Spectroscopic Synthesis and Fluorescence Analysis of 1-(2-Hydroxyphenyl) ethanone Schiff Bases and Their Metal Complexes

Udaysinha C. Patil*[a]

[a]P.G. Department of Chemistry, Shri Pancham Khemraj Mahavidyalaya, Sawantwadi; India.

*ucpatil26@gmail.com

Abstract:

Schiff bases, formed through addition and elimination reactions between aldehydes or ketones and amines, are significant ligands in chemistry due to their ability to form stable complexes with various metal ions. In this study, reduced Schiff bases were prepared from the reaction of 1-(2-Hydroxyphenyl) ethanone with diamine derivatives, followed by reduction with NaBH4, resulting in the formation of Co (II), Ni (II), Cu (II), and Zn (II) complexes. These ligands and metal complexes were characterized using techniques such as FTIR, 1H and 13C-NMR, MS, XRD, TGA, UV-Visible, Fluorescence, and elemental analysis. Schiff bases exhibit versatile structural and chemical properties, making them valuable in fields such as biological, inorganic, and analytical chemistry. They have notable applications in industry and pharmacology, attributed to their stability and diverse reaction profiles. Transition metal complexes with Schiff bases play crucial roles in biological systems, contributing to advancements in medical treatments, including cancer therapy and antibacterial applications. The structural variability and chelating properties of Schiff bases, particularly those derived from aromatic aldehydes and amines, highlight their potential for further research and development in various scientific domains.

Key words: Schiff bases, FTIR, UV-Visible, Fluorescence, Elemental analysis, Structural variability, chelating properties

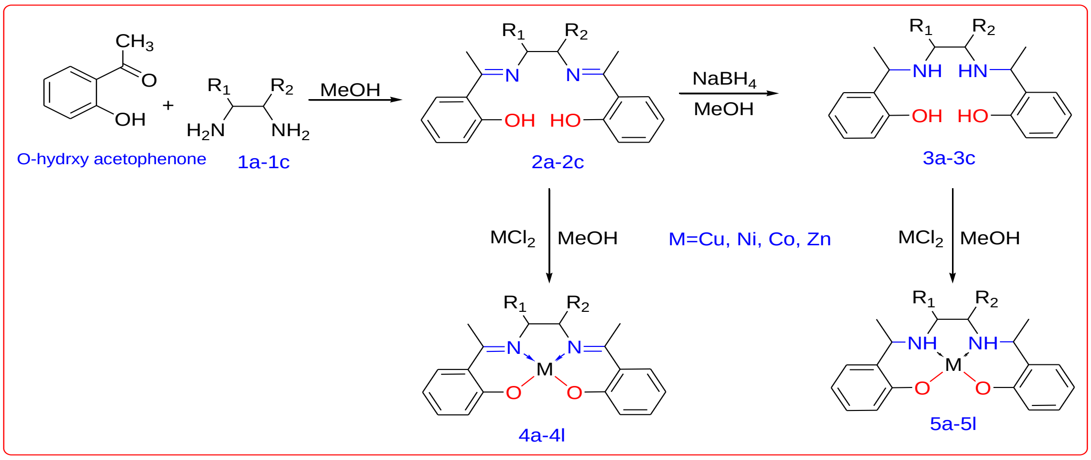
1. Introduction

Schiff bases, formed by the reaction of a metal with a cluster of ions or molecules, are extensively used for the preparation of complex compounds [3]. These compounds serve as excellent ligands, forming complexes with various metal ions due to their proton-donating ability and multiple bonding sites, which lead to diverse stereochemical structures and provide kinetic and thermodynamic stability to the metal complexes. While monodentate Schiff base ligands have been synthesized and studied for complexation with several metal ions, multidentate ligands (bi, tri, and tetradentate), known for their chelating properties, offer additional stability and exhibit intriguing geometries. Schiff bases are notable in chemistry for their useful physical and chemical properties and their involvement in numerous reactions. They have significant industrial applications due to their pharmacological activity and exhibit characteristics and structural similarities with natural biological substances. Their simple preparation procedures and synthetic flexibility allow the design of suitable structural scaffolds [1]. The synthesis of coordination compounds of Schiff base ligands with N, S-donor binding sites has garnered considerable attention for their potential biological activities [4]. Key features of these compounds include preparative accessibility, diversity, structural variability, and versatile coordinating properties [5]. Schiff bases derived from aromatic aldehydes are more stable than those from lower aliphatic aldehydes and primary aromatic amines. They have diverse applications in fields such as biological, inorganic, and analytical chemistry and are used in optical and electrochemical sensors, as well as various chromatographic methods, due to enhanced selectivity and sensitivity [1]. The chelating abilities and analytical and biological applications of Schiff bases have attracted significant attention [7]. These compounds are widely used in biological, inorganic, analytical, and drug synthesis fields, serving as bidentate ligands in coordination chemistry [2]. Schiff bases also play roles in the degradation of organic compounds and radiopharmaceuticals [8]. Initial research focused on simple Schiff base ligands like salophen, salen, and acacen, but interest has shifted to more intricate species with additional functional groups, side chains, and more methylene groups in the amine backbone [9]. Schiff bases derived from salicylaldehyde are well known as polydentate ligands coordinating in neutral forms [10,31]. Tetradentate Schiff bases derived from salicylaldehyde derivatives and various diamines (1:2 ratio) have shown that increasing the methylene chain length provides sufficient flexibility for the complexes to transition from planar to distorted or pseudo-tetrahedral motifs. The longer chains also decrease ligand field strength [18]. Schiff bases with multiple donor sites play a key role in investigating the geometrical structure of coordination compounds, which is the backbone of structural chemistry. Tetradentate Schiff bases with an N_2O_2 donor atom set are known to coordinate with various metal ions, attracting significant research interest [19]. The ligand was synthesized by condensing 2-hydroxyacetophenone with ethylenediamine, as reported [20]. The complexing behavior of bidentate and tridentate Schiff bases with different donor atoms and varying electronegativities has been well studied. Recent years have seen considerable interest in the complexing behavior of quadridentate Schiff bases [21]. Studies have highlighted the synthesis of first-row transition metal complexes with new Schiff bases.Limited work has been done on metal complexes of Schiff bases derived from 2-hydroxy-1-naphthaldehyde and anisidines [22,33]. Complexes of transition metal (II) derivatives of salicylaldehyde and diamine have received attention for their potential as catalysts for oxygen insertion into organic substrates [24,35]. The electrochemical synthesis of metal complexes was introduced by Dennis G. Tuck in 1982 [25]. Transition metals exhibit varied utility and interesting chemistry. Coordination compounds are crucial due to their roles in biological and chemical systems. Metal complexes with suitable ligands are more chemically significant and specific than the metal ions and their original forms [28]. The significance of metal ions in biological systems has become prominent, as they are more potent enzyme inhibitors compared to uncomplexed biologically active compounds. Evidence supporting the use of metal complexes in combating cancer, tumors, viruses, and bacteria has further fueled research interest in this area. Numerous metal complexes have demonstrated anticancer, antitumor, and antibacterial properties [29,31,32]. Complexation with metallic elements can render biologically inactive compounds active or enhance the activity of already active compounds. Further investigation is needed to understand the mechanisms involved in enhancing biological activity upon complexation [30,34].

2. Materials and Methods:

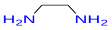
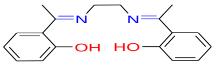
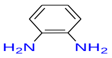
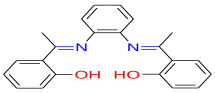
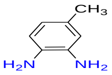
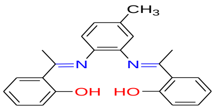
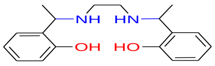
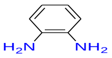
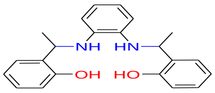
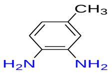
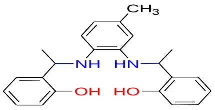
Series of reduced Schiff bases have been prepared from the reaction of two equivalents of 1-(2-Hydroxyphenyl) ethanone with one equivalent diamine derivatives followed by reduction with $NaBH_4$. The Co (II), Ni (II), Cu (II) and Zn (II) complexes of these ligands have been prepared. All the synthesized ligands and metal complexes were characterized by FTIR, ^{1}H and ^{13}C-NMR, MS, XRD, TGA, UV-Visible, Fluorescence and elemental analysis.

Figure 1.1: Preparation of hydrazones and metal complexes.



