



BIO-ACTIVE SCHIFF BASE TRANSITION METAL COMPLEXES DERIVED FROM 4- AMINO BENZAMIDE AND 3,5-DICHLORO-2- HYDROXYACETOPHENONE

Abstract: Coordination transition metal complexes of Co(II) and Zn(II) ions with Schiff base ligand formed by condensation reactions using 3,5-dichloro-2-hydroxyacetophenone and 4-amino benzamide. The synthesized Schiff base is bidentate (ON) donor ligand to the metal ions. Both the ligand and the metal complexes are characterized by the various physico-chemical methods such as elemental analysis, molar conductance, UV, IR, NMR, powder XRD and ESR spectra. The spectral studies reveals that the complexes obtained as mononuclear structure and are four-coordinated metals center moieties with square planar geometry. Synthesized compounds are screened for their anti-bacterial activity against Gram positive and Gram negative bacteria by the well diffusion method.

Index Terms - Component, formatting, style, styling, insert.

I. INTRODUCTION

In current years much attention has been dedicated by coordination transition complexes due to their biological importance especially in the designing of long acting drugs in metabolism. The bidentate Schiff base metal complexes have been frequently studied recently because of their industrial applications^{1, 2}. Transition Schiff base metals are extensively studied due to their interesting biological activities and crucial for normal functioning of living organism. They have been reported to be useful in pharmacological field and catalyst. They are known to exhibit potent antibacterial, antiulcer and analgesic activities³. Additionally some Schiff bases show pharmacologically helpful actions similar to anticancer, anti-tuberculosis and antioxidant activities⁴. A grand deal of consideration in this area has been listening carefully, spectral characterization and anti-bacterial activities of novel Heterocyclic Schiff base mononuclear metal complexes obtained by the condensation of 3,5-dichloro 2-hydroxyacetophenone and 4-amino benzamide by conventional methodology as described in the literature. Many studies reported several metal complexes of Schiff base derived from 3,5-dichloro 2-hydroxyacetophenone and their biological activity.

II Experimental

2.1 Materials and methods

According to the literature here we have synthesized and explored the structural determination of ligands (having oxygen and nitrogen donors), derived from 3,5-dichloro 2-hydroxyacetophenone with various derivative of 4-aminobenzamide and its mononuclear Co(II) and Zn(II) metal complexes. These metal complexes were structurally characterized by various chemical and analytical techniques such as elemental analysis, conductivity, UV-VIS, FT-IR, ESR, XRD, and ¹HNMR spectra. The antibacterial activity of the ligand and the mononuclear metal complexes had also been researched.

2.2 Synthesis of Schiff base ligand

The unsymmetrical Schiff base ligand was prepared by the condensation of 3,5-dichloro 2-hydroxyacetophenone (0.820g, 4mmol) and 4-aminobenzamide (0.5446g, 4mmol) in the molar ratio of 1:1, using methanol as a solvent with constant stirring and refluxed for 3 hours and cooled at the room temperature. The isolated orange colour solid product was separated by the slow evaporation method.

2.3 SYNTHESIS OF METAL COMPLEXES

The Schiff base metal complexes were prepared by refluxing the appropriate molar quantities of the Schiff base ligand synthesized and the metal acetate following the standard procedure.

2.3.1 Synthesis of [Co L]

A methanolic solution of ligand L (0.3053g, 1mmol) was added to a solution of cobalt acetate (0.4758 g, 1mmol) in 20 ml of methanol. The stirring mixture was refluxed for 3 hours the solution was allowed to cool at room temperature and the solid product obtained was dried in air.

2.3.2 Synthesis of [Zn L]

A methanolic solution of ligand L (0.3053g, 1mmol) was added to a solution of zinc acetate (0.4758 g, 1mmol) in 20 ml of methanol. The stirring mixture was refluxed for 3 hours the solution was allowed to cool at room temperature and the solid product obtained was dried in air.

