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Zr (IV) Complex derived from Salicylaldehyde and 2,4-dinitrophenylhydrazine Schiff base Ligand: Synthesis, Characterization and Biological Evaluation

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Abstract

The Schiff base complex of Zirconium (IV) nitrateis synthesized with ligand obtained by condensation of Salicylaldehyde and 2,4-dinitrophenylhydrazine. The ligand and complex are characterized using Spectroscopic techniques, including FTIR, UV-Visible, ^{1}HNMR and^{13}CNMR. The biological activities of the metal-ligand complex have been investigated in relation to both gram-positive and gram-negative bacteria as well as various fungal species.

Keywords: Spectroscopic techniques, Schiff base, transition metal complex synthesis, biological activity.

Introduction

The 4d-series metals have more nuanced coordination chemistry than 3d-series. The 4d-metals are more likely to create stable complexes[1]. Condensation between aldehydes and amines form an imine bond stereogenic centre whichcan be prepare Schiff base ligand for use in new synthetic complex[2]. As Schiff bases readily form metal complexes, they are essential in inorganic chemistry[3]. Schiff bases are versatile ligands because they have multiple potential donors are flexible and can coordinate in a neutral or deprotonated state from those that contain (-C=N-) bond form a strong chelate ring, leading to delocalization linked to extended conjugation[4,5].

Owing to its antibacterial and antifungal properties, as well as the complexes made from them, ligands with oxygen and nitrogen donor atoms are used in medicine[6-11]. The molecule is efficient and a stereospecific catalyst for oxidation, reduction, and hydrolysis because it contains nitrogen and oxygen donor atoms and it also exhibits bioactive properties[12-15]. Schiff bases are useful in various fields as antiviral, anticancer, antimicrobial activities and macrocyclic moieties.

Materials and Methods

Materials: All chemicals and reagents were used of highest purity. Salicylaldehyde and 2,4-dinitrophenylhydrazine was purchased from Sigma Aldrich. Ethanol, diethyl ether, n-hexane and toluene were used of analytical grade. All the solvents were freshly dried and distilled prior to use. The progress of the reactions was monitored by TLC on the pre – coated Kieselgel 60HF TLC plates.

Measurements: The solid state Fourier transformation infrared (FTIR) spectra were recorded on a Perkin Elmer spectrum. FTIR Spectrophotometer used KBr pallets. ^{1}H and ^{13}C NMR spectra were recorded by Bruker 300 MHz ultra-shield Spectrophotometer in DMSO-d_6 at room temperature. The effective field strength for ^{13}C NMR spectra was 75 MHz, UV-Visible spectrum was recorded by UV-Visible Spectrophotometer model TCC-240 A, using chloroform as solvent.

Synthesis of Schiff Base Ligand (B_2L): The ethanolic solution of the salicyaldehyde (4 millimole, 0.4884 g) is added slowly to the 2, 4dinitrophenylhydrazine (4 millimole, 0.7924g) solution. The reaction mixture is continuously stirred while being heated in a reflux environment for six hours. The reaction mixture is then exposed to the TLC method through which completion of reaction can be known. After the solvent is evaporated to one fourth of its original volume then it is filtered and obtained as an orange colour solid washed with ethanol followed by ether. The proposed reaction for ligand formation is given in Scheme-1.

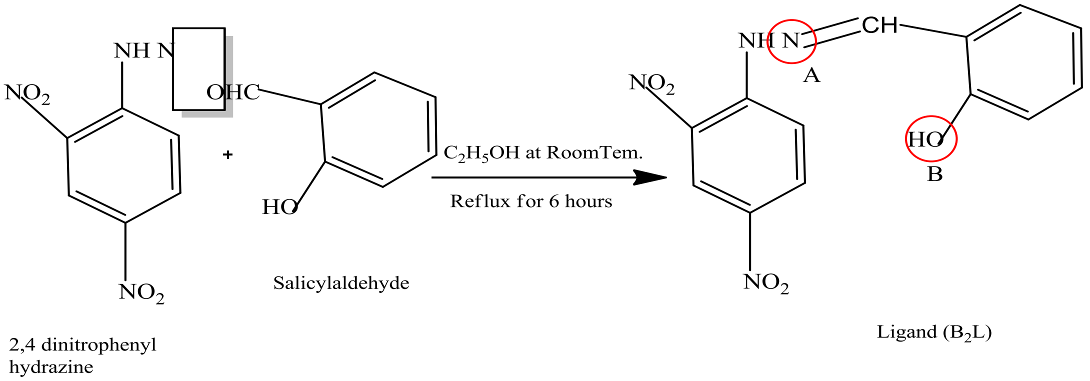
Synthesis of Complex: Complex was synthesized by refluxing ethanolic solution of ligand and hydrated zirconium nitrate ($ZrO(NO_3)_2.xH_2O$) in (1 metal: 1ligand) ratio. The resulting mixture was refluxed for 9 hours. The product was isolated after reduction of original volume by evaporation. It was filtered, washed with ethanol and ether dried under vacuum.