To prepare reduced Schiff bases, dissolve 2.27 mmol of the Schiff base in 10 mL of dichloromethane and cool the solution to 0°C. Add a methanolic solution of 2.0 mmol NaBH4 containing a few drops of concentrated KOH to the cooled solution. Adjust the pH to 6.0 and stir the mixture until the yellow color disappears. Evaporate the solvent to dryness and add 10 mL of cold water to the residue. Adjust the pH to 4–5 using 3M HCl. Filter the resulting white solid, wash it with cold water, ethanol, and diethyl ether, and then dry it under vacuum.

Table 1.1: Structure of Schiff bases [2a-2c] and reduced form [3a-3c]

Entry	Diamine	Product	Yield (%)
2a			94
2b			92
2c			95
3a			74
3b			85
3c			76

a) Preparation of 2-((E)-1-(2-((E)-1-(2-hydroxyphenyl) ethylideneamino) ethylimino) ethyl) phenol [SB07]

M.P.:190-192 ^{0}C; Colour: Yellow; MS [M+2]: 296.32; FTIR(KBr cm^{-1}): 3458, 3242, 3093, 2902, 1662, 1604, 1574, 1475, 1382, 1337, 1288, 1182, 1146, 1072, 1039, 934, 808, 656, 576;^{1}H-NMR (300 MHz, DMSO-d$_6$) δ: 2.608(s, 3H), 2.481(s, 3H), 3.895(s, 4H), 6.829-6.884(m, 4H), 7.271-7.409(m, 4H), 13.358(s, 2H); Elemental analysis [$C_{18}H_{20}N_2O_2$]: observed (calculated): C 72.70% (72.95%), H 6.84% (6.80%), N 9.42% (9.45%).

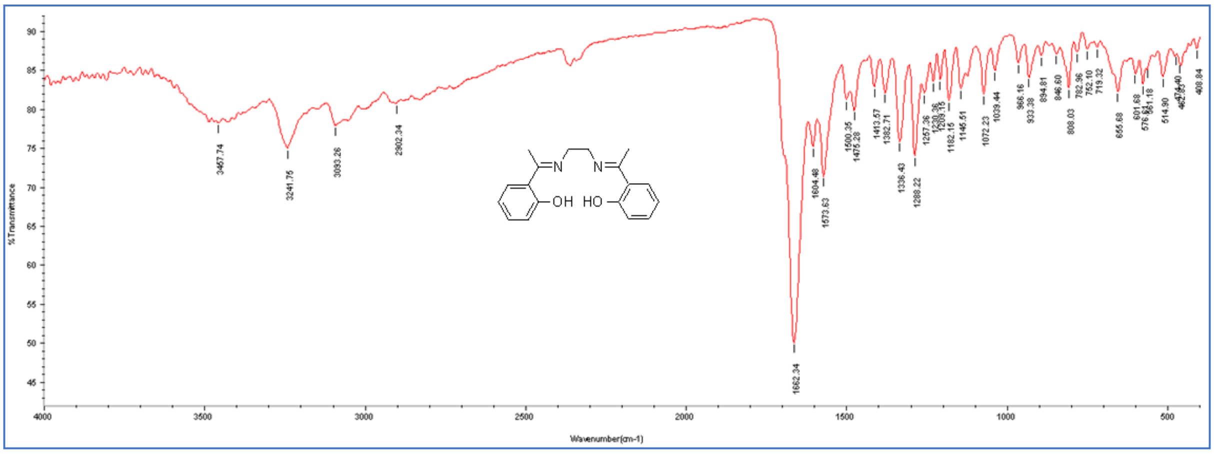


Figure 1.2: FTIR spectra of [SB07]

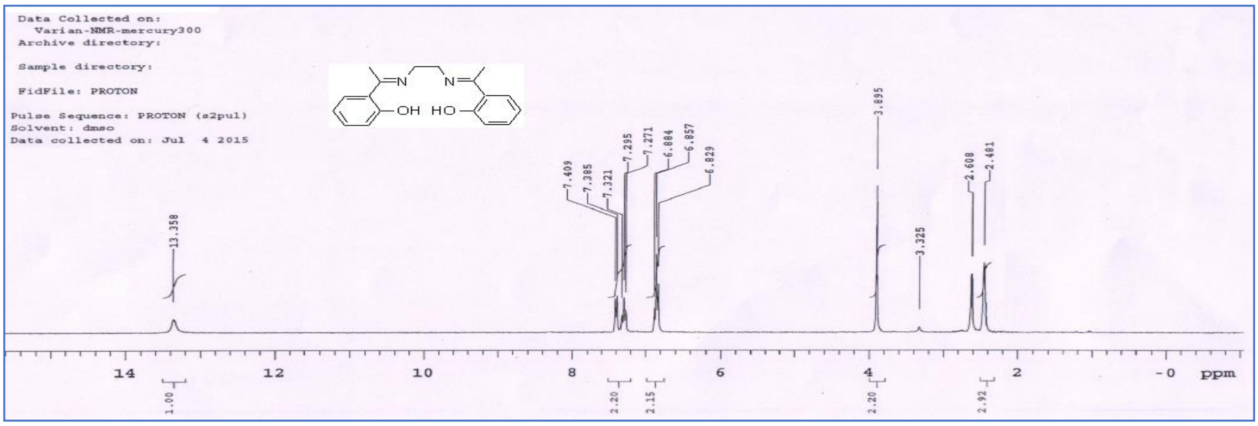


Figure 1.3: ^{1}H-NMR spectra of [SB07]

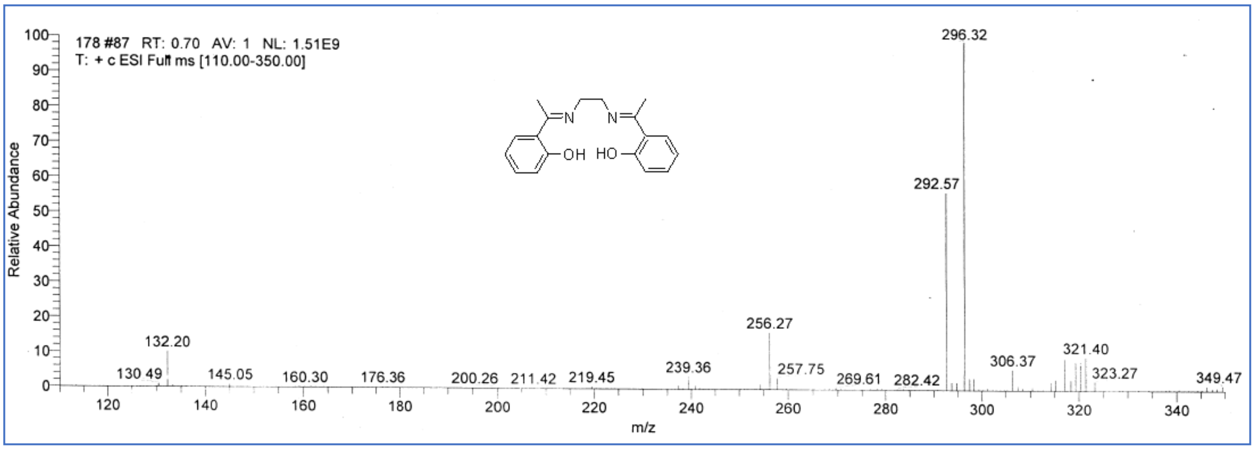


Figure 1.4: Mass spectra of [SB07]

b) Preparation of 2-((E)-1-(2-((E)-1-(2-hydroxyphenyl)ethylideneamino)phenylimino) ethyl)phenol [SB08]

M.P.: 194-196 ^{0}C; Colour: Yellow; MS [M+2]: 345.34; FTIR(KBr cm^{-1}): 3319, 3157, 2983, 2877, 2829, 1660, 1612, 1551, 1479, 1394, 1321, 1290, 1184, 1070, 1004, 933, 816, 752, 682, 634, 586.;^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 2.316(s, 6H), 6.607-6.963(m, 4H), 7.360-7.410(m, 4H), 7.735-7.761(m, 4H), 15.025(s, 2H); Elemental analysis [$C_{22}H_{20}N_2O_2$]: observed (calculated): C 76.79% (76.73%), H 5.88% (5.85%), N 8.18% (8.13%).