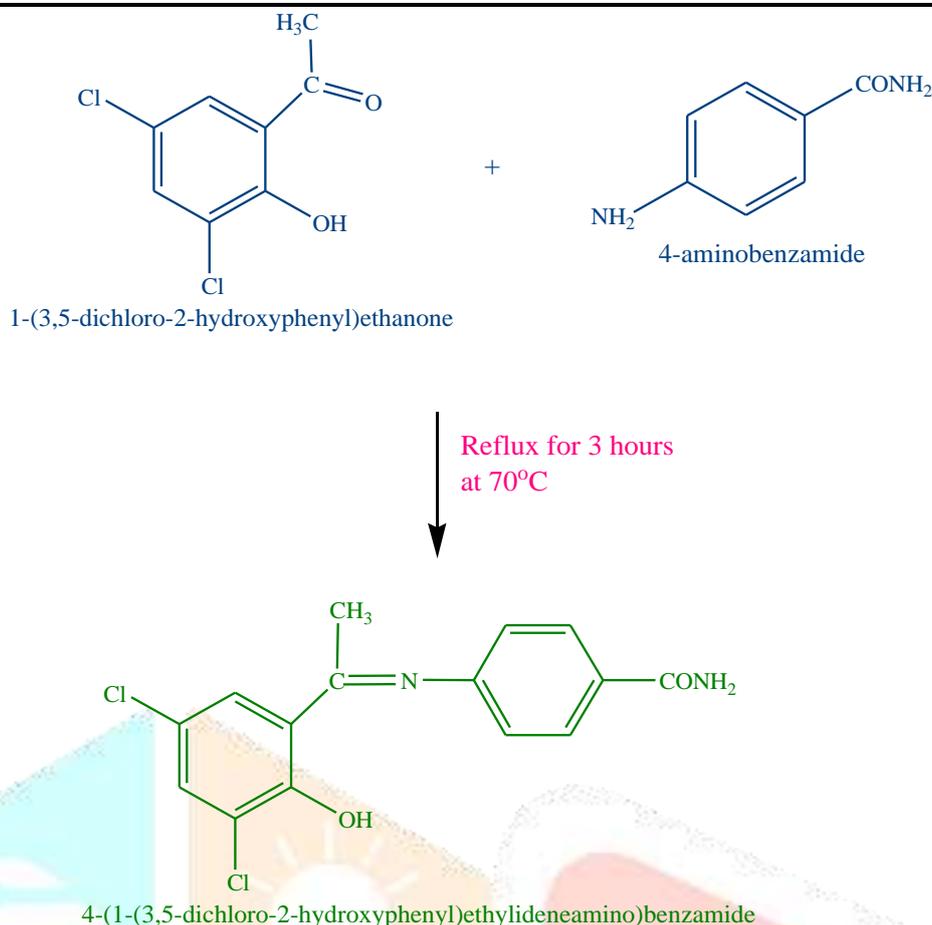


Fig:1 Synthetic route for the preparation of Schiff base ligand

III RESULT AND DISCUSSION

The color, melting point, elemental analysis and empirical formulae of the prepared Schiff base and its complexes are listed in Table 2. The results of the elemental analysis are in good agreement with the calculated values. The metal contents of the complexes were determined according to literature methods. The mononuclear complexes were stable in air, non-hygroscopic, insoluble in water and most organic solvents, but are easily soluble in ethanol and DMSO.

3.1 ELEMENTAL ANALYSIS

The elemental analyses shows that, the Co(II) and Zn(II) complexes have 1:2 stoichiometry of the type ML where in L acts as a bidentate. The elemental content of the present complexes were compared with the formulation. The difference between the two values was found to be greater than acceptable limits of experimental errors. All the carbon, hydrogen, nitrogen, oxygen, sulphur and metal contents of the complexes have been determined and the results, which were in good agreement with those calculated for the suggested formulae. The isolated mononuclear Schiff base metal complexes have general composition $[ML_2]$, where M is Co(II) & Zn(II), L= Schiff base ligand. The melting point of the Schiff base ligand was below 170°C and their metal complexes were above 250°C.

