

# Novel Schiff Base Ligand and their Fe (III), Co (II) and Ni (II) Complexes: Spectroscopic Investigation and Biological Applications

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**Abstract:** Novel Schiff base ligand derived from condensation reaction between 3-Amino-4-Hydroxy Benzoic Acid and 2-hydroxy-5-nitrobenzaldehyde. Fe (III), Co (II) & Ni (II) metal complexes were formed from the synthesized ligand. FT-IR, UV-Visible <sup>1</sup>H-NMR & HRMS Characterization studies were carried out for the confirmation of the structure and bonding of the synthesized ligand and its complexes. Complexes were tested for their antibacterial and antifungal activities using gram positive bacterial strains i.e. Staphylococcus aureus and Bacillus subtilis, gram negative bacterial strains i.e. Escherichia coli and Pseudomonas aeruginosa by disc diffusion method and antifungal activity was carried out using Aspergillus Niger fungal strain. It has been found that complexes and ligand show potent antibacterial and antifungal activities.

**Keywords:** Schiff base, Metal complexes, Antibacterial activity, Antifungal activity

## 1. Introduction:

A variety of Schiff bases with azomethine groups and their complexes have been found for their chelating and biological characteristics [1]. Schiff bases are ketone- or aldehyde-like substances that substitute the carbonyl group with an imine or azomethine group. Schiff bases are ligands formed by combining amino compounds with carbonyl compounds. They were initially described by Hugo Schiff in 1864 [2-3]. These days Schiff bases are used to synthesise amino acids and metal complexes with various structures [4]. The imine group [-C=N-] in Schiff bases has a unique role in producing compounds with diverse biological activities [5]. In addition to their diverse industrial applications, they show a wide range of physiological activities, including anti-inflammatory, antibacterial, antiproliferative, antifungal, antipyretic, and antiviral characteristics [6]. Due to their ease of synthesis and metal

complexation, they have attracted the scientific community's curiosity [7]. The vast majority of Schiff bases are popular ligands because they effectively produce complexation with most transition metals owing to the variable stereo-electronic structures [8]. A variety of in vivo biological reactions are studied using Schiff base complexes produced from amino acids. Schiff bases' biological activity changes depending on whether they are chelated with metal ions. Acid solutions are commonly used in industrial activities, as well as for auxiliary purposes such as acid cleaning, acid pickling, acid descaling, and oil well acidification. Schiff base complexes of the same hydrazone are used as plasticisers and stabilisers for polymers and polymerisation inhibitors, antioxidants, and other applications [9]. SB ligands and their metal complexes have recently been used as efficient catalysts for cross-coupling reactions in modern organic synthesis, including Suzuki-Miyaura, Heck, Sonogashira, Buchwald-Hardwig, Negishi, Stille, and Kumada reactions that form C—C, C—N, C—O, and C—S bonds. The metal complex of SBs has been used as an effective catalyst for a variety of polymerisation reactions [10]. Biologically active molecules with the azomethine group have established a niche in medicinal chemistry. This class of chemicals, known as Schiff bases (SB), offers the potential for a wide range of pharmacological applications, including antibiotics and cancer treatment [11].

In this study we have synthesized Schiff base ligand by the condensation reaction between 3-Amino-4-Hydroxy Benzoic Acid and 2-hydroxy-5-nitrobenzaldehyde. Metal complexes of Fe (III) Co (II) and Ni (II) were synthesized from this ligand.

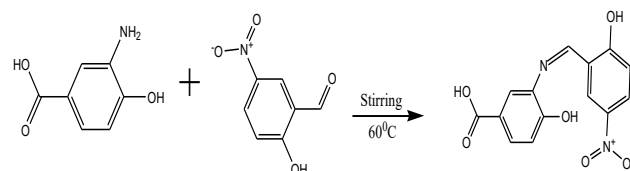
## 2. Materials and Methods:

All the chemicals required for the synthesis of ligand and its complexes were purchased from Thermo-Fischer scientific company pvt. Ltd. All the chemicals were obtained in pure form and no further purification were done. FT-IR analysis was done by using Perkin Elmer, NMR analysis on Bruker advance neo 500 MHz spectrometer UV-Visible spectrum was done on Shimadzu double beam spectrometer.