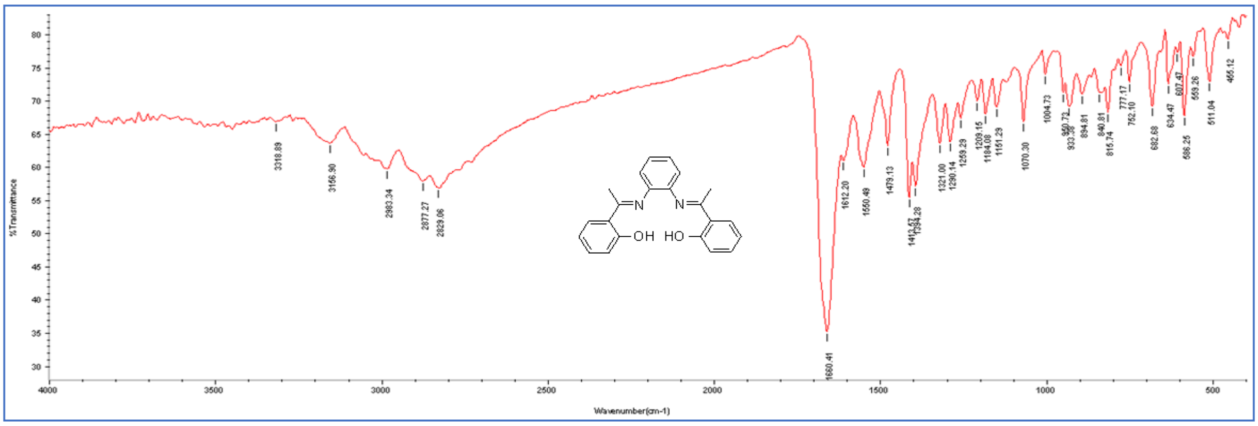


Figure 1.5: FTIR spectra of [SB08]

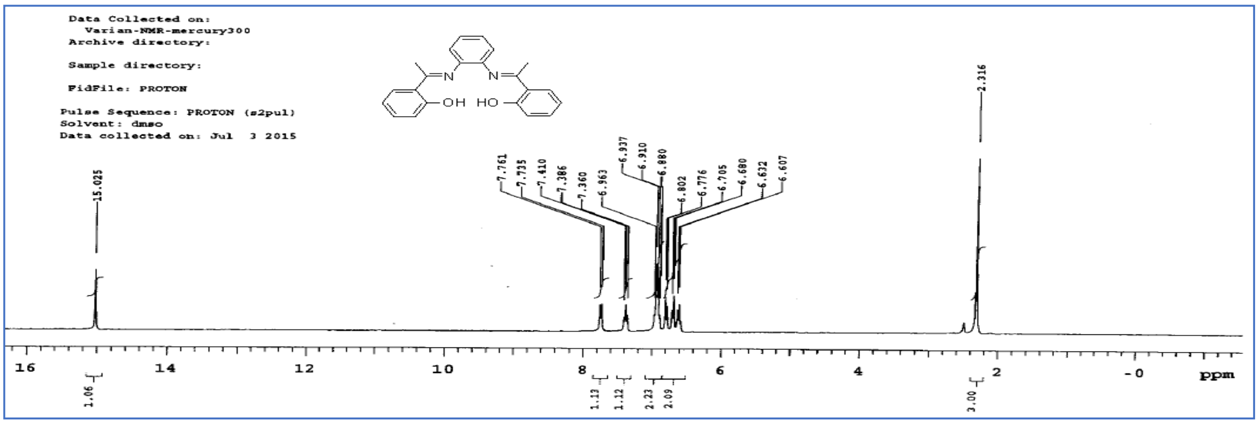


Figure 1.6: ^{1}H-NMR spectra of [SB08]

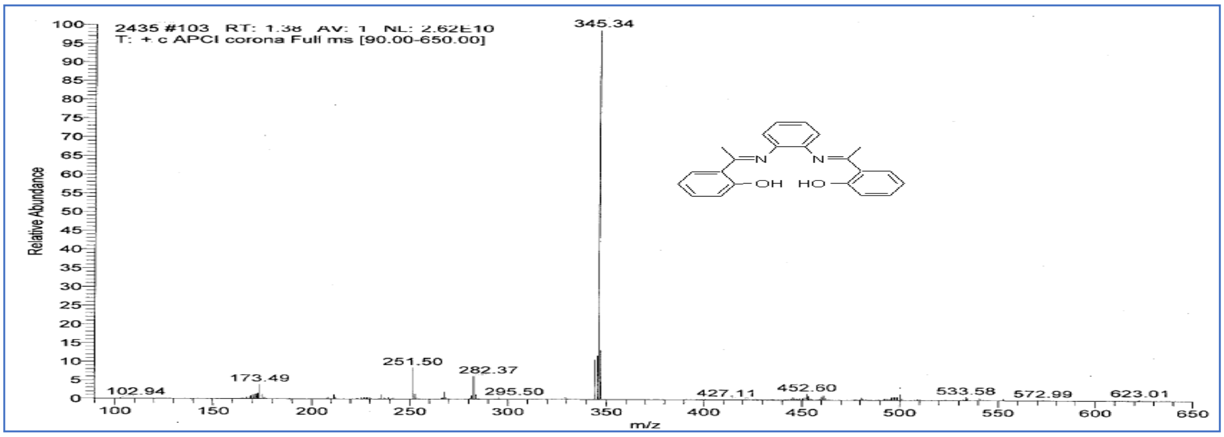


Figure 1.7: Mass spectra of [SB08]

c) Preparation of 2-((E)-1-(2-((E)-1-(2-hydroxyphenyl)ethylideneamino)-4-methyl phenyl imino)ethyl) phenol [SB09]

M.P.: 193-195^{0}C; Colour: Yellow; MS [M+H]: 359.50; FTIR(KBr cm^{-1}): 3186, 3053, 2922, 2843, 1662, 1616, 1566, 1479, 1415, 1255, 1209, 1178, 1103, 980, 945, 820, 770, 667, 599, 588; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 2.196(s, 6H), 2.389(s,3H), 6.918-6.962(m, 4H), 7.228-7.404(m, 4H), 7.539(m, 3H), 12.910(s, 1H), 13.091(s, 1H); Elemental analysis [$C_{23}H_{22}N_2O_2$]: observed (calculated): C 77.40% (77.07%), H 6.13% (6.19%), N 7.80% (7.82%).

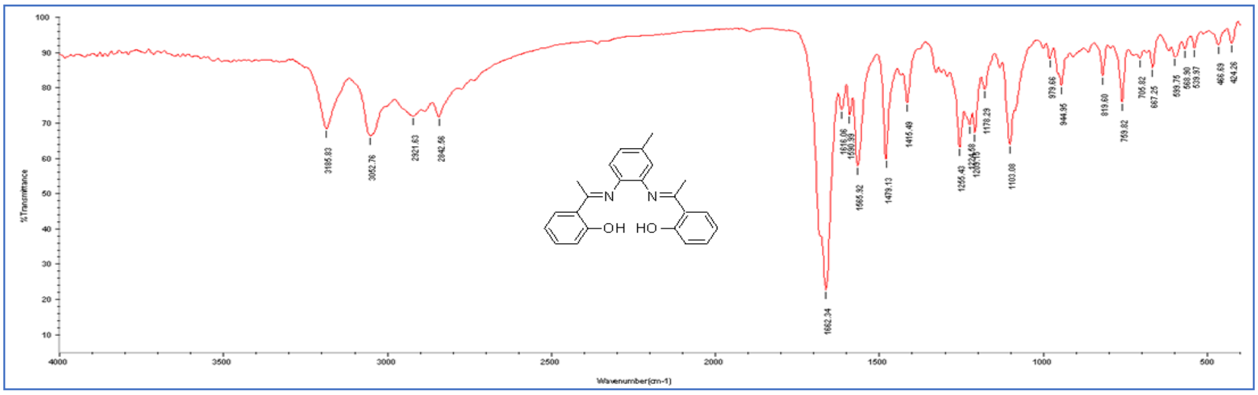


Figure 1.8: FTIR spectra of [SB09]

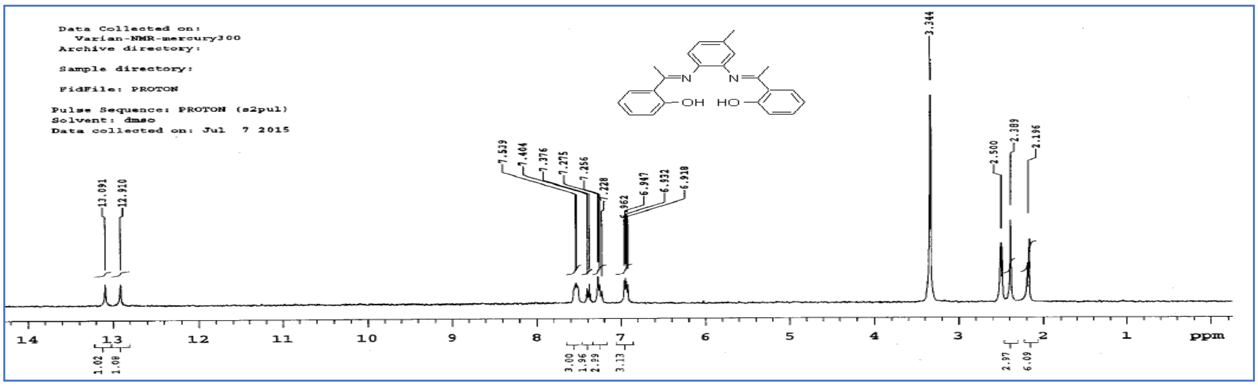


Figure 1.9: ^{1}H-NMR spectra of [SB09]

