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Synthesis, characterization and antimicrobial activity of Cobalt(II), Nickel(II) and Zinc(II) complexes with azo ligand derived from 1-(4-amino phenyl) ethanone

S. Karthikeyan^{1*}, N. Sampath Kumar¹, R. Ebenezer², S. Chandra Mohan³
and P. Balasubramanian⁴

¹Department of Chemistry, SSM Institute of Engineering and Technology, Dindigul, Tamil Nadu, India

²Department of Chemistry, The American College, Madurai, Tamil Nadu, India

³Research and Development Centre, Bharathiar University, Coimbatore, Tamil Nadu, India

⁴Department of Chemistry, Saiva Bhanu Kshatriya College, Aruppukottai, Tamil Nadu, India

ABSTRACT

The azo base of 1-(4-amino phenyl) ethanone and their complexes were synthesized and well characterized by elemental analysis, spectral studies, conductivity and magnetic measurements. All the complexes have lower molar conductance values, indicating their non-electrolytic nature. The synthesized ligands, along with their metal complexes were screened for their in-vitro antibacterial activity against Gram-negative (*Escherichia coli*) and a Gram-positive (*Staphylococcus aureus*) bacterial strains and for in-vitro antifungal activity against *Candida albicans*. The results of these studies revealed that all the compounds and their metal complexes showed significant antibacterial and antifungal potency.

Keywords: Azo ligand, metal complexes, Antibacterial, Antifungal, 1-(4-amino phenyl) ethanone

INTRODUCTION

Metal complexes of azo dye ligand have played a central role in the development of co-ordination chemistry [1]. The systematic synthetic study of azo dye ligand complexes was commenced by Farben Fabriken Bayer et. al [2] and Kraska et.al [3]. A survey of the literature reveals that much work has been done on the synthesis and physico-chemical studies of metal complexes of number of azo dye ligand [4-8]. Recent studies revealed that studies of azo based ligand and its metal complexes are used for organometallic application. The azo base of 4-amino phenyl ethanone and their complexes have received most of the attention, because of the magnetic, spectroscopic, biological and photosensitive properties. Lot of studies has been under taken on azo base ligands and their respective complexes. 4-amino phenyl ethanone have shown a wide variety of anticancer, antimicrobial, antifungal, antidepressant, antitumor, antibacterial, anti-inflammatory and anticonvulsant activities [9]. In addition 4-amino phenyl ethanone are widely used for various optical application including holographic recording materials and fluorescent probes for sensing of metal ions.

The objectives of this paper were to synthesize azo ligand and their metal (II) complexes and study their spectral and biological activity. The ligand and its complexes characterized by various physico-chemical techniques such as elemental analysis, conductance, magnetic moment, UV-VIS, ¹H-NMR, IR and mass spectroscopy. The

antibacterial activity of ligand and their metal (II) complexes studied by agar cup plate method and the zone inhibition recorded.

MATERIALS AND METHODS

Electronic Spectrometric Measurement

In many applications other techniques could be employed but none rival UV-Visible spectrometry for its simplicity, versatility, speed, accuracy and cost-effectiveness. The electronic spectra of ligand and their metal complexes were recorded using Jasco V-530 spectrophotometer with 1 cm matched quartz cell in the range 190-1100 using DMSO as a solvent.

Infrared Spectrophotometric Measurement

The infrared spectra of all complexes were recorded in KBr disc on a Shimadzu double beam infrared spectrophotometer and measuring the relative intensity of transmitted light energy versus wave number in the region of 4000-400 cm^{-1} .

$^1\text{H-NMR}$ Spectrometric Measurement

The proton NMR spectra of the ligand was recorded in ^1H NMR spectra were recorded in CDCl_3 using Bruker DRX-300, 300MHz NMR spectrometer.

Conductometric Measurement

Conductivity measurements were made using a Toshniwal conductivity bridge (CL 01/02 A) with a dip-type cell fitted with a platinised platinum chloride. Approximately 1×10^{-3} m solution of the complexes was employed for the conductivity measurements. All the measurements were taken at room temperature on freshly prepared solutions

Experimental Work

The experimental work mainly concerns with the synthesis of Co (II), Ni (II) and Zn (II) complexes from its corresponding ligand.