3.2 MOLAR CONDUCTIVITY STUDIES

The solution conductivity measurements were performed to establish the charge type of the complexes⁵. The complexes were dissolved in DMSO and the molar conductivities of 10^{-3} M of their solutions at 29°C were measured. The conductance of the metal complexes was carried out in DMSO and the values were found to be in the range 30-46 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ suggesting that the complexes belong to non-electrolytes.

3.3 INFRARED SPECTRA

The IR spectra provide valuable information regarding the nature of functional group and mode of bonding to the metal atom⁶. The IR spectra of the Schiff base metal complexes are compared with the free ligand to determine the coordination sites may be involved in the chelation. The important IR frequencies exhibited by the Schiff base ligand and their corresponding metal complexes are tabulated (Table 1 and Fig.2). The broad band in the range 1674 cm^{-1} were observed due to $\nu(\text{C}=\text{N})$ which has been shifted towards lower region at around $1640\text{-}1594\text{ cm}^{-1}$ in the complexes indicating the participation of the azomethine group in the complex formation⁷, this shift is also due to the reduction of double bond character of carbon-nitrogen bond of azomethine group. The Schiff base ligands shows an intensity band at around 3431 cm^{-1} due to phenolic $\nu(\text{-OH})$ which is absence in metal complexes indicating the coordination through the phenolic oxygen atom and also due to the conversion of hydrogen bonded structure into a covalent metal bonded structure. The band at $3465\text{-}3203\text{ cm}^{-1}$ was due to the presence of amide group. The coordination through nitrogen of azomethine and oxygen of $\nu(\text{C-O})$ of ligand are further evidenced by the appearance of non-ligand bands around $457\text{-}550\text{ cm}^{-1}$ and $550\text{-}555\text{ cm}^{-1}$ are due to M-N and M-O bonds respectively.

3.4 ELECTRONIC SPECTRA AND MAGNETIC MOMENT

The nature of the ligand field around the metal ion was deduced from the electronic spectra⁸. The Schiff base ligand shows an absorption bands of $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ in the region from 215 and 303 nm. On complexation these bands were shifted. The electronic spectra of Co(II) complex display the absorption band in the range 246, 320, 473 nm due to the presence of $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, $L \rightarrow M$ transition and the d-d transition bands in the region 679 nm, which are due to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition⁹. The measured value of the magnetic moment for Co(II) complex was 3.91 BM. The electronic spectra of Zn(II) complex show the absorption bands in the range 450, 326 and 245 nm. The Zn(II) ions with its d^{10} configuration does not show any d-d transition. Due to the d^{10} system of Zn(II) complex shows diamagnetic in nature because of unavailability of unpaired electrons in the system. These absorption spectra and the magnetic moment values suggest that the both the metal complexes possess square planar geometry¹⁰.

3.5 ¹H NMR SPECTRA

The ¹H NMR spectra of Schiff base (C₁₅H₁₂Cl₂N₂O₂) ligand was recorded in DMSO at room temperature (Fig. 3). The chemical shifts were recorded with respect to TMS. Presence of phenolic hydrogen was confirmed by the singlet peak appears at 12.5 ppm. The multiplet in the region of 6.8–7.9 ppm is due to aromatic protons. The singlet signal formed at the region of 2.7 ppm showed that the presence of methyl proton. A singlet peak appears at 6.5 ppm indicates that the presence of amide (–CONH₂) in the prepared Schiff base ligand. All these observations support the infrared and electronic conclusions¹¹.