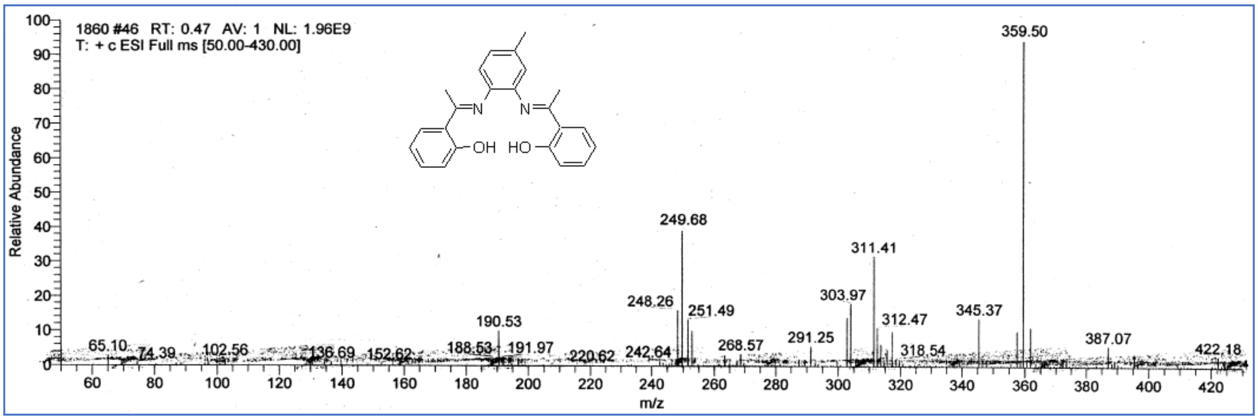


Figure 1.10: Mass spectra of [SB09]

d) Preparation of 2-(1-(2-(1-(2-hydroxyphenyl)ethylamino)ethylamino)ethyl)phenol [RSB07]

M.P.: 121-123 ^{0}C; Colour: white; MS [M+1]: 301.23; FTIR(KBr cm^{-1}): 3227, 3153, 3045, 2998, 2944, 2892, 2840, 1617, 1556, 1488, 1432, 1413, 1290, 1261, 1213, 1151, 1071, 956, 898, 846, 755, 684, 636, 603, 426; ^{1}H NMR (300 MHz, DMSO-d$_6$) δ: 1.288 (s, 6H), 3.836 (m, 4H), 3.857 (s, 2H), 5.05 (s, 2H), 6.360-6.723 (m, 4H), 6.992-7.056 (m, 4H),12.259 (s, 2H); Elemental analysis [$C_{18}H_{24}N_2O_2$]: observed (calculated): C 71.90% (71.97%), H 8.10% (8.05%), N 9.39% (9.33%).

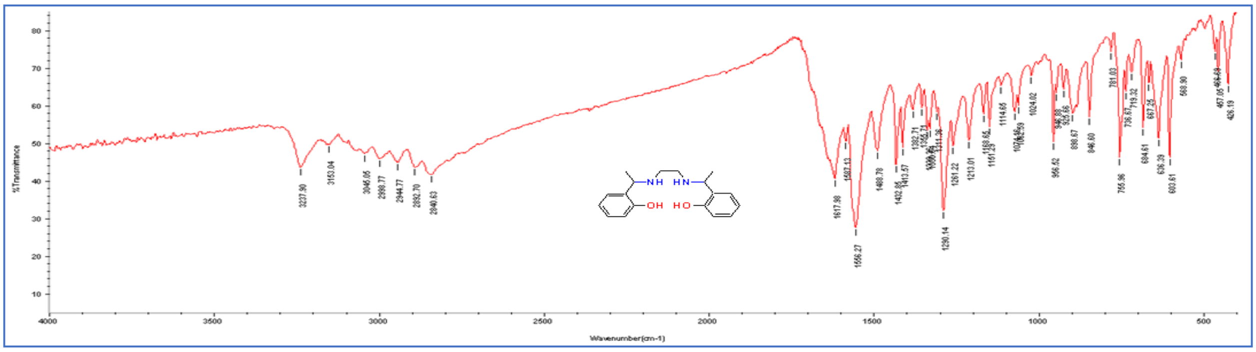


Figure 1.11: FTIR spectra of [RSB07]

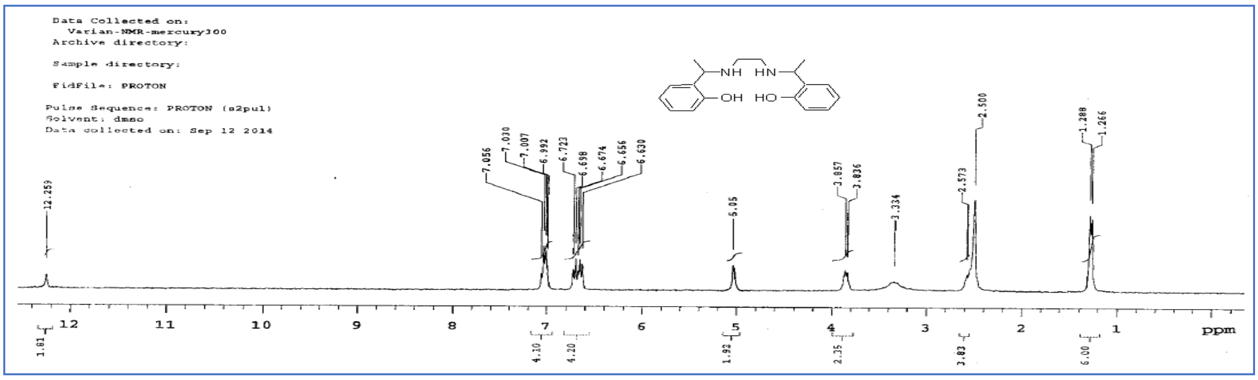


Figure 1.12: ^{1}H-NMR spectra of [RSB07]

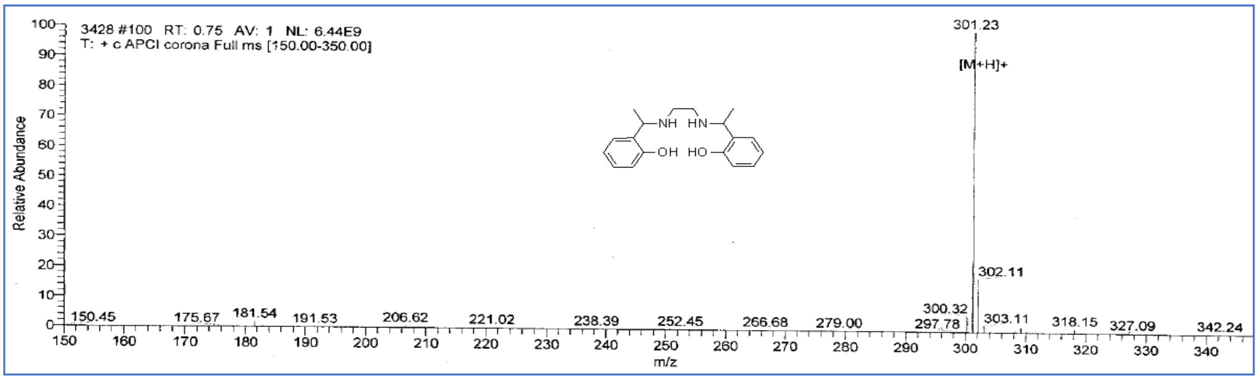


Figure 1.13: Mass spectra of [RSB07]

e) Preparation of 2-(1-(2-(1(2hydroxyphenyl)ethylamino)phenylamino)ethyl)phenol [RSB08]

M.P.: 136-138 ^{0}C; Colour: white; MS [M+]: 348.78; FTIR(KBr cm^{-1}): 3417, 3273, 3190, 1620, 1579, 1508, 1454, 1402, 1299, 1232, 1165, 1082, 1057, 1014, 879, 804, 687, 613, 518; ^{1}H NMR (300 MHz, DMSO-d_6) δ: 2.045(s,6H), 2.861(s,2H), 5.214(s, 2H), 6.664-7.343(m, 4H), 7.508-7.532(m, 4H),7.735-7.849(m,4H),12.031(s, 2H); Elemental analysis [$C_{22}H_{24}N_2O_2$]: observed (calculated): C 75.78% (75.83%), H 6.90% (6.94%), N 8.10% (8.04%).