### A) Synthesis of ligand:

3-Amino-4-hydroxy benzoic acid (0.002 mol) was dissolved in ethanol and this solution was mixed with ethanolic solution of 2-hydroxy-5-nitro benzaldehyde (0.002 mol) and stirred continuously at 60°C for 30 min. A brown coloured solid product was obtained. This

product is dried in desiccators after being repeatedly washed with methanol. The melting point of the synthesized product was taken.



Synthesis of Schiff base ligand (L) : (E)-4-hydroxy-3-((2-hydroxy-5-nitro benzylidene) amino) benzoic acid

### B) Synthesis of Complex:

To the ethanolic solution of Schiff base (L) (0.002 mole) with sodium hydroxide solution (0.002 mole), ethanolic solution of metal nitrate (0.002 mole) slowly added with constant stirring on hot plate at 60°C for half an hour. The precipitate obtained was filtered and washed with ethanol and methanol and then dried on desiccators over anhydrous CaCl<sub>2</sub>.

### 3. Analytical Studies of Metal Complexes

The C, H, and N levels of metal complexes were measured using the Flash EA 1112 Elemental Analyser. Tables 3.1 indicate the percentages of C, H, and N detected in metal complexes, as well as theoretically computed values. The molecular stoichiometry of each complex is determined through elemental analysis. Table 3.1 depict the elemental analysis of metal complexes.

Table 3.1 Analytical studies of metal complexes

Molecular formula (Complex)	Mol. Wt.	Calculated / Found%			
		C	H	N	M
[Fe(III) L (H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	430.14	39.09/39.06	4.22/4.21	6.51/6.49	12.98/ 12.99
[Co(II) L (H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	433.23	38.81/38.82	4.19/ 4.20	6.47/6.48	13.60/ 13.61
[Ni(II) L (H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	432.99	38.93/38.93	4.19/4.20	6.47/6.43	13.56/ 13.55

## 4.Result and Discussion

### IR spectral studies

IR spectroscopy is used to investigate the structure of metal complexes. It is advised that when metal ions react with ligands to create complexes, The vibrational spectra are predicted to alter. Changes in vibration can be attributed to either molecule symmetry or individual frequency. The metal

complexes spectra are compared with the ligand spectra.

The IR spectral analysis of Fe (III) complexes revealed notable shifts indicative of ligand coordination. Stretching vibrations attributed to  $\nu(\text{C}=\text{N})$  appeared in the range of 1646 cm<sup>-1</sup> for the complex, shifted to 1619cm<sup>-1</sup> in the free ligand,

confirming nitrogen coordination to the metal center. Aromatic C=C stretching bands observed in the  $1531\text{ cm}^{-1}$  region exhibited minor shifts compared to the uncoordinated ligands, likely due to changes in electron distribution upon complexation.

O–H stretching bands present in the  $3210\text{ cm}^{-1}$  range in free ligands disappeared in the complexes, indicating deprotonation and coordination via phenolic oxygen. Corresponding shifts in phenolic C–O stretching frequencies further supported this; bands shifted from  $1197\text{ cm}^{-1}$  in ligands to  $1182\text{ cm}^{-1}$  in complexes. Notably, the C–O frequency decreased by  $15\text{ cm}^{-1}$ , this shift confirming metal–oxygen bond formation.

The FT-IR spectral analysis of Co(II) complexes reveals significant shifts in key vibrational bands, confirming the coordination of ligand donor atoms with the metal center. The azomethine (C=N) stretching frequencies of the free ligands, originally observed in the range of  $1646\text{ cm}^{-1}$ , shift to  $1612\text{ cm}^{-1}$  in the complexes, indicating nitrogen coordination. The FT-IR spectra of Ni (II) complexes exhibit significant vibrational shifts, confirming the coordination of functional groups with the Ni (II) ion. The azomethine (C=N) stretching bands of the free ligands appear in the range of  $1646\text{ cm}^{-1}$ , which shift to  $1589\text{ cm}^{-1}$  upon complexation, indicating the coordination of the azomethine nitrogen to the metal center.

The disappearance of O–H stretching bands  $3210\text{ cm}^{-1}$  in the complex signifies phenolic deprotonation and coordination through oxygen. The phenolic C–O stretching bands, originally in the range of  $1197\text{ cm}^{-1}$  in ligands, shift to  $1101\text{ cm}^{-1}$  in the complex.

Ni (II) complex show broad absorption bands at  $3400\text{ cm}^{-1}$ , confirming the presence of coordinated

coordination to Co(II). Aromatic C=C stretching bands, present in the  $1531\text{ cm}^{-1}$  region, show variations attributed to changes in electron distribution upon complexation.

