



## Synthesis, Characterization and antimicrobial activity of Co(II), Ni(II) and Cu(II) complexes of schiff bases derived from 4-aminoacetophenone and furane 2- carboxaldehyde

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**Abstract :** The new three complexes of Co(II), Ni(II) and Cu(II) with a schiff base 2,4-Furyliminobenzylacetophenone(FIBA) derived from the condensation of 4-aminoacetophenone and furane 2- carboxaldehyde in methanol have been synthesized. The ligand and their metal complexes have been characterized by their elemental analysis, molar conductance, magnetic moments, I.R., NMR, electronic spectral studies; purity of the compounds has been ascertained by determining their repeated melting points of a sample, running TLC for single spot. The ligand and their metal complexes were screened for antibacterial and antifungal activities against bacteria *Staphylococcus aureus* (ATCC 25923), and *Staphylococcus aureus* (ATCC 3160) and common fungi; *Candida albicans* (227) and *Staphylococcus cerevisiae* (361) by the agar well diffusion method. The Schiff base showed varied antibacterial and antifungal activity against one or more strains respectively and their activity was enhanced on coordination or chelation.

**Key words:** Schiff base ligand, complexes, I.R., NMR, Electronic spectra, Magnetic moment and Biocidal studies.

### I. INTRODUCTION

Compound containing an azomethine group ( $-\text{HC}=\text{N}$ ) are known as Schiff bases. Schiff bases are generally bi or tri dentate ligands capable of forming very stable complexes with transition metals. Schiff bases have been widely used as bidentate ligands in the field of Co-ordination chemistry<sup>(1-5)</sup>. The Schiff base complexes have been used in catalytic reactions<sup>(6)</sup> and as models for biological systems<sup>(7, 8)</sup>. Multidentate Schiff base ligands and their metal complexes have been extensively studied for many years<sup>(9-12)</sup>. The multidentate Schiff base ligands and their metal complexes play an important role in the development of coordination chemistry<sup>(13, 14)</sup> and possess characterized by important properties such as biological activity<sup>(14, 15)</sup>, catalytic activity<sup>(16)</sup> and photochromic properties<sup>(17)</sup>. Schiff bases of 4-aminoantipyrine and its complexes are known for their variety of applications<sup>(18-24)</sup> in the areas of catalysis, clinical applications and pharmacologically. Antipyrine and its derivatives<sup>(25-32)</sup> show antibacterial and antitumor activities.

### II. EXPERIMENTAL

#### Material and Methods

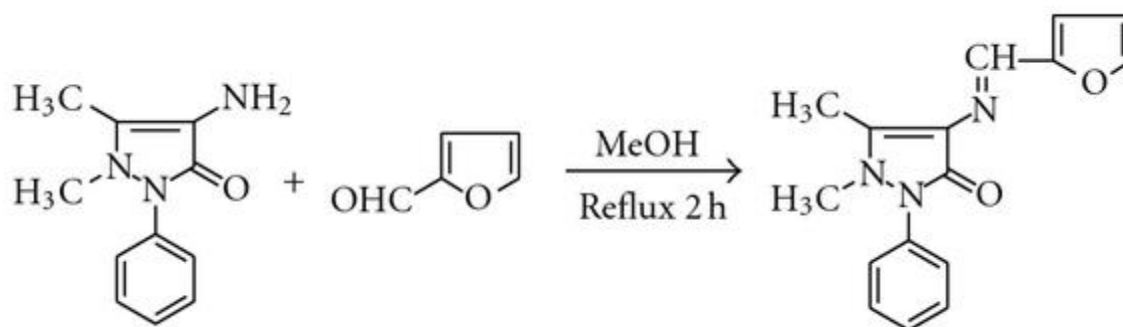
All the chemicals and solvents used were analytical grade Chemicals and solvents were used without further purification. Elemental analysis (C, H and N) of the ligand and complexes were carried out in micro analytical laboratory on CarloErba-1106 elemental analyzer. Metals were estimated following standard procedures<sup>(33)</sup>.