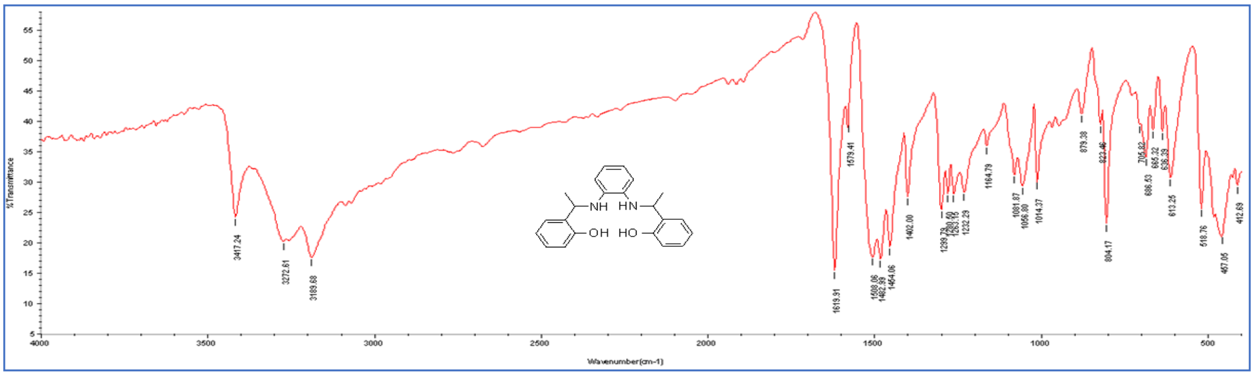


Figure 1.14: FTIR spectra of [RSB08]

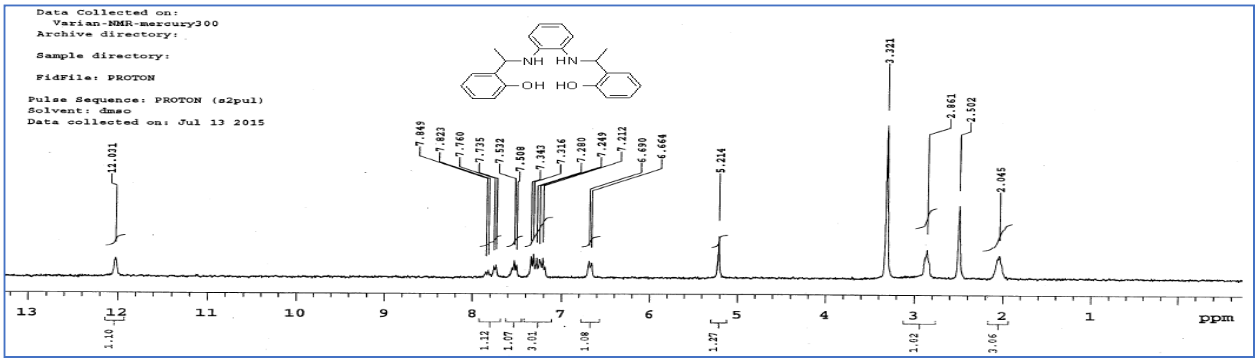


Figure 1.15: ^{1}H-NMR spectra of [RSB08]

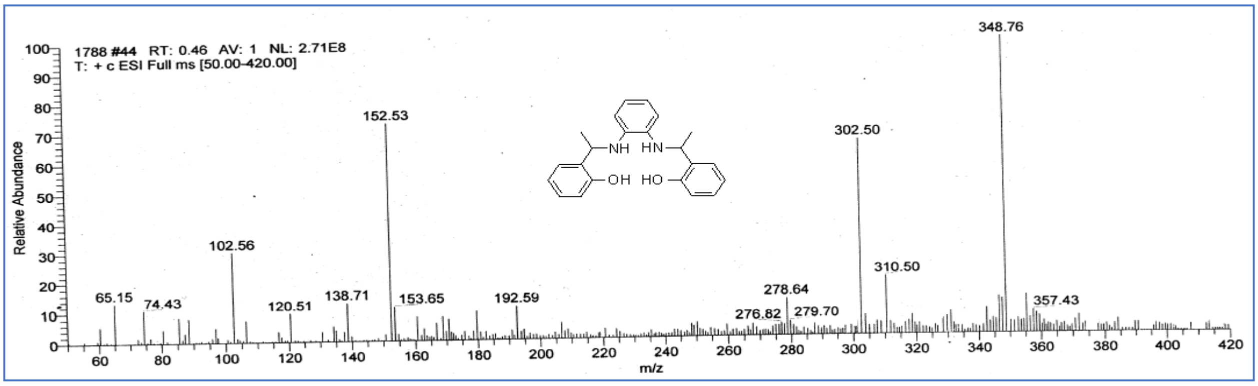


Figure 1.16: Mass spectra of [RSB08]

f) Preparation of 2-(1-(2-(1-(2-hydroxyphenyl) ethylamino)-4-methylphenylamino) ethyl) phenol [RSB09]

M.P.: 124-126 ^{0}C; Colour: white; MS [M+H]: 363.24; FTIR(KBr cm^{-1}): 3539, 3433, 3118, 3003, 2938, 2843, 1657, 1564, 1471, 1425, 1329, 1292, 1263, 1232, 1182, 1101, 976, 865, 738, 595; ^{1}H-NMR (300 MHz, DMSO-d$_6$) δ: 2.371 (s, 6H), 2.555 (s, 3H), 3.338 (s, 2H), 5.107 (s, 2H), 7.201-7.253 (m, 4H), 7.331-7.508 (m, 4H), 7.708 (m, 3H), 11.781 (s,1H), 12.388 (s, 1H); Elemental analysis [$C_{23}H_{26}N_2O_2$]: observed (calculated): C 76.32% (76.26%), H 7.22% (7.23%), N 7.70% (7.73%).

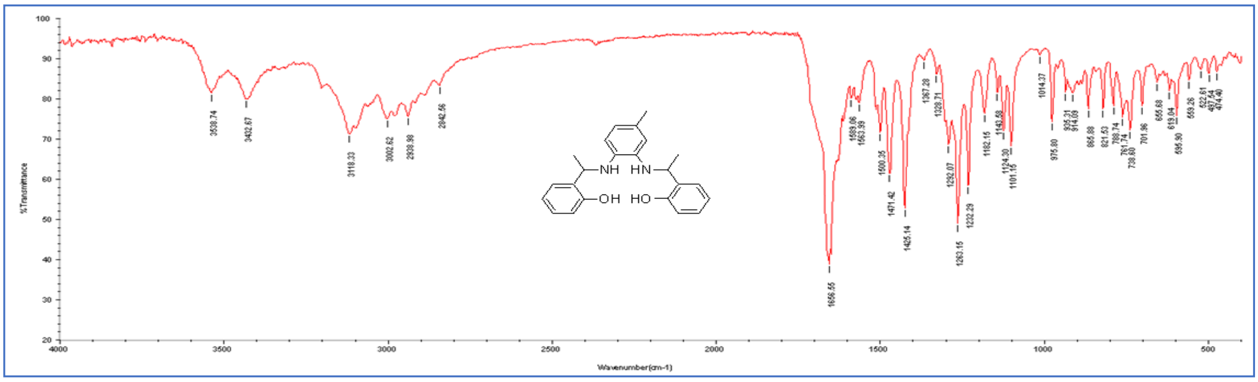


Figure 1.17: FTIR spectra of [RSB09]

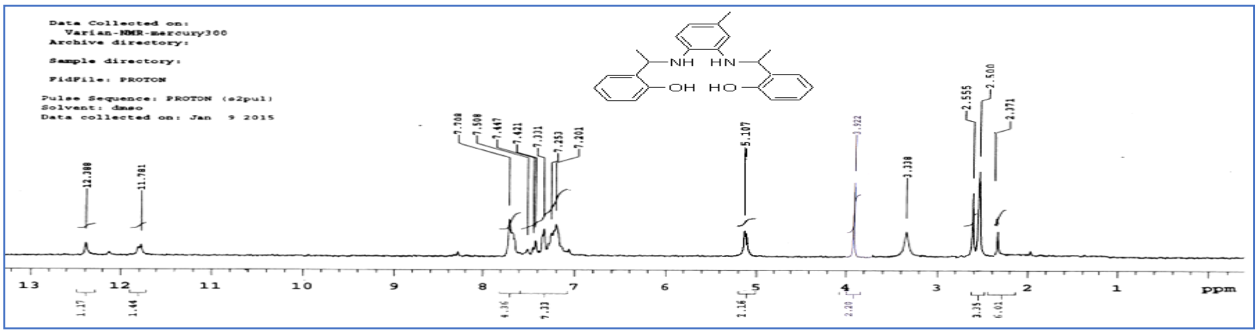


Figure 1.18: ^{1}H-NMR spectra of [RSB09]