3.6 ESR SPECTRA

The X-band EPR spectra of mononuclear Co(II) complex were recorded at room temperature (Fig.4). The g tensor values of this cobalt(II) complex can be used to derive the ground state. In square-planar complexes, the unpaired electron lies in the dx²–y² orbital giving g_{||} > g_⊥ > 2 while the unpaired electron lies in the dz² orbital giving g_⊥ > g_{||} > 2. From the observed values, it is clear that g_{||} > g_⊥ > 2 suggesting that the complex is square-planar. This is also supported by the fact that the unpaired electron lies predominantly in the dx²–y² orbital¹².

The g values observed for mononuclear Co(II) complex g_{||} = 2.3425, g_⊥ = 2.0833, G = 4.11. The g_{||} and g_⊥ values are greater than 2.04 which confirmed the existence of unpaired electron in the dx²–y²orbital corresponds to square planar geometry around the Co(II) center is an important function for indicating covalent character of M-L bonds. For ionic character, g_{||} > 2.30 while in covalent character g_{||} < 2.30. In the present compounds, the g_{||} < 2.30 indicating the presence of unpaired electrons is localized in the dx²–y²orbital. The exchange interaction between cobalt centers are measured by the expression G = (g_{||} - 2)/(g_⊥ - 2). The G value (4.11) indicates that there is no exchange interaction between the metal complex and Schiff base ligand.

3.7 X-RAY DIFFRACTION:-

Powder XRD analysis of Schiff base metal complexes Co(II), and Zn(II) were recorded (2θ range from 10-80) using Cu Kα radiation (λ = 1.5406 Å). The average crystal size of the samples was calculated by using the Debye-Scherrer formula.

$$D = (0.9\lambda) / (\beta \cos\theta)$$

where λ is the wavelength (Cu Kα), β is the full width at the half maximum (FWHM) of the metal oxide line and θ is the diffraction angle. The metal complexes Co(II) and Zn(II) shows the sharp crystalline peaks due to their crystalline phase (Fig.5). The Diffraction peaks of the Co(II) complex could be well indexed as face-centered cubic phase at about 2θ = 10.61, 12.34, 21.43, 22.32, 32.40 and 48.50 which are attributed to [100], [100], [200], [200], [200], [300] and [420] crystal planes, respectively (Table 2.1). Likewise the Zn(II) also shows the well indexed diffraction peaks as face-centered cubic phase at about 2θ = 12.65, 22.50 and 48.11 which are allotted to [100], [111] and [321] (Table 2.2). The average crystallite size of the Co(II) and Zn(II) were 20.39 nm and 32.19 nm insinuating nano crystalline nature.

3.8 ANTIBACTERIAL ACTIVITY

An antimicrobial is a substance that kills or inhibits the growth of microorganisms such as bacteria, fungi or protozoan's. In recent times numerous antimicrobial drugs have been developed to kill or inhibit the growth of pathogenic microbes. The microbes have the ability to bind to metal ions present in the external environment at the cell surface and to transport them into the cell for various intracellular functions. This unique property of the metal complexes could be applied safely in the treatment of infections caused by microbes¹³. It is difficult to make out an exact structure activity relationship between the microbial activity and structure of these complexes. The in-vitro anti-bacterial activity of the investigated compounds was tested against S. aureus, B.suptilis (Gram+ve) and K.pneumonia, P.aeruginosa (Gram-ve) by the well diffusion method. At present much consideration has been focused to the synthesis of new metal complexes and the evaluation of these agents for antibacterial activity¹⁴. A comparative study of the ligand and its metal complexes indicates that the complexes exhibit higher antibacterial activity than the free ligand. This may be due to the change in structure due to coordination and chelation of the metal complexes. The variation in the effectiveness of different compounds against different organisms depends either on the impermeability of the cells of the microbes or on differences in ribosome of microbial cells (Fig.6). Also the difference in antibacterial activity of the synthesized compounds is due to difference in the number of protons in the mononuclear Co(II) and Zn(II) metal complexes probably points the difference in the sizes of the +2 oxidation state of these metal ions, with the different polarizing due to its different sizes.