Molar conductance measurements were carried out for the  $10^{-3}\text{M}$  solutions of the complexes in DMF solvent at 300 K using a Systronics direct reading digital conductivity bridge – 304 with a dip type cell. Molecular weights were determined by cryoscopic method using Beckmann's thermometer and

magnetic measurements of the complexes at 300K were made by Gouy magnetic balance using Hg [Co (NCS)<sub>4</sub>] as calibrant. The purity of the compound was checked by TLC using ethyl acetate and hexane in 1:2 ratio. IR spectra were recorded on a FTIR spectrophotometer model IR-550 NICOLET-45A in the 4000-400 cm<sup>-1</sup> region employing KBr pellets. The electronic spectra were recorded on a Varian CARY 50 Bio UV-visible spectrophotometer.

### Synthesis of ligands: -

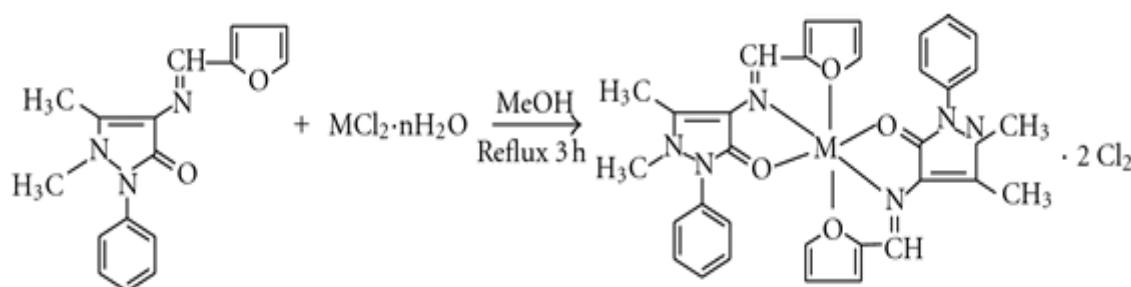
In a round bottom flask, furan-2-carboxaldehyde (0.01 mmol, 0.35 mL) in methanol (15 mL) and 4-aminoantipyrine (0.1 mmol, 0.203 g) in methanol (15 mL) were stirred by a magnetic stirrer for about 30 minutes. The mixture was refluxed for 2 hour on the heating mental at 50°C. After completion of the reaction monitored through TLC, it was cooled at room temperature to afford a yellow solid product which was filtered, washed with cold methanol then with ether and dried and obtained product, yield: 50% (Scheme 1).



*Scheme 1: Route for the synthesis of the 2, 4-Furyliminobenzylacetophenone.*

### Synthesis of Metal Complexes

For the synthesis of metal complexes, a solution of 2,4-Furyliminobenzylacetophenone ligand (0.1 mmol, 0.317 g) in methanol (50 mL) was added to a magnetically stirred solution of MCl<sub>2</sub>·nH<sub>2</sub>O (0.1 mmol) in methanol (30 mL) at a required equimolar ratio of M : L (1 : 2). The mixture was refluxed for 3 h and then cooled to room temperature. On cooling, a colored solid product was formed. The solid was filtered, washed with ethanol then several times with ether and dried. Crystallization from methanol gave the desired metal complexes (Scheme 2).