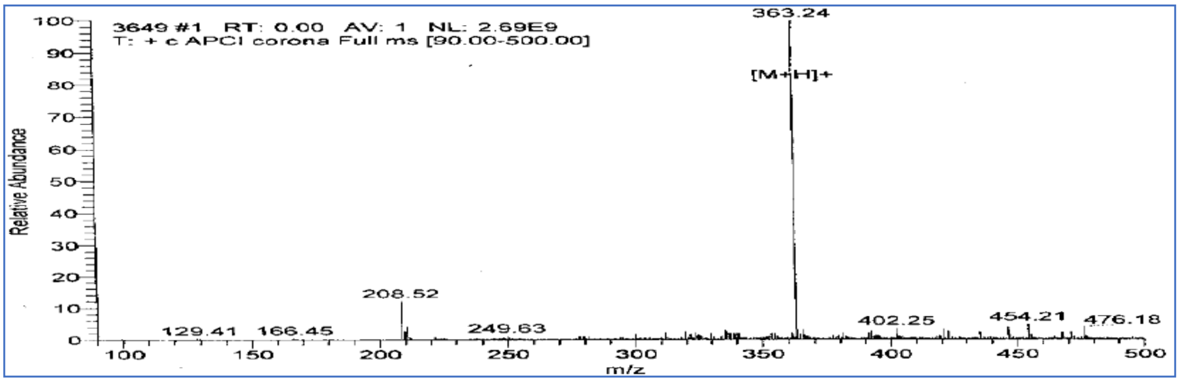


Figure 1.19: Mass spectra of [RSB09]

Table 1.2: Structures of metal complexes of schiff bases [4a-4l]

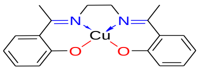
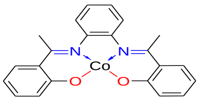
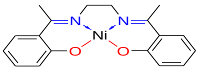
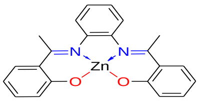
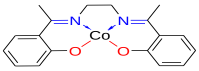
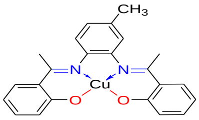
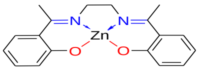
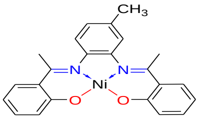
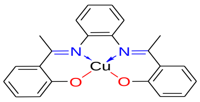
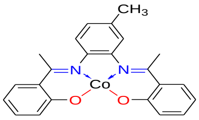
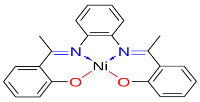
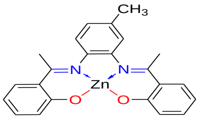
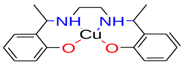
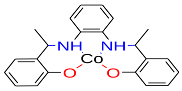
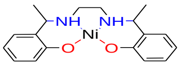
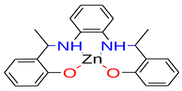
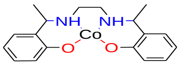
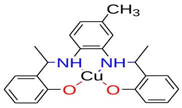
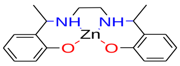
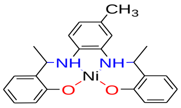
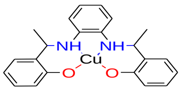
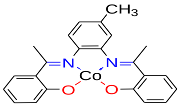
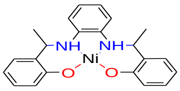
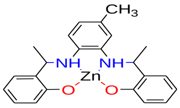
Entry	Complex	Colour	Entry	Complex	Colour
4a		Green	4g		Grey
4b		Shiny Red	4h		Yellow
4c		Grey	4i		Green
4d		Yellow	4j		Red
4e		Green	4k		Grey
4f		Shiny Red	4l		Yellow

Table 1.3: Structures of metal complexes of reduced schiff bases [5a-5l]

Entry	Complex	Colour	Entry	Complex	Colour
5a		Grey	5g		Grey
5b		Brown	5h		Grey
5c		Grey	5i		Grey
5d		Grey	5j		Brown
5e		Grey	5k		Grey
5f		Brown	5l		Grey

3. Results and Discussion:

The synthesis of the target transition metal complexes (4a-4l and 5a-5l) is shown in Figure 1.1. First, Schiff bases (2a-2c) were made by reacting 1-(2-Hydroxyphenyl) ethanone with diamines (1a-1c) in warm ethanol at 70°C. The imine bonds in these Schiff bases were then reduced using sodium borohydride, resulting in reduced Schiff base ligands (3a-3c). The structures of these products were confirmed through various analyses, including FT-IR, 1H and 13C-NMR, MS, UV-Visible, and Fluorescence.

The FT-IR spectra of Schiff bases 2a-2c showed strong absorption bands at 1612-1662 cm−1, corresponding to the imine (-HC=N-) function. These bands disappeared in the IR spectra of the reduced Schiff bases 3a-3c, confirming the reduction. Additionally, the FT-IR spectra of the reduced Schiff base ligands 3a-3c showed broad peaks at 3539-3433 cm−1 and 3417 cm−1, attributed to amino (-NH-) and hydroxyl groups, respectively. The 1H-NMR spectra of Schiff bases 2a-2c included singlets at δ 6.91 and 12.95 ppm, assignable to the azomethine proton (-CH=N-) and hydroxyl proton (-OH), respectively. New singlets at δ 5.05 and 5.2 ppm in the reduced Schiff bases 3a-3c confirmed the presence of $–CH_2$- and –NH- groups. The 13C-NMR spectra of Schiff bases 2a-2c displayed a characteristic peak at δ 161.5 ppm assignable to the imine carbon, which was absent in the spectra of 3a-3c. The mass spectra further confirmed the molecular weights of the target compounds.

The Schiff bases (2a-2c) and reduced Schiff base ligands (3a-3c) were then reacted with transition metal chlorides in methanol at a 1:1 molar ratio, forming metal complexes (4a-4l and 5a-5l). The FT-IR spectra of all metal complexes showed broad peaks in the region of 3330-

3517 cm−1 due to water of crystallization. The coordination mode of hydrazones with central metal ions was clarified based on FT-IR studies, showing medium intensity bands at 443-485 cm−1 due to υM–O vibrations and prominent bands at 501-620 cm−1 due to υM–N stretching. Elemental analysis of the metal complexes matched theoretical values, as shown in Table 1.4.

Table 1.4: Molar Conductance (Λm) and % Content of Metal in Complexes:

Complex	**Metal**	**% Metal Observed (Calculated)**	**Molar conductance Λm (Ω^{-1} mol^{-1} cm^2)**	**Complex**	**Metal**	**% Metal Observed (Calculated)**	**Molar conductance Λm (Ω^{-1} mol^{-1} cm^2)**
4a	Cu	17.80(17.76)	10.02	5a	Cu	17.63(17.56)	11.39
4b	Ni	16.70(16.63)	9.70	5b	Ni	16.50(16.44)	10.20
4c	Co	16.73(16.68)	9.50	5c	Co	16.55(16.49)	9.78
4d	Zn	18.23(18.18)	8.30	5d	Zn	18.04(17.98)	6.50
4e	Cu	15.71(15.65)	11.13	5e	Cu	15.56(15.50)	11.24
4f	Ni	14.68(14.63)	10.01	5f	Ni	14.55(14.49)	10.61
4g	Co	14.75(14.68)	9.57	5g	Co	14.58(14.54)	9.20
4h	Zn	16.10(16.04)	10.18	5h	Zn	15.96(15.88)	6.90
4i	Cu	15.17(15.13)	10.95	5i	Cu	15.06(14.99)	10.96
4j	Ni	14.20(14.14)	10.09	5j	Ni	14.03(14.00)	11.20
4k	Co	14.27(14.19)	8.93	5k	Co	14.25(14.19)	9.56
4l	Zn	15.56(15.50)	6.70	5l	Zn	15.39(15.33)	7.16

The molar conductance (Λm) of the metal complexes was calculated using the relation Λm = K/C, where C is the molar concentration of the metal complex solutions. Dissolving the complexes in DMF to prepare 10^{-3} M solutions, the molar conductivities were measured at 25±2°C. The study showed negligible molar conductance values, indicating that the complexes are non-electrolytes. The thermal behaviour of metal complex 5d was studied in the temperature range of 250–1000°C. TG-DTA studies revealed three stages of decomposition: weight loss below 100°C corresponding to lattice cell water, weight loss at 110–200°C due to coordinated water elimination, and a stable plateau above 600°C indicating the formation of zinc oxide.