IV CONCLUSION

Schiff base ligand was synthesized from 4-amino benzamide and 3,5-dichloro-2-hydroxyacetophenone in 1:1 molar ratio. The molar conductivity data of the complexes indicates that all the complexes were non-electrolytic in nature. Based on spectral data Square planer geometry was proposed for the metal complexes. Proposed structure of Schiff base ligand and metal complexes further confirmed by ¹H-NMR and ESR spectra. The antibacterial activity result shows that the activity of the complexes was more than that of the ligand.

Table 1: IR Spectroscopic studies of Schiff base ligand and its metal complexes:

S.No	Compounds	-C=N (ν , cm^{-1})	-CONH ₂ (ν , cm^{-1})	M-O (ν , cm^{-1})	M-N (ν , cm^{-1})
1.	Ligand	1647.58	3465.15	-	-
2.	Co-complex	1640.96	3465.78	550.76	457.84
3.	Zn-complex	1594.93	3203.74	555.46	550.76

Table 2.1: P-XRD studies of Schiff base Co(II) metal complex:

1	12.656	13.9507	194.622	5.13816	1	100	1.4745
2	22.508	7.8529	61.668	16.2158	3.1559	111	0.4460
3	48.112	3.6950	13.653	73.243	14.2547	321	0.2632

Table 2.2: P-XRD studies of Schiff base Zn(II) metal complex:

No. of Peaks	2θ	d-spacing	d^2	$1000/d^2$	$h^2+I^2+K^2$	hkl	width
1	10.614	16.632	276.72	3.6150	1	100	0.8138
2	12.340	14.307	204.70	4.8851	1.3513	100	0.2101
3	21.430	8.246	68.008	14.7041	4.0675	200	0.1538
4	22.476	7.864	61.842	16.1702	4.4730	200	0.2290
5	23.323	7.579	57.447	17.4073	4.8152	200	0.3577
6	32.405	5.463	29.845	33.4963	9.2659	300	0.6879
7	48.502	3.665	13.437	74.4186	20.5860	420	0.4157