*Scheme 2: Route for the synthesis of the Metal complexes*

Table 1: Analytical data of ligand and their metal complexes

S.No.	Compound	Yield	Colour	M.P. (°C)	Mol. Wt.	Analytical data Found (calc.)			$\mu_{\text{eff}}$ (B. M)	Am ( $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ )
						C	H	N		
1	FIBA ( $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$ )	50 %	yellow	239	281	62.32 (61.70)	5.33 (5.01)	14.94 (13.89)	-	-
2	$[\text{Co}^{\text{II}}(\text{L}_2)]\text{Cl}_2$ ( $\text{CoC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2$ )	28 %	Dark Green	318	870	44.13 (43.25)	3.44 (3.11)	9.65 (9.05)	1.05	10.3
3	$[\text{Ni}^{\text{II}}(\text{L}_2)] \text{Cl}_2$ ( $\text{NiC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2$ )	36 %	Dark Green	317	869	44.18 (43.95)	3.45 (3.01)	9.66 (9.11)	2.13	16.09
4	$[\text{Cu}^{\text{II}}(\text{L}_2)]\text{Cl}_2$ ( $\text{CuC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2$ )	30 %	Light Green	344	802	47.88 (46.38)	3.74 (3.13)	10.47 (10.09)	3.17	16.14

Table-2: I.R. Spectral bands of ligand and their metal complexes

S.No.	Compound	$\nu_{\text{HC-N}}$	$\nu_{\text{C=O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{C-O}}$	$\nu_{\text{M-Cl}}$	$\nu_{\text{N-N}}$	UV-vis (DMSO): $\lambda_{\text{max}}$ ( $\text{cm}^{-1}$ )
1	FIBA ( $\text{C}_{16}\text{H}_{15}\text{N}_3\text{O}_2$ )	1630	1690	-	-	1528	-	1298	
2	$[\text{Co}^{\text{II}}(\text{L}_2)]\text{Cl}_2$ ( $\text{CoC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2$ )	1590	1645	560	446	-	389	-	15000, 16389 and 27249
3	$[\text{Ni}^{\text{II}}(\text{L}_2)] \text{Cl}_2$ ( $\text{NiC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2$ )	1586	1648	500	450	-	387	-	14992, 16668 and 27779
4	$[\text{Cu}^{\text{II}}(\text{L}_2)]\text{Cl}_2$ ( $\text{CuC}_{32}\text{H}_{30}\text{N}_6\text{O}_4\text{Cl}_2$ )	1600	1677	-	-	1532	396	-	14918, 16389 and 27249

**Table-3:  $^1\text{H}$  NMR Spectral data of ligand and their metal complexes. (DMSO- $d_6$ ):  $\delta$  ppm**

S.No.	Compound	s,3H, H <sub>3</sub> C–C	s,3H,H <sub>3</sub> C– N	m, 9H, Ar	s, 3H, H <sub>3</sub> C–O	s,1H, CH=N
1	FIBA (C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> )	1.131	1.812	6.217– 6.984	3.27	8.91
2	[Co <sup>II</sup> (L <sub>2</sub> )]Cl <sub>2</sub> (CoC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	1.065	1.812	6.217– 6.984	3.27	8.24
3	[Ni <sup>II</sup> (L <sub>2</sub> )] Cl <sub>2</sub> (NiC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	1.131	1.812	6.217– 6.984	3.27	8.24
4	[Cu <sup>II</sup> (L <sub>2</sub> )]Cl <sub>2</sub> (CuC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	1.131	1.812	6.217– 6.984	3.27	8.24

**Table-4:  $^{13}\text{C}$  NMR Spectral data of ligands and their metal complexes of 2,4-Furyliminobenzylacetophenone schiff base. (DMSO- $d_6$ ):  $\delta$  ppm**

S.No.	Compound	1C,CH <sub>3</sub> - C	1C, CH <sub>3</sub> -N	1C, CH <sub>3</sub> -O	12C, CH-Ar	1C, C-N	1C, C=O	1C, CH=N
1	FIBA (C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> )	11.23	19.27	58.39	128.52– 123.29	142.22	158.88	171.14
2	[Co <sup>II</sup> (L <sub>2</sub> )]Cl <sub>2</sub> (CoC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	11.23	19.27	58.39	128.52– 123.29	142.22	158.88	165.35
3	[Ni <sup>II</sup> (L <sub>2</sub> )] Cl <sub>2</sub> (NiC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	11.23	19.27	58.39	128.52– 123.29	142.22	158.88	165.35
4	[Cu <sup>II</sup> (L <sub>2</sub> )]Cl <sub>2</sub> (CuC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	11.23	19.27	58.39	128.52– 123.29	142.22	158.88	165.05