Synthesis of ligand (Scheme I)

10 mmol of 1-(4-amino phenyl) ethanone and 5ml of distilled water were taken in a round bottom flask. Then 5 ml of diluted hydrochloric acid solution was added drop wise with continuous stirring in a magnetic stirrer for 30 mins. The reaction mass was cool to 273K. Then 1mmol of sodium nitrite in water was added slowly to the reaction mixture. The reaction mass was stirred for 30 mins at 0°C . Then 10 mmol of salicylaldehyde taken in distilled water was added to the reaction mass. The whole reaction mixture was stirred at same temperature for one hour. The precipitate was filtered and washes with distilled water then dried.

Yield: 96%, Melting point: 178°C , Elemental analysis: $\text{C}_{15}\text{H}_{12}\text{O}_3\text{N}_2$, Calc: C 67.16, H 4.51, O, 17.89, N, 10.44, Found: C 67.13, H 4.48, O 17.86, N 10.42; NMR (δ in ppm): 6-9 (m) - aromatic ring protons, 2.8 (s)- CH_3 protons, 11.4 (s) - CHO protons, 10.0 (s) - OH protons; IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})_a$ 1672cm^{-1} , $\nu(\text{C}=\text{C})$ 1488cm^{-1} , $\nu(\text{N}=\text{N})$ 1598cm^{-1} , UV-Vis (Freq, cm^{-1}): 27777, 26881 cm^{-1}

Synthesis of Complexes (Scheme II)

[Co (L)₂] Complex:

The pale green complex [Co (L)₂] was synthesized by the reaction of 1mmol (0.536g) of ligand and 1mmol (0.474g) of cobalt chloride in 20 ml of ethanol. It was stirred for 3 hours. A powdery substance was obtained. It was filtered and dried.

Yield: 87%; Melting point: $>360^\circ\text{C}$; Elemental analysis: $\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4\text{Co}$ Calc: C 60.72, H 3.74, O 16.18, N 9.44; Found: C 60.70, H 3.72, O 16.16, N 9.42; IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})_a$ 1656cm^{-1} , $\nu(\text{Co}-\text{O})$ 416cm^{-1} , $\nu(\text{C}=\text{C})$ 1499cm^{-1} , $\nu(\text{N}=\text{N})$ 1591cm^{-1} , UV-Vis (Freq, cm^{-1}): 23364, 23041, 13495 cm^{-1} , Conductivity: 1.95 μS .

[Ni (L)₂] Complex:

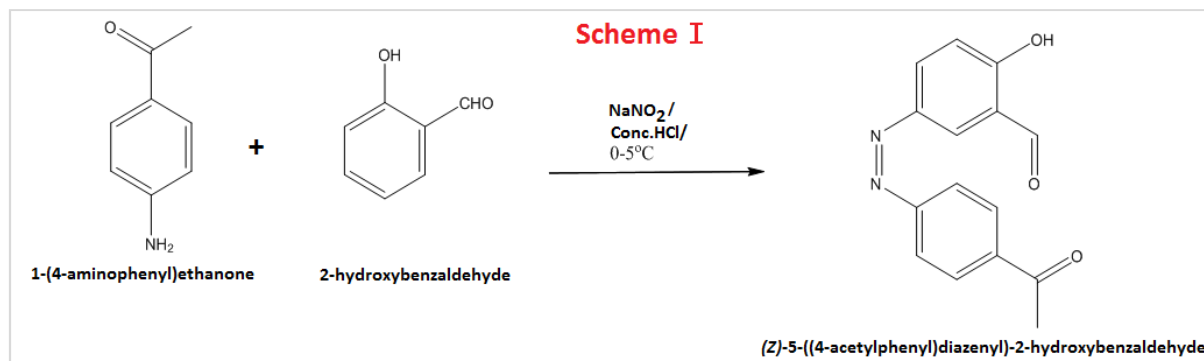
The green complex [Ni (L)₂] was synthesized by the reaction of 1mmol (0.268g) of ligand and 1mmol (0.237g) of nickel chloride in 20 ml of ethanol. It was stirred for 3 hours. A powdery substance was obtained. It was filtered and dried.