The proposed reaction for synthesis of complex is given in (Scheme-2).

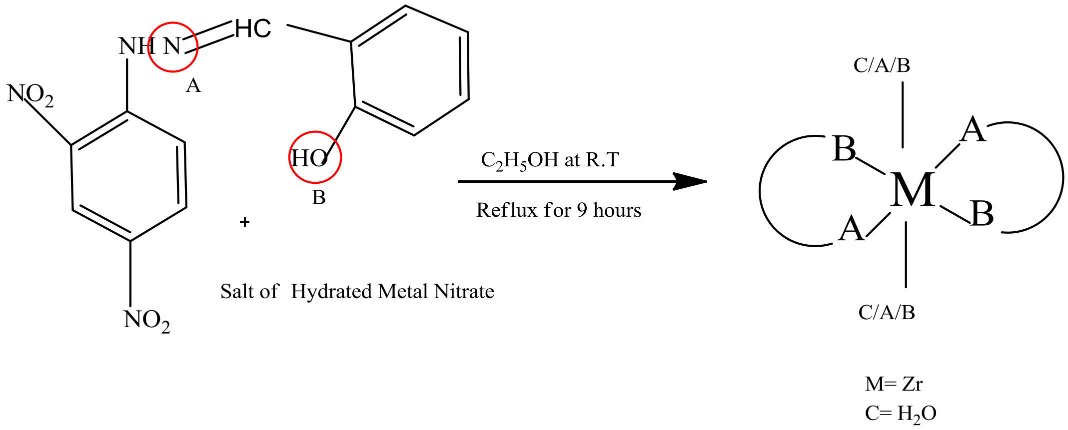
Results and Discussion

The spectral characterization of the Schiff base ligand (B_2L) and metal complex and their applications in antibacterial and antifungal activities are discussed below.

FTIR Spectra of ligand: FTIR Spectral image of synthesized Schiff base ligand is shown in (Figure-1). Schiff base (B_2L) displayed the characteristic absorption bands for -OH stretching at 3418.07cm^{-1}, aromatic C-H stretching at 3103.78 cm^{-1}and –NH stretching at 3269.68 cm^{-1}. The imine -C=N group is observed at 1618.16cm^{-1}, which is characteristic peak for the Schiff base. The aromatic C=C stretching’s are observed at 1486.17cm^{-1} and the aromatic nitro group stretching observed at 1514.03 cm^{-1} and 1593 cm^{-1}. FTIR data revealed successful synthesis of Schiff base ligand.



Scheme-1: Synthesis of Schiff base ligand (B_2L).



Scheme-2: Synthesis of complex.