### Antimicrobial Activity:

#### Antibacterial Activity

The newly synthesized ligands and their metal complexes were screened for their antibacterial activity against *Staphylococcus aureus* (ATCC 25923) and *Staphylococcus aureus* (ATCC 3160) bacterial species using the agar well diffusion method. 10–24 hour bacterial solution containing  $\sim 10^4$ – $10^6$  colony forming units (CFU)/mL were used. The test sample's (1 mg/mL in DMF) concentration (100  $\mu$ L) was introduced in the petric disc. New petric dishes were incubated immediately at 37°C for 24 h activities was determine by measuring the diameter of zones showing complete inhibition (mm). Growth inhibition was compared with the standard drug.

**Table-5: Antibacterial screening data of ligand and their metal complexes**

Compound	Average % inhibition after 48 h. (conc. in ppm)			
	Staphylococcus aureus (ATCC 25923)		Staphylococcus aureus (ATCC 3160)	
	500	1000	500	1000
FIBA (C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> )	29	42	30	35
[Co <sup>II</sup> (L <sub>2</sub> )]Cl <sub>2</sub> (CoC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	43	51	41	53
[Ni <sup>II</sup> (L <sub>2</sub> )] Cl <sub>2</sub> (NiC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	43	50	41	44
[Cu <sup>II</sup> (L <sub>2</sub> )]Cl <sub>2</sub> (CuC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	42	51	42	55
Bavistin	84	100	80	99

### Antifungal Activity

Antifungal activities of all compounds were studied against two fungal cultures *Candida albicans* (227) and *Staphylococcus cerevisiae* (361) fungal species. Sabouraud dextrose agar was seeded with 10<sup>5</sup> mL<sup>-1</sup> fungal spore suspension and transferred to petric plates. Dishes soaked in 20 mL (10 µg/mL in DMF) of the entire agar surface. The plates were incubated at 32°C for 24 h. the results were recorded as zones of inhibition (mm) and compared with the standard drug Streptomycin.

**Table-5: Fungicidal screening data of ligand and their metal complexes.**

Compound	Average % inhibition after 48 h. (conc. in ppm)			
	<i>Candida albicans</i> (ATCC 227)		<i>Staphylococcus cerevisiae</i> (ATCC 361)	
	500	1000	500	1000
FIBA (C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> )	5	8	6	10
[Co <sup>II</sup> (L <sub>2</sub> )]Cl <sub>2</sub> (CoC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	7	14	7	15
[Ni <sup>II</sup> (L <sub>2</sub> )] Cl <sub>2</sub> (NiC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	8	11	7	16
[Cu <sup>II</sup> (L <sub>2</sub> )]Cl <sub>2</sub> (CuC <sub>32</sub> H <sub>30</sub> N <sub>6</sub> O <sub>4</sub> Cl <sub>2</sub> )	9	17	10	12
Streptomycin	16	18	16	18

### III. MINIMUM INHIBITORY CONCENTRATION

Compounds showing antibacterial activity over 8% were selected for minimum inhibitory concentration studies. The MIC was determined using the disc diffusion technique by prepared uses containing 500 and 1000  $\mu\text{g/mL}$  of the compounds (Figure 1).