Yield: 86%; Melting Point: $>360^\circ\text{C}$; Elemental analysis: $\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4\text{Ni}$; Calc: C 60.74, H 3.74, O 16.18, N 9.44; Found: C 60.72, H 3.71, O 16.15, N 9.41; IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})_a$ 1655cm^{-1} , $\nu(\text{Ni}-\text{O})$ 407cm^{-1} , $\nu(\text{C}=\text{C})$ 1459cm^{-1} , $\nu(\text{N}=\text{N})$ 1592cm^{-1} , UV-Vis (Freq, cm^{-1}): 23809, 12674 cm^{-1} , Conductivity: 1.45 μS

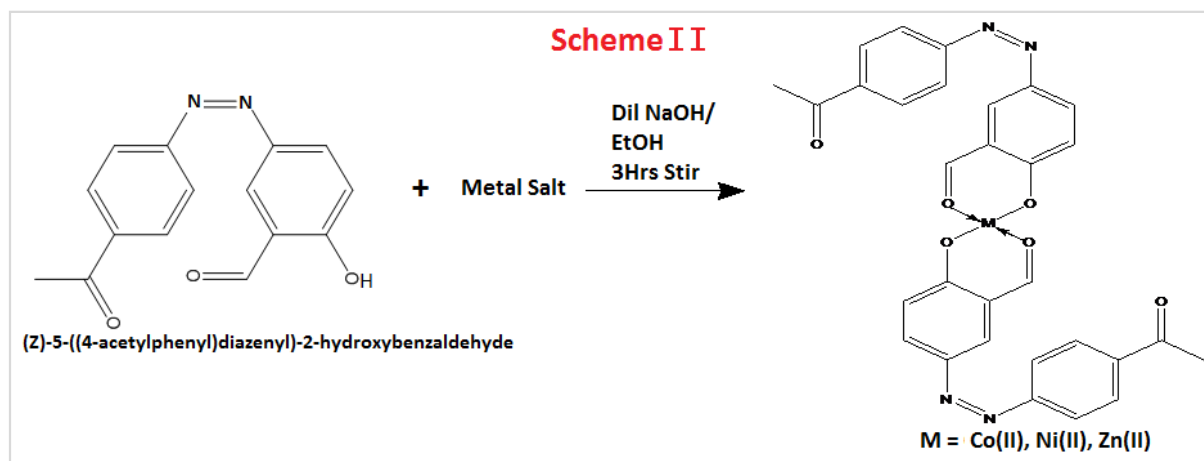
[Zn (L)₂] Complex:

The orange complex [Zn (L)₂] was synthesized by the reaction of 1mmol (0.268g) of ligand and 1mmol (0.136g) of zinc chloride in 20 ml of ethanol. It was stirred for 3 hours. A powdery substance was obtained. It was filtered and dried.

Yield:86%;Melting point:>360°C;Elemental analysis:C₃₀H₂₂O₆N₄ Zn;Calc: C 60.06, H 3.70, O 16.0, N 9.34;Found: C 60.03, H 3.68, O 15.58, N 9.32;IR (KBr, cm⁻¹): $\nu(\text{C}=\text{O})_a$ 1655cm⁻¹, $\nu(\text{Zn}-\text{O})$ 414cm⁻¹, $\nu(\text{C}=\text{C})$ 1457cm⁻¹, $\nu(\text{N}=\text{N})$ 1589 cm⁻¹;NMR (δ in ppm:6-9(m) - aromatic ring protons, 2.8(s) - CH₃ protons , 11.9(s) - CHO protons



Synthesis of ligand (Scheme I)



Synthesis of complexes (Scheme II)

Determination of antimicrobial activity

The antimicrobial activity was performed by agar cup plate method.

Microorganisms

Staphylococcus aureus (Gram-positive), *Escherichia coli* (Gram negative) and fungi as *Candida albicans* were the microorganisms used and they were obtained from the Microbiology Laboratory of the Thanjavur Medical College Hospital, Thanjavur. These microorganisms were identified and confirmed by Microbiologists, Department of Microbiology, Thanjavur Medical College, Thanjavur.