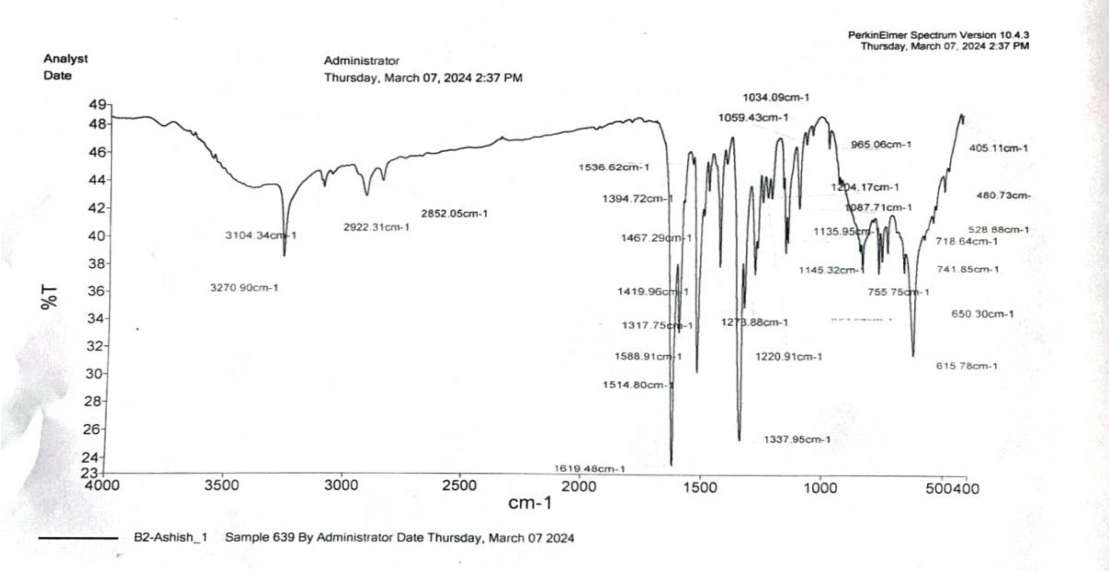


Figure-1: FTIR spectra of ligand (B_2L).

FTIR spectra of complex: FTIR spectra of complex are recorded in the range 4000–400 cm^{-1} and the values of important functional groups are shown and corresponding spectra in (Figure-2). The prepared complex exhibited the C-H stretching at 2921.90 cm^{-1} and these can be attributed to aliphatic C-H stretching vibrations. The aromatic C-H stretching vibration at 3108.5 cm^{-1} for the prepared compound and the imine -C=N group at 1621cm^{-1} for the complex.

The metal complex exhibits the high intensity band in the finger print region which can be attributed to the M-O stretching vibration at 616.23 cm^{-1} and M-N stretching vibration at 529.04 cm^{-1} chelation. The coordination of the nitrogen atom in complex is indicated in the fingerprint region of 600 to 1400 cm^{-1}.

UV-Visible spectra of ligand: Schiff base ligand (B_2L) is characterized by UV-Visible spectra at room temperature in DMSO and the graph obtained is shown in (Figure-3). The observed bands at 290 nm and 385 nm and can be assigned to $\pi \rightarrow \pi^*$ transition of the aromatic ring and $n \rightarrow \pi^*$ transition of the imines (azomethine) respectively.

UV-Visible spectra of complex: The UV-visible or electronic absorption spectra of the complex is recorded in DMSO at room temperature and shown in the (Figure-4). The prepared Schiff base ligand exhibited two absorption bands in the range of 300 nm and 390 nm, corresponding to the $\pi\rightarrow \pi^*$ and $n\rightarrow\pi^*$ transitions of the aromatic moiety and imine groups respectively. In the spectra of metal complexes, the bands are shifted to longer wavelengths (red-shift or bathochromic shift), indicating that ligands form a complex with metal ion.