Phenolic O–H stretching bands  $3210\text{ cm}^{-1}$  disappear in the metal complexes, signifying deprotonation and metal–oxygen coordination. The phenolic C–O stretching bands shift from  $1197\text{ cm}^{-1}$  in ligands to  $1068\text{ cm}^{-1}$  in complexes. Notably, C–O stretching frequencies in complex decrease by  $129\text{ cm}^{-1}$ , respectively, indicating coordination through phenolic oxygen.

C–N stretching bands of aryl azomethine moieties appear at  $1286\text{ cm}^{-1}$  in ligands and shift to  $1303\text{ cm}^{-1}$  in complex, supporting azomethine nitrogen involvement in coordination.

The disappearance of C=O (COOH) stretching bands and the emergence of asymmetric  $1544\text{ cm}^{-1}$  and symmetric  $1378\text{ cm}^{-1}$  COO<sup>−</sup> stretching frequencies in the complex, with  $\Delta(v_{\text{asym}} - v_{\text{sym}})$  at  $166\text{ cm}^{-1}$ , indicate bidentate coordination via the carboxylate group.

water molecules. These are further supported by medium-intensity bands in the  $818\text{ cm}^{-1}$  region.

Aryl azomethine C–N stretching vibrations appear at  $1286\text{ cm}^{-1}$  in ligand and shift to  $1302\text{ cm}^{-1}$  in Ni(II) complex, further confirming azomethine nitrogen coordination.

The disappearance of COOH C=O bands and the emergence of COO<sup>−</sup> asymmetric  $1546\text{ cm}^{-1}$  and symmetric  $1383\text{ cm}^{-1}$  stretching bands in the complexes suggest carboxylate involvement in coordination. The  $\Delta(v_{\text{asym}} - v_{\text{sym}})$  values at  $163\text{ cm}^{-1}$  imply bidentate binding of the carboxylate group to Ni (II).

**Table No. 4.1 Infrared spectral data for the Schiff base ligands and their complexes**

Ligand /Complexes	OH/H <sub>2</sub> O	C=O	C=N	Asym COO <sup>−1</sup>	Sym COO <sup>−1</sup>	C-N	C-O	C-Br	M-N	M-O
L	3210	1720	1619	-	-	1286	1197	-	-	-

LFe	3402	-	1646	1581	1383	1338	1182	-	536	454
LCo	3403	-	1612	1544	1378	1303	1068	-	543	468
LNi	3400	-	1589	1546	1383	1302	1101	-	532	477

