 9986	1578, 10, 21, 18	³ T _{1(g)} - ³ A _{2(g)} (v ₂) ³ T _{1(g)} - ³ T _{1(g)} (v ₃) ³ T _{1(g)} - ³ T _{2(g)} (v ₁)	3.453	3.896
[CuL ₁ L ₂ (NO ₃) ₂]	285, 538, 790	34342, 18640, 12812	1005, 4, 17	(C.T) ² T _{2(D)} - ² E _(D)	1.428	1.341
[ZnL ₁ L ₂ (NO ₃) ₂]	268	36225	1957	(C.T) (M-L)	Zero	Zero

Thermo gravimetric analysis

On heating the complexes up to 1000⁰C, the left over residue have higher weight than our expectation. This unexpected change may be attributed due to formation of mixture of metal carbide and metal oxides. The weight of the residue was in good agreement with the theoretically calculated weight of metal carbide as well as metal oxide [38].

Decomposition chart of Co(II) Complex

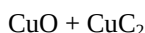
Metal Complex	Temp. range (°C)	wt. loss % found(cal.)
[CoL ₁ L ₂ (NO ₃) ₂]		
↓	108-297	13.68(13.23)
Intermediate		
↓	386-597	26.51 (26.01)
CoO + Co ₄ C ₃ + other		
Volatile oxides of C, H, N		
↓	987	55.17 (56.37)
CoO + Co ₄ C ₃		

Decomposition chart of Ni(II) Complex

Metal Complex	Temp. range (°C)	wt. loss % found(cal.)
[NiL ₁ L ₂ (NO ₃) ₂]		
↓	204-449	28.89 (30.65)
Intermediate		
↓	506-658	26.15(25.81)
NiO + Ni ₃ C + other		
Volatile oxides of C, H, N		
↓	987	37.75 (39.89)
NiO + Ni ₃ C		

Decomposition Chart of Cu(II) Complex

Metal Complex	Temp. range (°C)	wt. loss % found(cal.)
[CuL ₁ L ₂ (NO ₃) ₂]		
↓	179-384	12.98 (13.28)
Intermediate		
↓	468-575	32.18 (32.47)
CuO + CuC ₂ + other		
Volatile oxides of C,H,N		
↓	1003	49.03 (48.31)



Decomposition Chart of Zn(II) Complex		
Metal Complex	Temp. range (°C)	wt. loss % found(cal.)
$[\text{ZnL}_1\text{L}_2(\text{NO}_3)_2]$		
↓	221-343	13.77(14.40)
Intermediate		
↓	532-670	26.23(26.74)
$\text{ZnO} + \text{Zn}_2\text{C} + \text{other}$		
Volatile oxides of C,H,N		
↓	1008	39.84 (38.55)
$\text{ZnO} + \text{Zn}_2\text{C}$		

In thermo gravimetric analysis the TG curve for ligand was broader while the curve of its metal complexes were steeper, suggesting the faster decomposition rate of the metal complexes than that of the ligands, this may be due to catalytic action of metal present in them. The TGA curves of the mixed ligand metal complexes showed the decomposition of metal complexes follows the zero order kinetics. The value of energy of activation were calculated by using Freeman Carrolls [39], Horowitz Metzger's[40] and Coats Redfern's [41] equations (Table-3). The values of various thermodynamic parameters (ΔS , ΔG and ΔE) are given in Table-4.

Table 3. Average Energy of Activation of Co (II), Ni (II), Cu (II) & Zn (II) Complexes in Kcal mol⁻¹ from different Equations

Metal Complexes	Freeman Carolls	Coat Redferns	Horowitz Metzgers
$[\text{Co L}_1\text{L}_2(\text{NO}_3)_2]$	10.97	11.26	11.39
$[\text{Ni L}_1\text{L}_2(\text{NO}_3)_2]$	10.26	12.83	12.19
$[\text{Cu L}_1\text{L}_2(\text{NO}_3)_2]$	9.09	11.78	10.28
$[\text{Zn L}_1\text{L}_2(\text{NO}_3)_2]$	9.46	13.04	11.95

Table 4. Calculation of (ΔE), (ΔS), (ΔG) of the mixed ligand metal Complexes

Metal Complexes	Activation Energy (E) (K cal mol ⁻¹)	Entropy ΔS (e.u.)	Free Energy of Activation ΔG (Kcal mol ⁻¹)
$[\text{Co L}_1\text{L}_2(\text{NO}_3)_2]$	9.08	56.79	43.17
$[\text{Ni L}_1\text{L}_2(\text{NO}_3)_2]$	8.29	56.83	40.71
$[\text{Cu L}_1\text{L}_2(\text{NO}_3)_2]$	8.27	56.98	41.97
$[\text{Zn L}_1\text{L}_2(\text{NO}_3)_2]$	9.08	57.16	45.31

Antimicrobial Studies

The antibacterial and antifungal activities of synthesized mixed ligand metal complexes were screened in vitro, against various bacteria and fungi. The antimicrobial results show that the best zone of inhibition of all the metal complexes was 500 ppm. The percentage of growth of inhibition capacities of metal complexes follows the order given below against different bacteria and fungi.

Bactericidal activities of metal complexes

E. coli: $\text{Cu (II)} > \text{Zn (II)} > \text{Co (II)} > \text{Ni (II)}$
S. typhi: $\text{Cu (II)} \approx \text{Zn (II)} > \text{Co (II)} > \text{Ni (II)}$
S. aureus: $\text{Cu (II)} > \text{Zn (II)} \approx \text{Co (II)} > \text{Ni (II)}$
B. subtilis: $\text{Cu (II)} \approx \text{Zu (II)} > \text{Co (II)} \approx \text{Ni (II)}$

Fungicidal activities of metal complexes

A. flavous: $\text{Cu (II)} > \text{Zn (II)} > \text{CO (II)} > \text{Ni (II)}$
A. niger: $\text{Cu (II)} > \text{Zn (II)} > \text{Co (II)} > \text{Ni (II)}$
P. tritricina: $\text{Cu (II)} > \text{Zn (II)} > \text{Co (II)} \approx \text{Ni (II)}$
F. species: $\text{Cu (II)} > \text{Zn (II)} > \text{Co (II)} > \text{Ni (II)}$

The results indicate that the Cu (II) complex is more toxic compared to other complexes, as well as Cu (II) complex is more effective towards bacteria *S. aureus* compared to other microbes. The overall results

obtained from the above studies confirm that with increase in the concentration of the complexes above 500 ppm the activity almost remains unchanged or is slightly increased.

III. IV.CONCLUSION

The present study showed that the decomposition of newly synthesized mixed metal ligand complexes were of zero order kinetics and were nonelectrolytic in nature. The mixed ligand metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) were found to have octahedral geometry. All Cu (II) metal ligand complexes show the best antimicrobial activity at 500ppm as compared to other metal complexes.

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