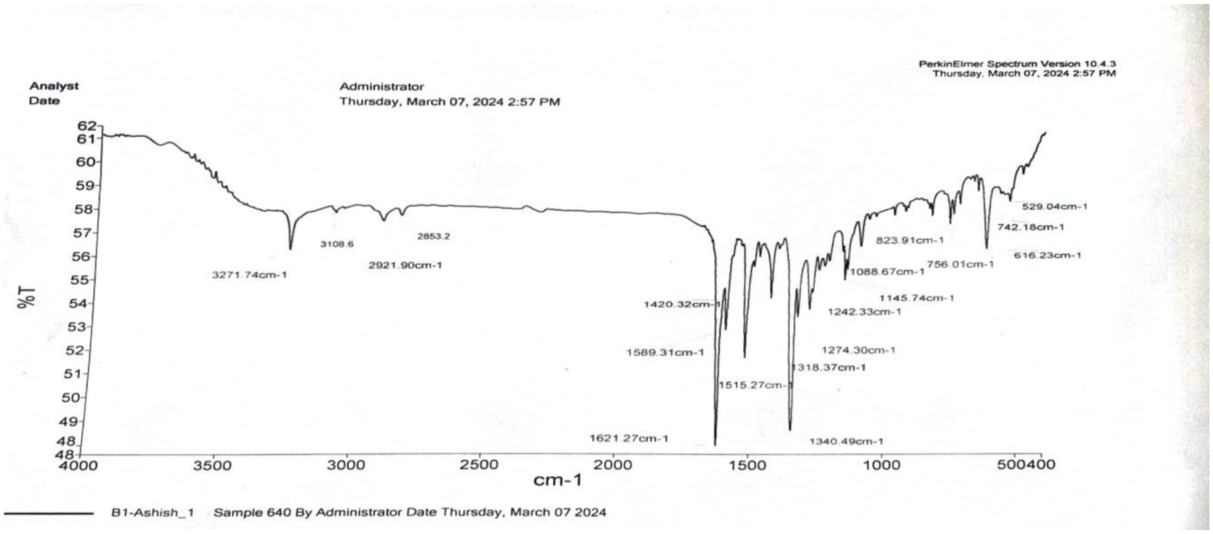


Figure-2: FTIR spectra of complex.

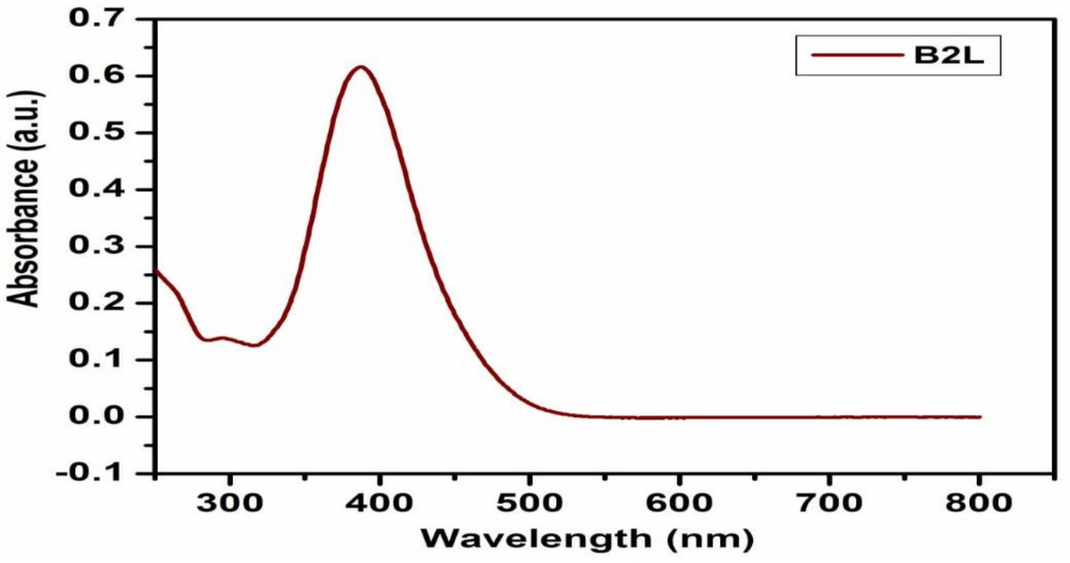


Figure-3: UV-Visible spectra of ligand (B_2L).

^{1}H NMR Spectra of ligand: The proton NMR spectra of the prepared Schiff base ligand recorded and the spectra are shown in (Figure-5). The chemical shift value of methylene hydrogens are observed at 1.2 ppm. The aromatic protons of the salicyaldehyde and 2, 4 dinitrophenylhydrazine rings are observed over a wide range of 6.8 ppm to 8.0 ppm. The hydroxyl proton is considered as a broad peak shifted at around 10.26 ppm. The -CH-N Proton peak appears at 8.4 ppm. NMR data confirmed the successful synthesis and structure of the Schiff base.

^{1}H NMR Spectra of complex: The proton NMR spectra of the prepared Schiff base metal complex is recorded and the spectrum shown in (Figure-6). The chemical shift value of methylene hydrogens are observed at 1.2 ppm. The aromatic protons of the salicyaldehyde and 2, 4 di- nitro phenyl hydrazine rings are observed over a wide range of 7.28 to 8.98 ppm with slight downfield shift. Hydrazine -NH peak appears at 11.7 ppm. The -CH-N Proton peak appears at 8.7 ppm due to metal coordination. Therefore the proton NMR data confirmed the successful synthesis and structure of the metal complex with the Schiff base.

^{13}C NMR Spectra of ligand: A crucial tool for understanding the carbon skeleton structure of substances is carbon NMR spectroscopy. In a DMSO-d6, the ^{13}C NMR spectra of the Schiff base is recorded using TMS as an internal standard. In Figure-7, the spectral image is displayed. One methylene at 40 ppm andaromatic ring showed the peak between 125 ppm 160 ppm. The carbon of the imine group is observed at 158 ppm. The data is consistent with the carbon skeleton of the prepared Schiff base.