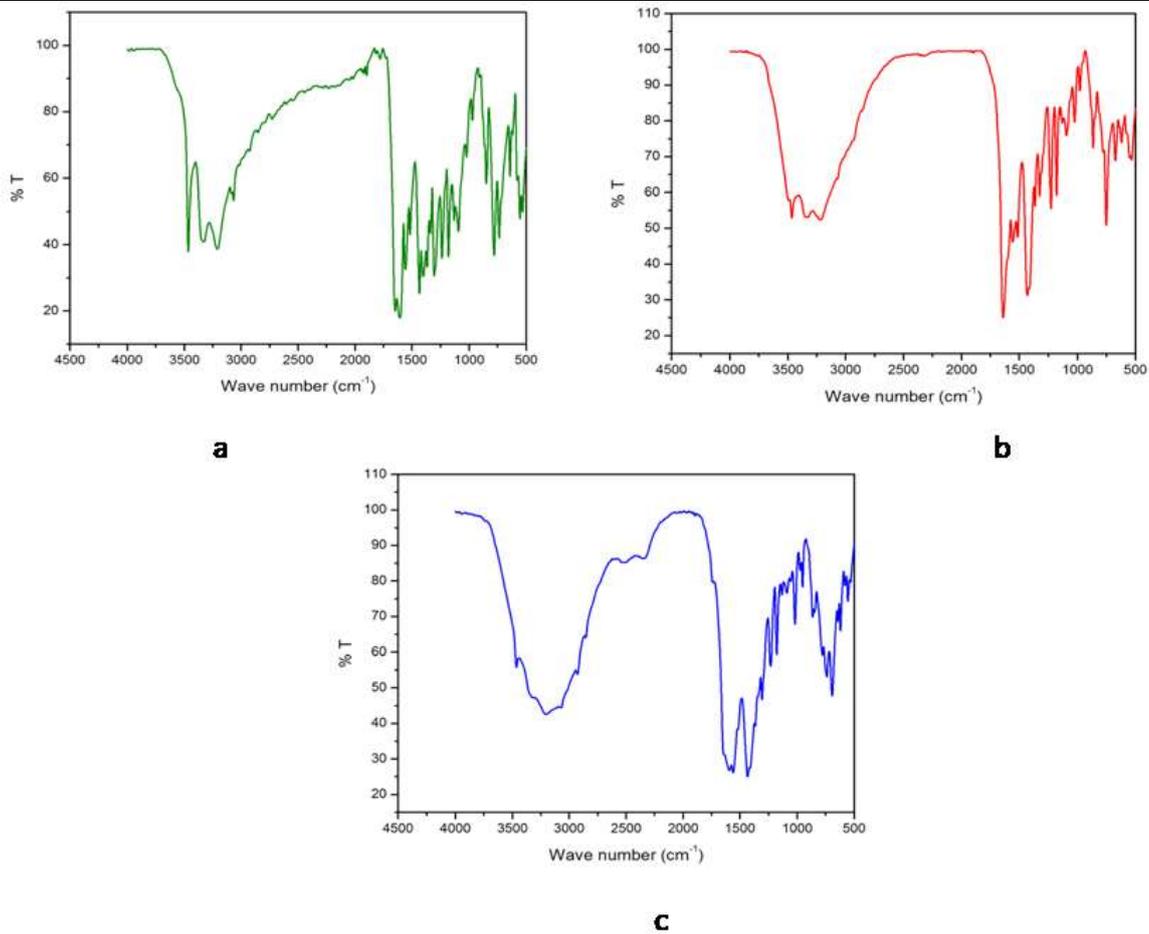


Fig. 2 IR Spectrum of Schiff base ligand (a), Co(II) complex (b) and Zn(II) complex (c)