Preparation of 24 hours pure culture

A loop full of each of the microorganisms was suspended in about 10ml of physiological saline in a Roux bottle. Each of these was streaked on to the appropriate culture slants and was incubated at 37°C for 24 hours except for *Candida albicans* which was incubated at 25°C for 24-48 hours. After completion of incubation period, when growth was observed the tubes were kept into 2-8°C until use.

Sample solutions for the experiment

The sample solution 150 μ l were used for the experiment. Standard antibiotic solution as *Chloromphenical* for bacteria and *Nystatin* (25mg/ml distilled water- 30 μ l) for fungi used to compare the test solution.

Preparation of dried filter paper discs

Whatman filter paper (No:1) was used to prepare discs approximately 6 mm in diameter, which are placed in hot air for sterilization. After sterilization, the discs were loaded with different concentrations of prepared sample solutions again kept under refrigeration for 24 hrs.

Application of discs to inoculated agar plates

Previously prepared paper discs were dispensed onto the surface of the inoculated agar plate. Each disc was pressed down firmly to ensure complete contact with the agar surface. The discs were placed on the medium suitably apart and the plates were incubated at 5°C for 1 hr to permit good diffusion and then transferred to incubator at 37°C for 24 hrs. After completion of 24hrs, the plates were inverted and placed in an incubator set to respective temperature for 24 hrs

Antimicrobial assay

Antibiogram was done by disc diffusion method [10,11]. Petri plates were prepared by pouring 30 ml of NA /PDA medium for bacteria/fungi. The test organism was inoculated on solidified agar plate with the help of micropipette and spread and allowed to dry for 10 mins. The surfaces of media were inoculated with bacteria/fungi from a broth culture. A sterile cotton swab is dipped into a standardized bacterial/ fungi test suspension and used to evenly inoculate the entire surface of the Nutrient agar/PDA plate. Briefly, inoculums containing *Escherichia coli* was spread on Nutrient agar plates for bacteria and *Candida albicans* was spread on potato dextrose agar for fungus strains. Using sterile forceps, the sterile filter papers (6 mm diameter) containing the sample (150µl and 30µl for respective standard) were laid down on the surface of inoculated agar plate. The plates were incubated at 37°C for 24 h for the bacteria and at room temperature (30±1)°C for 24-48 hr. Each sample was tested in triplicate.

Measurement of zone of inhibition

The antimicrobial potential of test compounds was determined on the basis of mean diameter of zone of inhibition around the disc in millimeters. The zones of inhibition of the tested microorganisms by the extracts were measured using a millimeter scale.

RESULTS AND DISCUSSION**Solubility**

The ligand was soluble in organic solvents such as dichloromethane, dimethylsulfoxide, acetonitrile and acetone. All the complexes are completely soluble in dimethylsulfoxide and sparingly soluble in all other organic solvents.

Elemental Analysis

The elemental analysis data of the ligands and their metal complexes are summarized in **Table 1**. With estimated values in good agreement with theoretical ones.

Conductance

The metal complexes discussed here were dissolved in dimethylsulfoxide (DMSO) and the molar conductivities of their solutions (10^{-3} M) at room temperature were measured to establish the charge of the metal complexes. The molar conductance values obtained for these complexes at the concentration of 10^{-3} m are in the range of 5 - 28 $\text{ohm}^{-1}\text{mol}^{-1}\text{cm}^2$. These values are too low to account for any ionization of the complexes in dimethylsulfoxide. Hence these complexes are non electrolytic in nature.