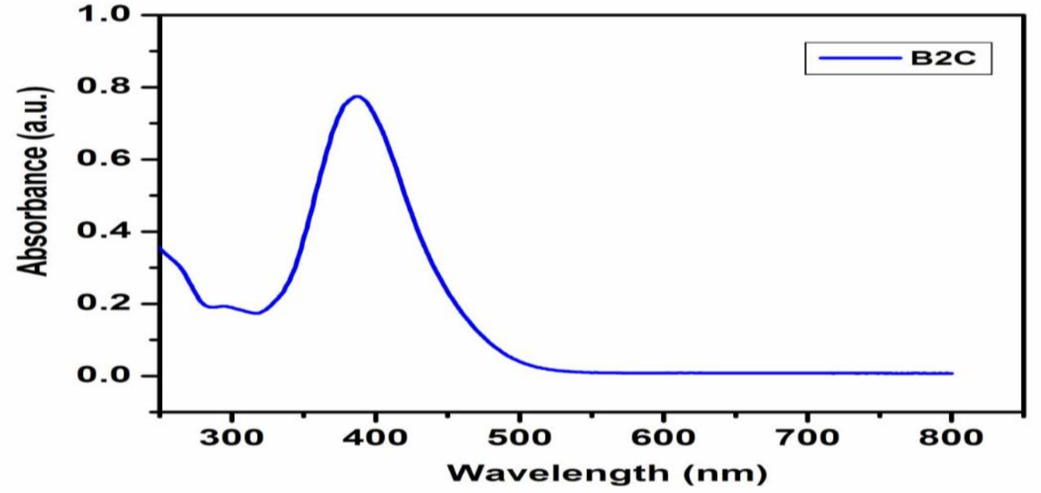


Figure-4: UV-Visible spectra of complex.

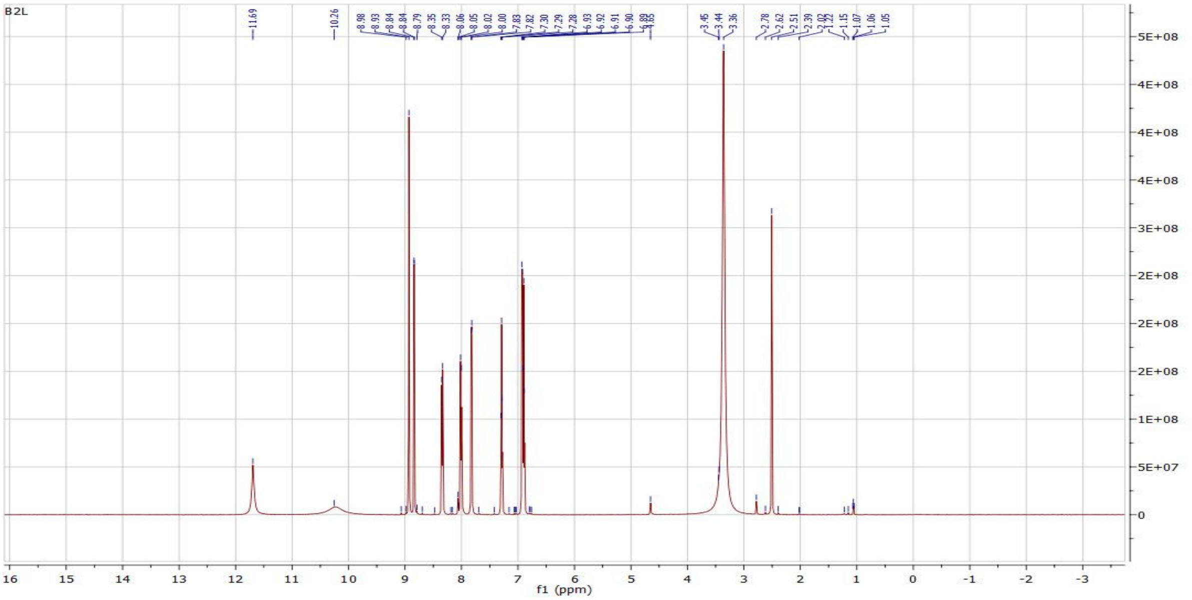


Figure-5: ^{1}H NMR spectra of ligand (B_2L).