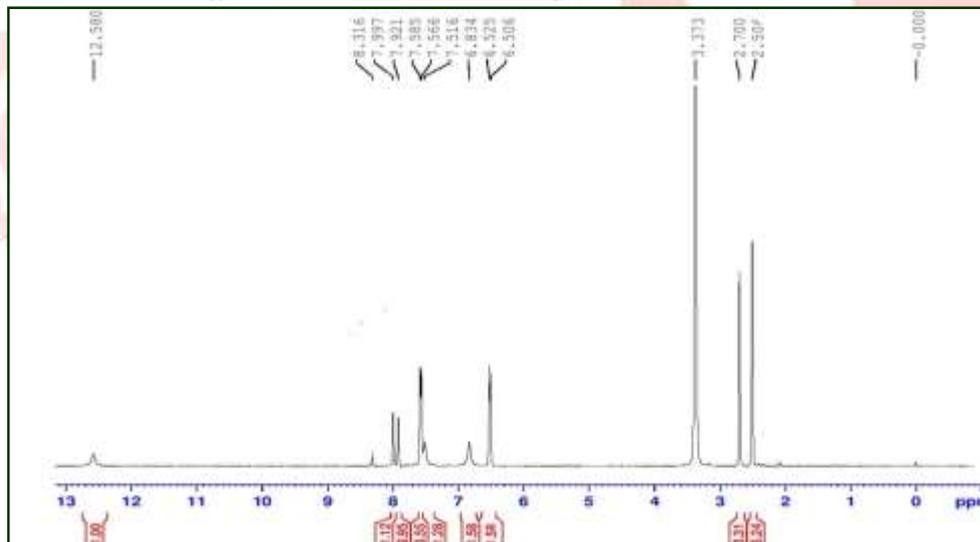


Fig. 3 ¹H NMR of Schiff Base ligand

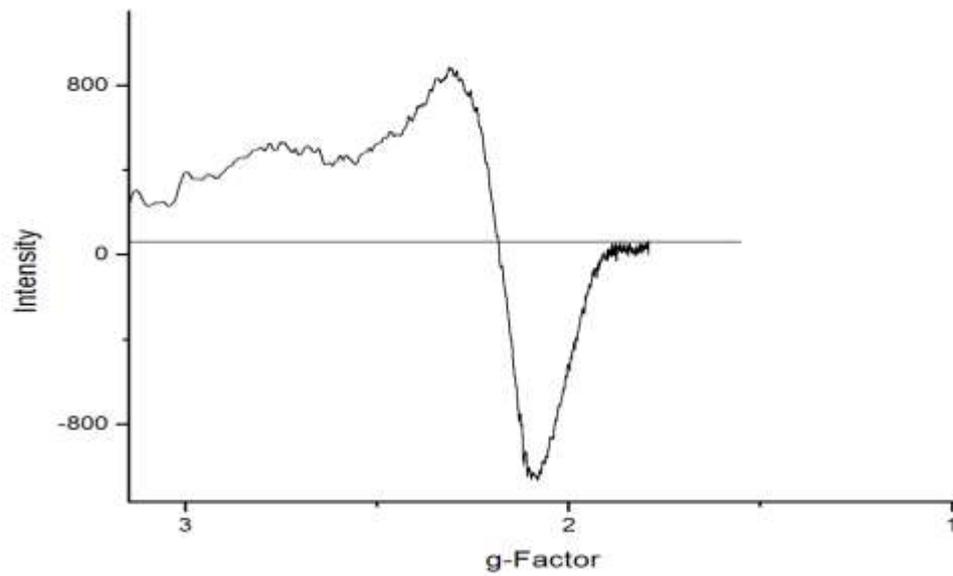


Fig. 4 ESR Spectra of Co(II) complex

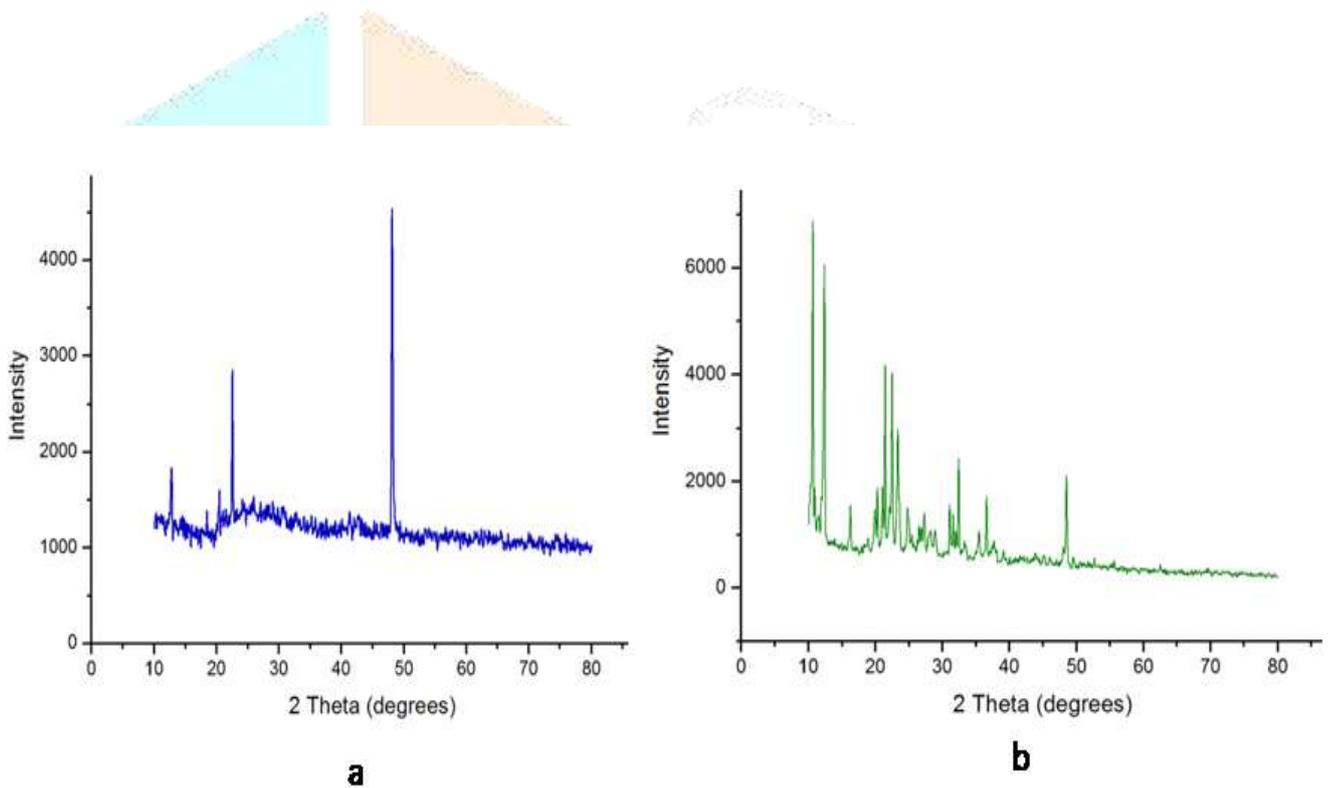