Table.1. Elemental analysis data of the ligand and their metal complexes

S.no	Compound	Colour	Experimental(cal)%				$\Lambda_M \text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$
			C	H	O	N	
1	$\text{C}_{15}\text{H}_{12}\text{O}_3\text{N}_2$	Dark orange	67.16 (67.13)	4.51 (4.48)	17.89 (17.86)	10.44 (10.42)	-
2	$\text{Co}[\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4]\text{Cl}_2$	Pale green	60.72 (60.70)	3.74 (3.72)	16.18 (16.16)	9.44 (9.42)	10
3	$\text{Ni}[\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4]\text{Cl}_2$	Green	60.74 (60.72)	3.74 (3.72)	16.18 (16.15)	9.44 (9.42)	11
4	$\text{Zn}[\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4]\text{Cl}_2$	orange	60.06 (60.03)	3.70 (3.68)	16.00 (15.58)	9.34 (9.32)	5

Infrared Spectra

In order to study the binding mode of the ligand in the metal complex, the IR spectrum of the free ligand was compared with the spectra of the corresponding transition metal complexes. One of the most important features of infra-red spectroscopy is that a wide variety of samples can be examined by this technique. Gases, liquids or

solutions, all can be handled and used for the measurement of the infra red spectra. In coordination chemistry, when a ligand was coordinated, the atom will undergo vibrations leading to change in bond length and bond angles. So the IR spectrum of a coordinated ligand will differ from that of free ligand. Vibrational spectra of metal chelate compounds can be divided into the high frequency (4000-650 cm^{-1}) region and the low frequency (650-50 cm^{-1}) or far Infrared region. In general, vibrations which occur in the high frequency region originate in the ligand itself, where as those occur in the low frequency region originate in the metal-ligand coordinate bonds.

Table.2. IR Spectral data (cm^{-1}) ligand and their Metal Complexes

S.no	Compound	Frequency(cm^{-1})			
		$\nu(\text{C}=\text{C})$	$\nu(\text{N}=\text{N})$	$\nu(\text{C}=\text{O})_a$	$\nu(\text{M}-\text{O})$
1	$\text{C}_{15}\text{H}_{12}\text{O}_3\text{N}_2$	1488	1591	1672	-
2	$\text{Co}[\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4]\text{Cl}_2$	1499	1591	1656	416
3	$\text{Ni}[\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4]\text{Cl}_2$	1459	1591	1655	407
4	$\text{Zn}[\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4]\text{Cl}_2$	1457	1589	1655	414

The IR spectra data of the ligand and their complexes are given in **Table.2** The $\nu(\text{C}=\text{O})$ stretching frequency which was observed at 1672 cm^{-1} in ligand was shifted to 1656 cm^{-1} , 1655 cm^{-1} and 1655 cm^{-1} in cobalt, nickel, zinc complexes respectively indicating the coordination of aldehydic carbonyl group. The $\nu(\text{N}=\text{N})$ was observed at 1591 cm^{-1} in the ligand and was found to be unaltered in the complex, there by indicating the non participation of nitrogens of -N=N- group. The oxygen coordination to the metal ion was proved by the bands that appeared in the range of 416-407 cm^{-1} assigned to M-O modes.

Electronic Spectra

The electronic absorption spectra provide quick and reliable information about the ligand arrangement in transition metal complex. The electronic spectra of complexes can provide valuable information related to bonding and structure. Four types of electronic transitions are observed: a) d-d transition b) Ligand transition c) Metal to ligand charge transition d) Inner ligand transition. The UV-Vis spectral data of ligand and complexes are summarized in **Table 3**. This includes absorption region, band assignment, geometry and magnetic moment.

Table.3: The electronic spectral data (cm^{-1}) and magnetic moment data of the ligand and their metal complexes

S.no.	Compound	Frequency (cm^{-1})	Transition	Proposed Geometry	Magnetic moment (μ_{eff} , BM)
1	$\text{C}_{15}\text{H}_{12}\text{O}_3\text{N}_2$	27777 26881	INCT INCT	-	-
2	$\text{Co}[\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4]\text{Cl}_2$	23364 23041 13495	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{p})$ ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$	Square Planar	1.95
3	$\text{Ni}[\text{C}_{30}\text{H}_{22}\text{O}_6\text{N}_4]\text{Cl}_2$	23809 12674	${}^3\text{T}_1(\text{F}) \rightarrow {}^2\text{A}_2(\text{F})$ ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$	Square Planar	Dia magnetic

INCT - Intravalence Charge Transfer.