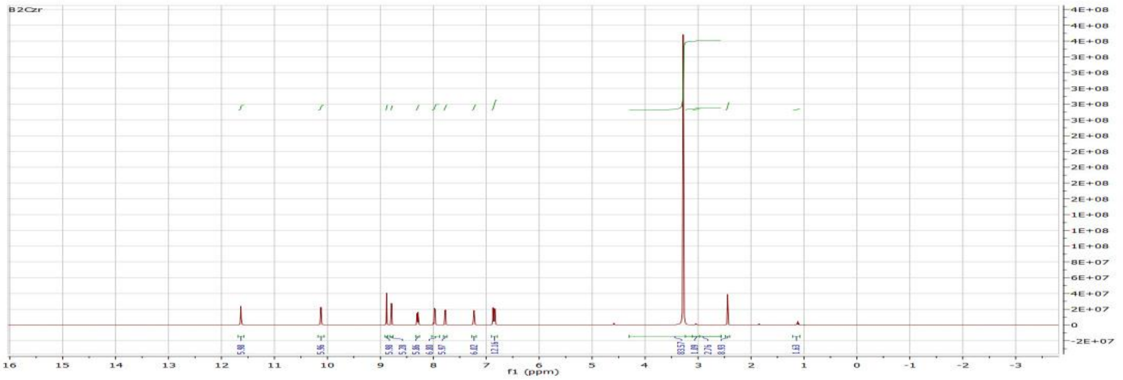


Figure-6: ^{1}H NMR spectra of complex.

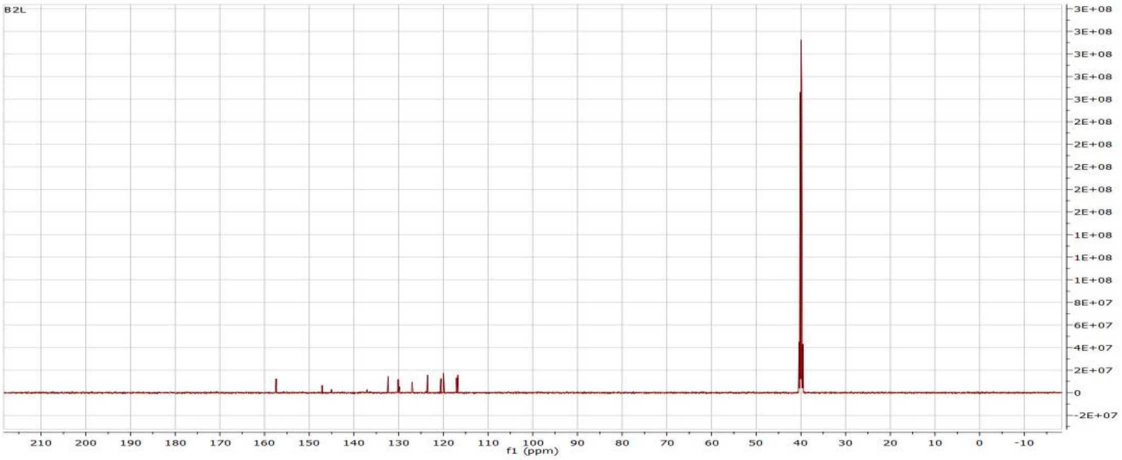


Figure-7: ^{13}CSpectra of ligand (B_2L).

Biological Activities: Antimicrobial – Schiff bases have antibacterial, antifungal and antiviral properties. Prepared Schiff base and their metal complex are screened for their antibacterial activities using petri disc method. Antibacterial activity is tested against two Gram-positive bacteria, *P. aeruginosa and S.aureus*, and one Gram-negative bacteria, *K.pneumoniae*. The synthesized complex is found to be active. The Schiff base metal complex is more active than the Schiff base ligand.

Conclusion

Ligand B_2L acts as a tetradentateligand coordinated to central metal through their phenolic oxygen and azomethyne nitrogen donor atoms. Ligand and complex are characterized by FTIR, NMR and UV- Visible spectroscopy. The synthesized ligand showed antimicrobial activities against to gram (+) bacteria *P. aeruginosa and S.aureus* and gram (-) bacteria *K. pneumoniae*. This result indicates synthesized complex may be more active against above bacterial species.

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