Fig. 5. P-XRD for Co(II) and Zn(II) Complexes

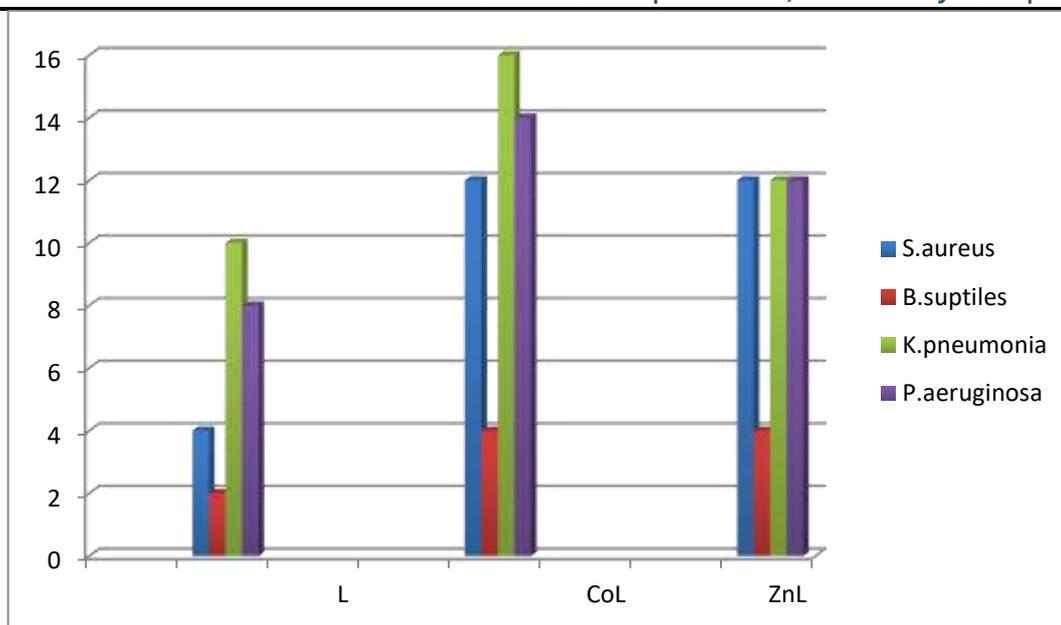


Fig. 6 Antibacterial activity of Schiff base ligand and its metal complexes

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