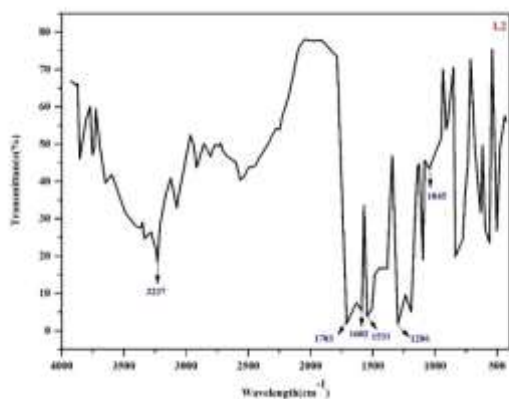


Figure 4.1 a) IR spectra of Schiff base ligand

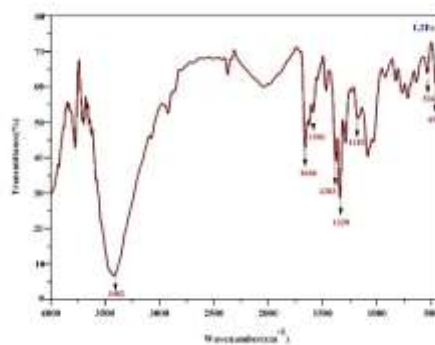


Figure 4.1 b) IR spectra of Fe(III) complex

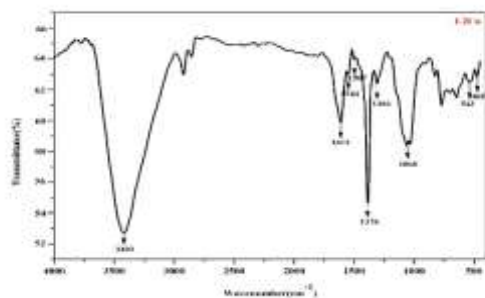


Figure 4.1 c) IR spectra of Co (II) complex

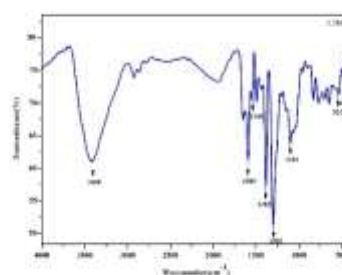


Figure 4.1 d) IR spectra of Ni (II) complex

### UV-visible spectra:

Synthesized ligand solution ( $1 \times 10^{-4}$ ) was prepared in dimethyl formamide solvent and used for the UV-Vis. Spectra. Free Schiff base ligand shows bands for  $\pi \rightarrow \pi^*$  transitions in the region 263

nm and for  $\eta \rightarrow \pi^*$  transitions show bands in the region 316 371, 429 nm. The electronic spectra of the synthesized ligand is shown in the table no. 4.2 and represented in the figure 4.2

Table 4.2 Absorption band for Schiff base ligand

Ligand	$\lambda$ max (nm)	Band Assignment
L	263 316 371, 429	$\pi \rightarrow \pi^*$ $\eta \rightarrow \pi^*$

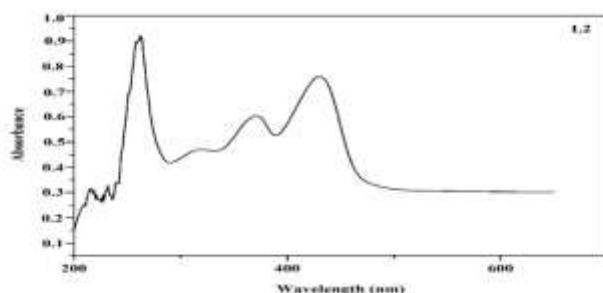


Figure 4.2 Electronic absorption spectra for Schiff base ligand

Electronic absorption studies of all the synthesized Fe (III), Co (II) and Ni (II) complexes exhibits two bands within the wavelength range of 258-306 nm

and 421-435 nm which are ascribed to  $\pi \rightarrow \pi^*$  and  $\eta \rightarrow \pi^*$  transitions respectively.

Table 4.3 Absorption band for complexes

Complex	Molar Conductance $\text{Ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$	$\mu_{\text{eff}}$ (B.M.)	$\lambda_{\text{max}}$ (nm) Absorbance	Band assignment
Fe (III)	16.50	5.80	258,263 435	$\pi \rightarrow \pi^*$ $\eta \rightarrow \pi^*$
Co (II)	12.25	5.21	270,306 421	$\pi \rightarrow \pi^*$ $\eta \rightarrow \pi^*$
Ni (II)	2.50	2.80	258,304 435	$\pi \rightarrow \pi^*$ $\eta \rightarrow \pi^*$

### NMR spectral studies for ligand

Ligand shows a singlet peak at  $\delta$  8.69 (s, 1H) due to  $-\text{CH}=\text{N}$  azomethine proton, a sharp peak at  $\delta$  12.66 (s, 1H) due to  $\text{Ar}-\text{COOH}$  proton, Singlet for 2H due to 2Ar-OH at  $\delta$  9.38 & 11.13 (s, 2H) and multiplet at  $\delta$  6.96 to 7.82 (m, 6H) due to Ar-H protons. Figure 4.3 shows the NMR spectra of the Schiff base ligand