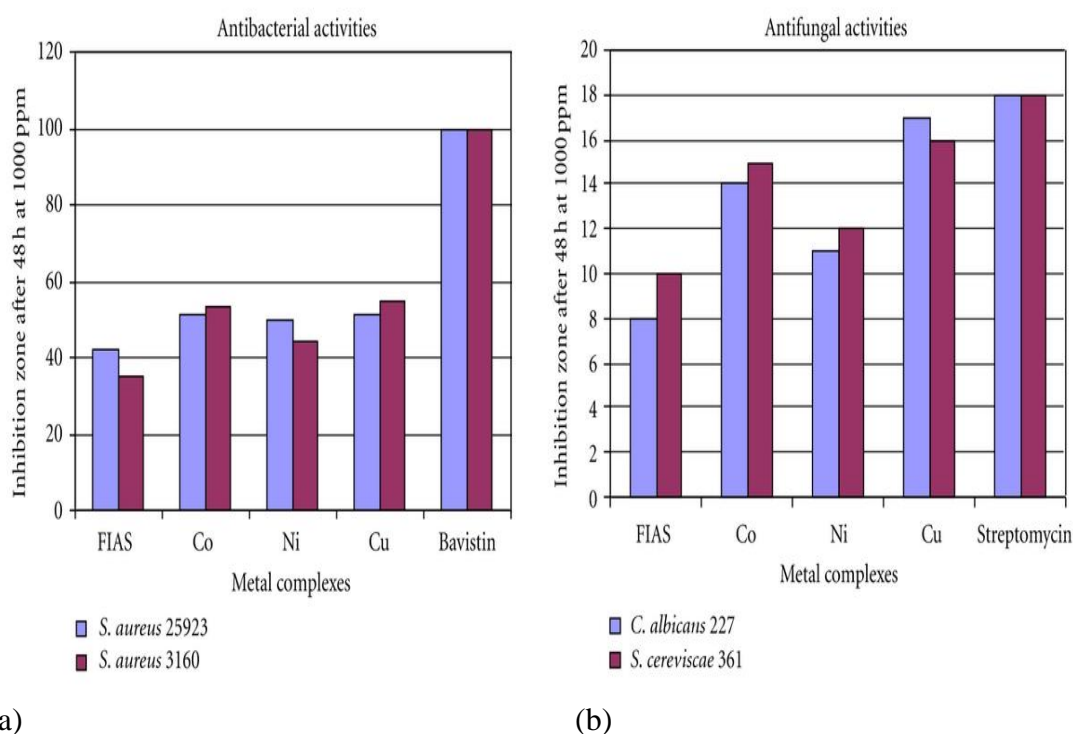


Figure 1: Plot of antibacterial (a) and antifungal (b) activity of ligand and their metal complexes in 1000 ppm conc.

### IV. RESULT AND DISCUSSION

The structure of newly synthesized ligand was established with the help of their IR, NMR ( $^1\text{H}$  &  $^{13}\text{C}$ ) and analytical data. All the metal complexes and Schiff base ligand were stable in air and moisture and they were synthesized by the stoichiometric reaction of the corresponding metal (II) chloride with ligand in a molar ratio M: L of 1: 2. All of the metal complexes were insoluble in the common organic solvents and only soluble in DMF/DMSO. Molar conductance value of the soluble complexes in DMF ( $10^{-3}$  M solution at  $25^\circ\text{C}$ ) indicated that chloride ion were in the outer sphere and show the non-electrolytic in nature. We agree with the proposed structure of the ligand on the basis of elemental analysis data in which the ligand contain three donor sites one is azomethine (HC=N) nitrogen, and other carbonyl (C=O) oxygen atom. IR spectra of the ligand observed at  $1615\text{ cm}^{-1}$  are assigned to the  $\nu(\text{C}=\text{N})$  mode and a band at  $810\text{ cm}^{-1}$  due to  $\nu(\text{C}-\text{N})$  pyrrolyl ring. The peak of azomethine group was found in the lower wave frequency in the IR spectra of the complexes which was evidence of the nitrogen bonding of the azomethine group to the central metal ions. The  $\nu(\text{C}=\text{O})$  carbonyl band in the ligand appeared at  $1645\text{ cm}^{-1}$ . This frequency was shifted to the lower frequency in the spectra of the complexes which was indicated the coordination of the carbonyl oxygen atom to the central metal ions. This is further confirmed by the appearance of the new band at  $515\text{--}525$  and  $425\text{--}430\text{ cm}^{-1}$  due to the  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{O})$ <sup>(34, 35)</sup>. The NMR spectrum of the ligand was done in DMSO- $d_6$ . The  $^1\text{H}$  NMR spectral data are reported along with the possible assignments in the experimental section. All the protons due to aromatic groups were found to be in their expected region. The conclusions of these studies lend further