The electronic spectrum of the cobalt complex of the ligand exhibits adsorption band at 23364 cm^{-1} , 23041 cm^{-1} and 13495 cm^{-1} these are assigned to ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{p})$, ${}^4\text{T}_{1g} \rightarrow {}^4\text{A}_{2g}$ and ${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}$ respectively suggesting a square planar geometry for the cobalt complex. The electronic spectrum of the nickel complex of the ligand exhibits adsorption band at 23809 cm^{-1} and 12674 cm^{-1} assigned to ${}^3\text{T}_1(\text{F}) \rightarrow {}^2\text{A}_2(\text{F})$ and ${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$ respectively their by suggesting the complex to have square planar geometry.

Magnetic Moment

Magnetic moment values for the complexes of ligand are shown in **Table.3**. The cobalt complex of the ligand showed magnetic moment value of 1.95BM, inferring a square planar geometry. The nickel complex showed diamagnetism suggesting square planar geometry.

${}^1\text{H-NMR}$ Spectroscopy

${}^1\text{H-NMR}$ spectral data (δ) of the Ligand

${}^1\text{H-NMR}$ spectral data of the ligand was recorded in d^6 -DMSO. Spectrum of the free ligand showed multiplet, observed between 6.0-9.0 ppm due to aromatic ring protons. The methyl signal appeared as singlet at 2.8 ppm. The hydroxyl signal appeared as singlet at 10.0 ppm and aldehydic proton appears as singlet at 11.4 ppm as singlet.

Mass Spectra

Mass Spectrum of Ligand

Ligand showed molecular ion (M^+) peak at m/z 268. The other fragments were observed at m/z 78, 93, 122, 136, 150, 208, and 254. The mass spectrum of ligand clearly confirms the structure of ligand as the reaction product.

Biological Activity

The azo-ligand is more antibacterial activity than metal complexes. Cobalt complex shows more antifungal activity than other compounds(**Figure1**).

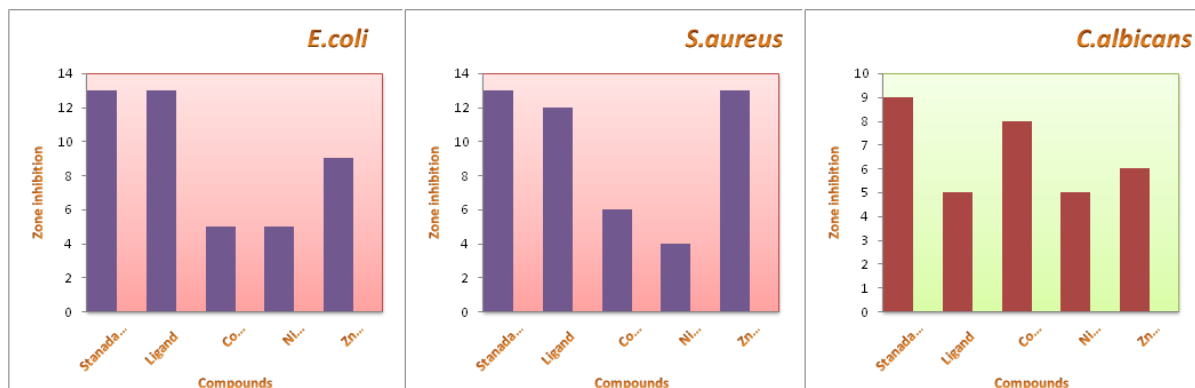


Figure1. Antimicrobial activity of ligand and metal complexes

CONCLUSION

The new cobalt (II), nickel (II) and zinc (II) complexes synthesized from ligand which was obtained by the condensation 1-(4-aminophenyl) ethanone and salicylaldehyde. The ligand and their metal complexes were characterized by spectral and analytical techniques. Low conductance values for all the complexes of ligand indicate that they are non-electrolytes. From these values it has been concluded that no anions are present outside the coordination sphere. Square planar geometry for all the complexes was proposed by spectral and magnetic moment data. The antibacterial studies indicate that the ligand showed more activity compared to complexes.

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