From the experimental study, it is evident that practical observations align well with the theoretical values calculated for a 1:1 metal: ligand stoichiometry. The various spectroscopic analyses suggest that the proposed geometry for the transition metal complexes with the general formula ML·2H2O is octahedral. The probable structures are shown in Tables 1.2 and 1.3.

4. Fluorescence Study:

The UV-Visible spectra of ligands 2a-2c and 3a-3c show bands around 332-336 nm and 302-307 nm. A broad band at 310 nm is seen in ligands 2a-2b due to an intra-ligand transition linked to the azomethine group, but this band is absent in ligands 3a-3c. Bands around 298-370 nm are related to ligand-to-metal charge transfer.

Ligands 2a-2c exhibit emission bands in the range of 461-463 nm, while ligands 3a-3c show strong emission at 360 nm. Complexes 4a-4l have emission bands between 378-516 nm, and complexes 5a-5l have emission bands between 431-516 nm. Zn(II) complexes show much stronger fluorescence than their parent ligands and other metal complexes.

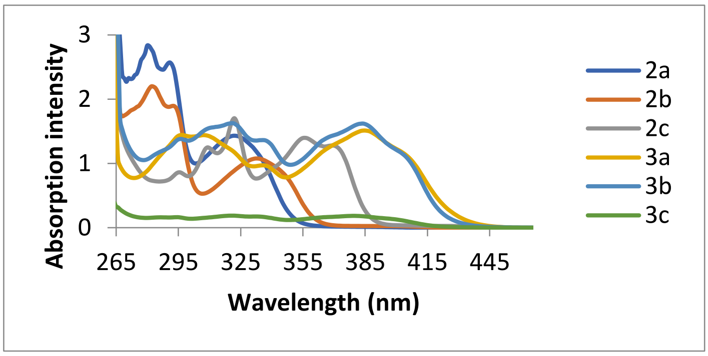
Adding metal increases the structural rigidity and fluorescence intensity of the complexes, making them suitable for photochemical applications.

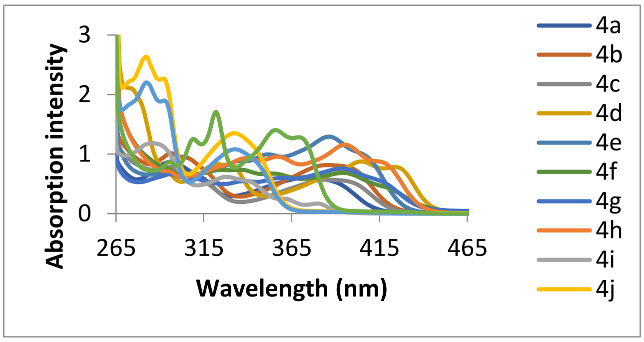
.

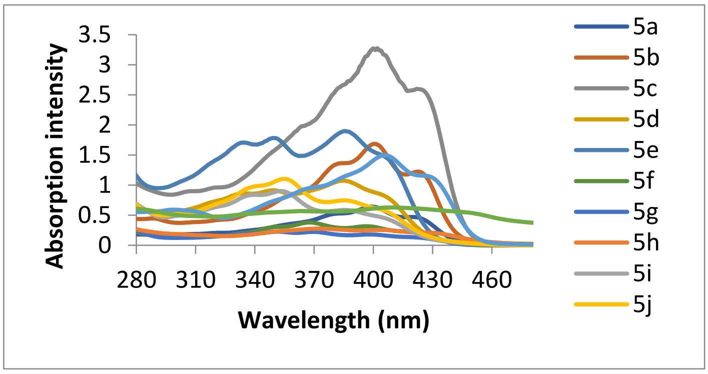
Table 2.5: The absorption and emission wavelength with intensity

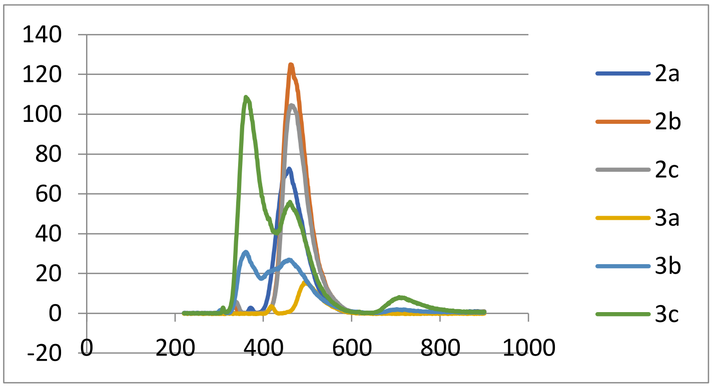
Hydrazone	Absorption λ_{max}(Intensity)	Emission λ_{max}(Intensity)	Complex	Absorption λ_{max}(Intensity)	Emission λ_{max}(Intensity)
2a	280(2.835)	458(72.704)	**3a**	385(1.513)	497(15.196)
2b	282(2.199)	460(123.34)	**3b**	321(1.626)	360(30.838)
2c	322(1.705)	467(104.219)	**3c**	320(0.188)	360(108.570)
4a	296(0.868)	455(415.269)	**5a**	399(0.643)	456(311.337)
4b	296(1.015)	485(446.254)	**5b**	401(1.687)	486(277.917)
4c	295(0.777)	500(401.611)	**5c**	403(3.239)	499(276.35)
4d	405(0.876)	465(658.786)	**5d**	385(1.072)	466(387.897)
4e	386(1.289)	532(3.469)	**5e**	385(1.897)	434(138.865)
4f	335(0.734)	378(2.562)	**5f**	367(0.381)	429(275.517)
4g	393(0.755)	500(3.376)	**5g**	351(0.228)	494(68.997)
4h	395(1.157)	486(303.76)	**5h**	373(0.279)	431(382.073)
4i	286(1.182)	516(43.061)	**5i**	353(0.902)	507(76.136)

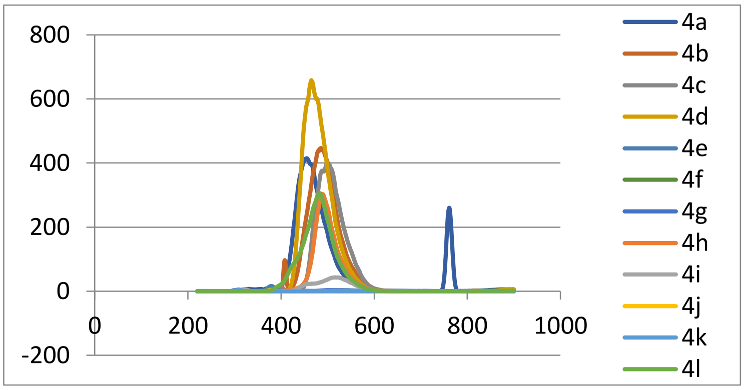
4j	282(2.629)	378(4.541)	**5j**	355(1.104)	516(172.644)
4k	282(2.199)	309(5.5)	**5k**	406(1.497)	504(231.897)
4l	322(1.705)	481(304.692)	**5l**	408(0.629)	482(172.958)

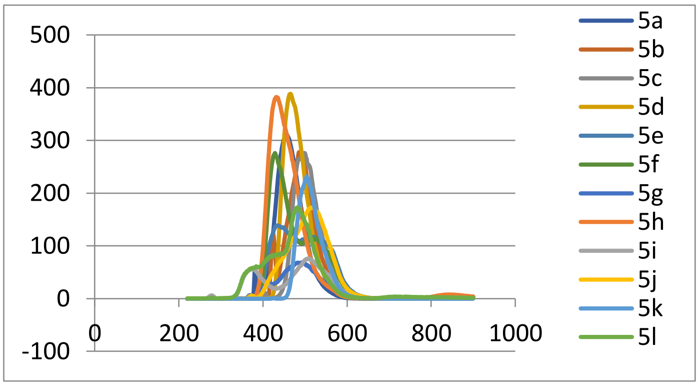












5. Acknowledgments

The authors thank Principal and Head Department of Chemistry, Shri Pancham Khemraj Mahavidyalaya, Sawantwadi for providing research and library facilities. The authors also thank Dr. Mustapha Mandewale, Dr. Ramesh Yamgar for encouragement and guidance during the research work.