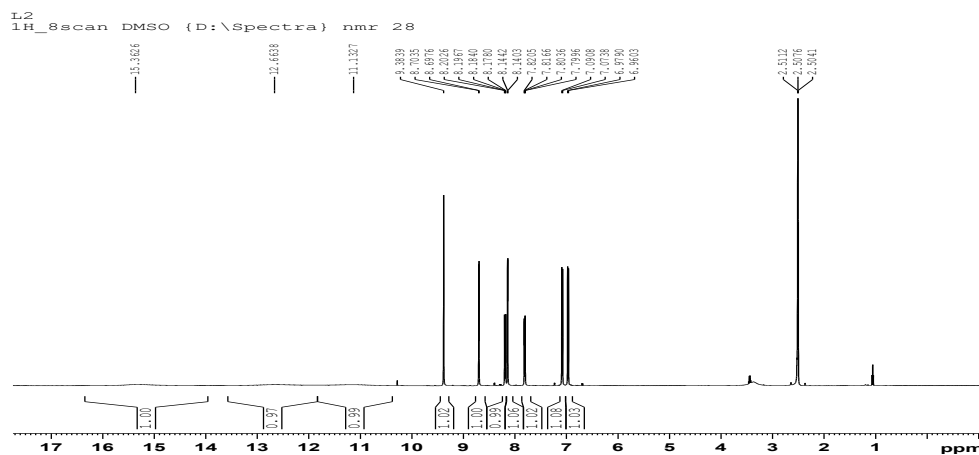


Figure 4.3 <sup>1</sup>H-NMR spectra of the Schiff base ligand

### HRMS of the Schiff base ligand

Older technology could only distinguish mass fragments up to the first digit; high-resolution mass spectrometry allows separation of mass fragments to the fourth or fifth decimal place. This point of view illustrates how the idea of precise mass, or exact mass, is obtained from basic physical rules, how the difference between integer mass and exact mass is caused by various atoms, and how these

characteristics may be utilised to identify molecules that are unknown.

High resolution mass spectroscopy (HRMS) was recorded on synapt -x at SAIF, Chandigarh. All the results received from SAIF; Chandigarh were compared with the calculated mass of the ligands. Results obtained are found in good agreement with calculated mass.

for ligand L calculated mass [M+H] is 303.0617 and observed mass [M+H] is 303.0619.

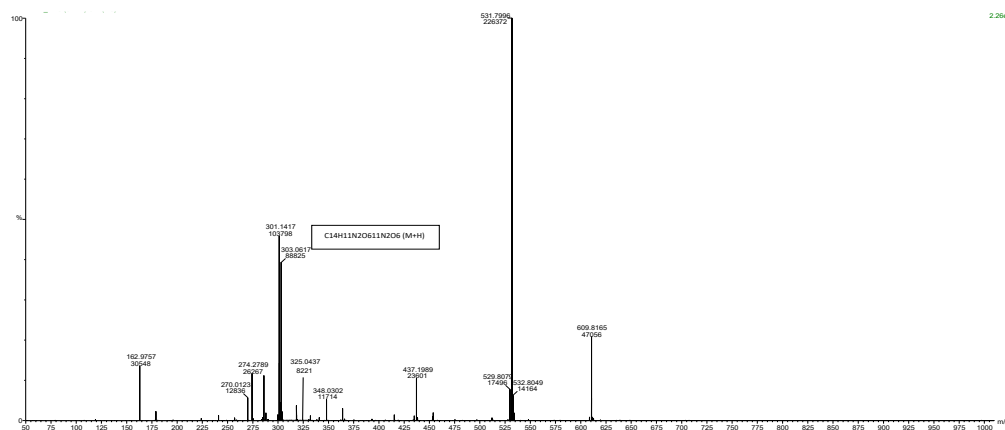


Figure 4.4 HRMS of Schiff base ligand

### Antimicrobial Studies:

In this study, the antibacterial and antifungal activities of the synthesized ligands and their complexes with Fe (III), Co (II) and Ni (II) were evaluated. The antibacterial tests were conducted using the disc diffusion method against two Gram-positive bacterial strains, *Staphylococcus aureus* and *Bacillus subtilis*, and two Gram-negative bacterial strains, *Escherichia coli* and *Pseudomonas aeruginosa*. For these tests, the concentration of the ligands and their metal complexes was set at 1000 ppm, and their efficacy was compared to the standard drug, Streptomycin. Antifungal activities

also evaluated by the same method for *Aspergillus niger* fungal strain and their efficacy was compared to the standard drug Amphotericin B



Table 4.4 Antimicrobial activity of Schiff base ligands

Test Compound	<i>S. aureus</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>A. Niger</i>
Ligand	14	16	14	00.00	10
Streptomycin	21	33	20	24	NA
Amphotericin B	NA	NA	NA	NA	12.58

Zone of inhibition = Diameter in mm calculated by Vernier Caliper NA = Not applicable

Table 4.5 Antimicrobial activity of Fe(III), Co (II) and Ni (II) complexes

Test Compound (Complex)	<i>S. aureus</i>	<i>B. subtilis</i>	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>A. Niger</i>
Fe (III)	33.00	00.00	00.00	00.00	00.00
Co (II)	12.00	00.00	00.00	00.00	00.00
Ni (II)	37.00	00.00	00.00	00.00	00.00
Streptomycin	21	33	20	24	NA
Amphotericin B	NA	NA	NA	NA	12.58