support to the mode of bonding discussed in their IR spectra.  $^{13}\text{C}$  NMR spectrum of the ligand, signals between 111.9 and 181.5 due to aromatic ring carbons. The peak of carbonyl carbon at 169.7 ppm was shifted to the lower frequencies. The UV-visible spectrum of  $\text{Cu}^{\text{II}}$  complex in DMSO solution displays a broad band at  $10718\text{ cm}^{-1}$  and a well-defined shoulder around  $22831\text{ cm}^{-1}$  attributable to  ${}^2\text{B}_{1g} \rightarrow {}^2\text{A}_{1g}$  transitions which strongly favor octahedral geometry around the  $\text{Cu}^{\text{II}}$  ion<sup>(36)</sup>. This is further supported by the magnetic susceptibility value (1.83 BM). The cobalt complex shows a d-d band at  $16216\text{ cm}^{-1}$  as signed to  ${}^2\text{A}_{1g} \rightarrow {}^2\text{B}_{1g}$  transition which confirmed square-planer geometry. This is further confirmed by its magnetic susceptibility value (3.85 BM). The electronic spectra of the nickel (II) complex exhibited<sup>(37-39)</sup> absorption bands at  $\sim 16,670$  and  $\sim 27,780\text{ cm}^{-1}$ , attributable to  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$ , transitions, respectively, in an octahedral geometry. The calculated values of the ligand field parameters lie in the range reported for an octahedral structure<sup>(40,41)</sup>. Also, the values of the magnetic moment (3.2–3.7 B.M.) may be taken as additional evidence for their octahedral structure. The magnetic moment values are of great significance in a structural context in the case of  $\text{Co}^{\text{II}}$  complexes. Magnetic moments of tetrahedral, octahedral and square planar complexes differ significantly and therefore structural type can be easily identified using magnetic data. In octahedral complexes, the ground state ( ${}^4\text{T}_{1g}$ ) is orbitally degenerate and this causes large orbital contribution to the magnetic moment. The  $\mu_{\text{eff}}$  value measured for the  $\text{Co}^{\text{II}}$  complex is 5.32 B.M, indicating octahedral geometry<sup>(42)</sup> of the  $\text{Co}^{\text{II}}$  ion in the complex. The reflectance spectrum of the complex showed a band at 656 nm and a shoulder at 477 nm, besides the ligand absorptions. The former band would be due to a  ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$  electronic transition, indicating an octahedral configuration around  $\text{Co}^{\text{II}}$  ions. On the basis of the above observations, it is tentatively suggested that all of the complexes show an octahedral geometry in which ligands act as bidentates. These possibly accommodate themselves around the metal atom in such a way that a stable chelate ring is formed giving, in turn, stability to the formed metal complexes.

## V. CONCLUSION

In this paper we have described that the all the synthesized transition metal complexes of Schiff base by condensation method. In the present investigations, all the complexes found to be mononuclear were obtained for  $\text{Co}^{\text{II}}$ ,  $\text{Ni}^{\text{II}}$  and  $\text{Cu}^{\text{II}}$  cations in presence of ligand. The results of antimicrobial activities show that the metal-complexes exhibit antimicrobial properties and it is important to note that they show enhanced inhibitory activity compared to parent ligand. All the investigated compounds showed less to good activity against *S. aureus*.

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