6. References:

1. Yamgar R., Kamat P., et. al. “Preparation of Schiff base zinc metal complex (DMAPIMP)2Zn and development of HPLC chromatographic method for its analysis” *J. Chem. Pharm. Res*. **2011**; 3*(1)*:188-198.
2. Sheikh A. A., Muhammad M., et. al. “Synthesis and analytical studies of sulfadimidine-imine Schiff base complexes with Ni(II) and Cu(II)” *The BIOL (E-Journal of Life Sciences)* **2010**; 1*(2)*:37-40.
3. Kumar S., Dhar D. N. et. al. “Applications of metal complexes of Schiff bases-A review” *Jornal of Scientific & Indusrial Research* **2009**; 68:181-187.
4. Rodrguez-Arguelles M. C., Touron-Touceda P., et. al. “Complexes of 2-acetyl-*γ*-butyrolactone and 2-furancarbaldehyde thiosemicarbazones: antibacterial and antifungal activity” *Journal of Inorganic Biochemistry* **2009**; 103*(1)*:35-42.
5. Chandra S. and Sharma A. “Antifungal and spectral studies of Cr(III) andMn(II) complexes derived from3, 3-thiodipropionic acid derivative” *Research Letters in Inorganic Chemistry* **2009**; Article ID 945670.
6. Shakru R., Subhashini N. J. P., et. al. “Synthesis, characterization and antimicrobial studies on Cobalt(II), Nickel(II), Copper(II) and Zinc(II) complexes of N, O, S donor Schiff bases” *J. Chem. Pharm. Res.* **2010**; 2*(1)*:38-46.
7. Ramana N., Mitub L., et. al. “Studies on DNA cleavage and antimicrobial screening of transition metal complexes of 4-aminoantipyrine derivatives of N2O2type” *J. Iran. Chem. Soc.* **2009**; 6*(4)*:738-748.
8. Kurtoglu N. “Synthesis, characterization, chelation with transition metal ions, and antibacterial and antifungal studies of the 4-[(*E*)--phenyldiazenyl]-2-[(*E*)-(phenylimino)methyl]phenol dye” *J. Serb. Chem. Soc.* **2009**; 74*(8–9)*:917–926.
9. Vafazadeh R. and Kashfi M. “Synthesis and characterization of Cobalt(III) octahedral complexes with flexible salpn Schiff base in solution. Structural dependence of the complexes on the nature of Schiff base and axial ligands” *Bull. Korean Chem. Soc*. **2007**; 28*(7)*:1227-1230.
10. Shaker S. A., Farina Y. et. al. “Synthesis and characterization of mixed ligand complexes of 8-hydroxyquinoline and *o*-hydroxybenzylidene-1- phenyl-2,3-dimethyl-4-amino-3-pyrazolin-5-on with Fe(II), Co(II), Ni(II) and Cu(II) ions” *European Journal of Scientific Research* **2009**; 33*(4)*:702-709.
11. Gao W. T. and Zheng Z. “Synthetic studies on optically active Schiff-base ligands derived from condensation of 2-hydroxyacetophenone and chiral diamines” *Molecules* **2002**; *7*:511-516.
12. O'Connor K. J., Wey S. et. al. “Alkene aziridination and epoxidation catalyzed by chiral metal salen complexes” *Tetrahedron Lett.* **1992**; 33*(8)*:1001-1004.
13. Jacobsen E. N., Zhang W., et. al. “Highly enantioselective epoxidation catalysts derived from 1,2-diaminocyclohexane” *J. Am. Chem. Soc.* **1991**; *113(18)*:7063-7064.
14. Kim G. J., Shin J. H. “Application of new unsymmetrical chiral Mn(III), Co(II,III) and Ti(IV) salen complexes in enantioselective catalytic reactions” *Cat. Lett*. **1999**; 63:83-89.

15. Sasaki C., Nakajima K., et. al. “Preparetion and characterization of optically active quadridentate Schiff base-Titanium(IV) complexes and asymmetric oxidation of methyl phenyl sulfide with organic hydroperoxides” *Bull.Chem. Soc.* **1991**; 64*(4)*:1318-1324.
16. Adam W., Fell R. T., et. al. “Synthesis of optically active α-hydroxy carbonyl compounds by the catalytic, enantiselective oxidation of silyl enol ethers and ketene acetals with (salen) manganese (III) complexes” *J. Am. Chem. Soc*. **1998**; 120:708-714.
17. Hayashi M., Inoue T., et. al. “Asymmetric carbon-carbon bond forming reactions catalyzed by chiral Schiff base-Titanium alkoxide complexes” *Tetrahedron* **1994**; 50:4385-4398.
18. Nathan L. C., Koehne J. E., et. al. “The X-ray structures of a series of copper(II) complexes with tetradentate Schiff base ligands derived from salicylaldehyde and polymethylenediamines of varying chain length” *Polyhedron* **2003**; 22:887-894.
19. Liu J., Zhang B., et. al. “The direct electrochemical synthesis of Ti(II), Fe(II), Cd(II), Sn(II), and Pb(II) complexes with N,N*’*-bis(salicylidene)-ophenylenediamine” *Turk J Chem* **2007**; 31:623-629.
20. Xavier K. O., Chacko J., et. al. “Zeolite-encapsulated Co(II), Ni(II) and Cu(II) complexes as catalysts for partial oxidation of benzyl alcohol and ethylbenzene” *Applied Catalysis A: General* **2004**; 258:251-259.
21. Rao N. R., Tyaga R., et. al. “Synthesis and characterisation of a physiologically active quadridentate Schiff base and its metal complexes” *Nat. Acad. Sci. Letters* **1985**; 8*(11)*:343-346.
22. Mittal R., Chaturvedi S., et. al. “Synthesis and studies of some first-row transition metal complexes with Schiff base derived from 2-hydroxy-1- naphthaldehyd and m-anisidine” *Current science* **1986**; 55*(6)*:312.
23. Benarjea D., “*Coordination Chemistry*” Tata, McGraw-Hill Publishing company Ltd., New Delhi.
24. Nishinaga A., Tojo T. et. al. “A model catalytic oxygenation for the reaction of quercetinase”*J. Chem. Soc., Chem. Commun.* **1974**; 896-897.
25. Said F. F. and Tuck D. G. **“**The direct electrochemical synthesis of some thiolates of zinc, cadmium and mercury**”** *Inorganica Chimica Acta.* **1982**; 59:1-4.
26. Labisbal E., Sousa-Pedrares A., et. al.“Structural studies of pyrazineformamide N4-methylthiosemicarbazone and its Zinc(II) and Cadmium(II) complexes formed by electrochemical oxidation**”** *Polyhedron* **2002**; 21:1553-1559.
27. Sanchez-Piso J., Garca-Vazquez J. A., et. al. “Electrochemical synthesis and crystal structures of nickel(II), copper(II), zinc(II) and cadmium(II) complexes with N,N'-bis[(4-methylphenyl)sulfonyl] ethylenediamine” *Inorganica Chimica Acta.* **2002**; 328:111-122.
28. Shahid S., Raza M. A. et. al. “Synthesis, characterization and antimicrobial potential of transition metal complexes of triacetic lactone” *African Journal of Biotechnology* **2009**; 8*(19)*:5116-5121.
29. Rosenberg B. “Some biological effects of platinum compounds: new agents for the control of Tumours” *Platinum Metals Rev.* **1971**; 15*(2)*:42-51.
30. Sander E. G., Wright L. D., et. al. “Evidence for function of a metal ion in the activity of dihydroorotase from *Zymobacterium oroticum****”*** *J. Biol. Chem.* **1965**; 240*(9)*:3628-3630.

31. Udaysinha Patil, Mustapha Mandewale, Bapu Thorat, Aarti Nagarsekar, Ramesh Yamgar, “Transition metal tetrahydro-salophen type complexes: synthesis, characterization and antitubercular studies” Asian Journal of Research in Chemistry, 2016; 9(9);425-434
32. Patil U, Khan A, Nagarsekar A, Mandewale M, Yamgar R. *Synthesis and Antibacterial Studies of Some Reduced Schiff Base Derivatives*. Orient J Chem 2018;34(6).
33. MC Mandewale, B Thorat, U Patil, R Yamgar *Review: Synthesis And Applications Of Schiff Bases* Int. J. Chem. Pharm. Sci, 2015
34. Akin, O., et al. (2017). "Schiff Base Metal Complexes: Synthesis, Characterization, and Biological Applications." *Coordination Chemistry Reviews*, 344, 123-145
35. Bose, P., et al. (2021). "Coordination Chemistry of Schiff Base Ligands: Synthesis, Characterization, and Biological Applications." *Coordination Chemistry Reviews*, 426, 213506.
36. Vasquez, M., et al. (2020). "The Role of Schiff Base Metal Complexes in Medicinal Chemistry: Anticancer and Antibacterial Applications." *Bioinorganic Chemistry and Applications*, 2020, 7854360.