Zone of inhibition = Diameter in mm calculated by Vernier Caliper NA = Not applicable

The synthesized Schiff base ligand exhibited moderate antibacterial activity against *Staphylococcus aureus*, *Bacillus subtilis*, and *Escherichia coli* strains, when compared to the standard antibiotic Streptomycin. Additionally, the ligand demonstrated moderate antifungal activity against *Aspergillus niger*. Among the metal

### Conclusion

The Schiff base ligand is synthesized from 3-amino-4-hydroxy benzaldehyde and 2-hydroxy-5-nitro benzaldehyde. Fe (III), Co (II) and Ni (II) metal complexes are also synthesized from this ligand. Synthesized ligand characterized by using IR, UV-visible, <sup>1</sup>H-NMR and HRMS spectroscopic techniques. All the synthesized metal complexes are also characterized using UV-visible and IR

complexes, the Fe (III) and Ni (II) complexes displayed superior antibacterial activity, surpassing that of the standard drug. In contrast, the Co (II) complex showed moderate antibacterial efficacy, comparable to or slightly lower than that of Streptomycin.

spectroscopic methods. All the spectroscopic results are in good agreement with the literature which confirms the purity of the synthesized compounds. Ligand shows moderate antibacterial and antifungal activity against *S. aureus*, *B. subtilis*, *E. coli* and *A. niger*. All metal complexes shows moderate antibacterial activity against *S. aureus* bacterial strain.

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### References:

1. Ibatte, S. N. (2017). Synthesis and Characterization of N2O2 type Metal Complexes derived from 4-Aminoantipyrine, 4-Nitrobenzaldehyde and Acetylacetone. *Asian Journal of Research in Chemistry*, 10(2), 166-173.
2. Katwal, R.; Kaur, H.; Kapur, B. K., Applications of copper— Schiff's base complexes: a review.
3. Mahmud, T., Synthesis and characterization of the amino acid Schiff bases and their complexes with copper (II). 2010.
4. Paul, T., & Hossen, M. F. (2020). Schiff base metal complexes: Synthesis, characterization, thermal analysis and antibacterial activity. *Asian Journal of Research in Chemistry*, 13(4), 265-274.

5. Boulechfar, C., Ferkous, H., Delimi, A., Djedouani, A., Kahlouche, A., Boubli, A., ... & Benguerba, Y. (2023). Schiff bases and their metal Complexes: A review on the history, synthesis, and applications. *Inorganic Chemistry Communications*, 150, 110451.
6. Plesch, G., Kettmann, V., Sivy, J., Švajlenová, O., & Friebe, C. (1998). Coordination geometries and cooperative ordering effects in copper (II) complexes with tridentate Schiff base dianions—VI Structure and EPR spectra of (imidazole)(N-salicylidene-beta-alaninato) copper (II). *Polyhedron*, 17(4), 539-545.
7. Golcu, A., Tumer, M., Demirelli, H., & Wheatley, R. A. (2005). Cd (II) and Cu (II) complexes of polydentate Schiff base ligands: synthesis, characterization, properties and biological activity. *Inorganica Chimica Acta*, 358(6), 1785-1797.
8. Chaviara, A. T., Christidis, P. C., Papageorgiou, A., Chrysogelou, E., Hadjipavlou-Litina, D. J., & Bolos, C. A. (2005). In vivo anticancer, anti-inflammatory, and toxicity studies of mixed-ligand Cu (II) complexes of dien and its Schiff dibases with heterocyclic aldehydes and 2-amino-2-thiazoline. Crystal structure of [Cu (dien)(Br)(2a-2tzn)](Br)(H<sub>2</sub>O). *Journal of inorganic biochemistry*, 99(11), 2102-2109.
9. Singh, A., Gogoi, H. P., & Barman, P. (2023). General Applications of Schiff Bases and Their Metal Complexes. *Schiff Base Metal Complexes: Synthesis and Applications*, 119-128.
10. Saranya, S., & Vedachalam, S. (2023). Application as Catalyst. *Schiff Base Metal Complexes: Synthesis and Applications*, 149-168.
11. Sarkar, P., Sutradhar, S., & Ghosh, B. N. (2023). Application in Pharmacological Field. *Schiff Base Metal Complexes: Synthesis and Applications*, 129-147.