

Synthesis and Characterization of Novel Fluoro Azomethines and its Solution Study with Co(II), Ni(II), and Cu(II)

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ABSTRACT

Two new azomethine compounds, L₁ and L₂, were prepared by the condensation of 5-fluoro-2-hydroxyacetophenone with furan-2-carbohydrazide and thiophene-2-carbohydrazide, respectively. The structure of the synthesized compounds (ligands) was characterized by different techniques such as CHN(S) analysis, UV-Vis. spectrophotometry, FT-IR spectroscopy, ¹H-NMR spectroscopy, and mass spectrometry. Formation of binary complexes of the divalent transition metal ions Co (II), Ni (II) and Cu (II) with Schiff bases was investigated by the conventional potentiometric technique. The proton-ligand stability constant (pK_f^H) of the Schiff bases and the metal-ligand stability constant ($\log K_f$) of their complexes with Co (II), Ni (II), and Cu (II) have been extensively determined through Calvin-Bjerrum pH-metric titration technique.

Key words: Potentiometric titration, Azomethine, Proton-ligand stability constant, Metal-ligand stability constant.

1. INTRODUCTION

The compounds having the azomethine functional group (-C=N-) are generally known as Schiff base [1,2]. Multifarious Schiff bases have been synthesized since it was first reported in 1864 by Noble prize winner scientist Hugo Schiff [3]. Schiff bases are synthesized by a reversible acid/base-catalyzed condensation reaction of different primary amino groups with active carbonyl groups (aldehydes or ketones) [4,5]. Schiff bases are a vital category of organic compounds that have attracted considerable attention in many fields such as biological, clinical, medicinal, analytical, and pharmacological and have a broad assortment of applications in different regions such as biological chemistry, organic, and inorganic chemistry [6,7].

Hydrazone Schiff bases are a class of organic compound with the structure R₁R₂CO = NNH₂ and are generally prepared by reacting a stoichiometric amount of hydrazide with a carbonyl compound [8,9]. Hydrazone Schiff bases generally have extra chelating center. Hydrazones act as multi-dentate ligands and have nature to form stable metal complexes with transition metal ions due to the complexing ability of ligand through keto-enol tautomerism and availability of other donor sites in the ligand [10,11]. Due to its biological potency, pharmacological properties and synthetic flexibility of Schiff base derived from acid hydrazide hydrazones, hydrazones ligands, and their metal complexes are biologically active compounds as antiproliferative effects, antibacterial, antiviral, antifungal, antimicrobial, anti-inflammatory, anticonvulsant, antitubercular, antioxidative effects, antidepressant, anti-neoplastic, antileukemic, antimalarial, and antitumor agent [9,12-16]. They are utilized in therapy of schizophrenia, cancer, mental disorders and used as corrosion inhibitors, herbicides, insecticides, nematicides, rodenticides, plant growth regulators, optical sensors for a variety of chemical stimuli [9,17-21], and widely used to design compounds for molecular magnetism and in catalysis [22]. On the other hand, compounds containing thiophene and furan nucleus have been familiar as an essential part in the synthesis of heterocyclic compounds which shows potential pharmacological characteristics.

Thiophene and furan moiety and their derivatives are known as best pharmacophore in the diabetes mellitus, antimicrobial, hepatitis-B virus inhibitors, cholesterol inhibitors, antiviral, antitumor, and antitubercular agents [23,24]. Literature survey shows that the presence of halogen atom in the molecule increases the lipophilicity of the molecule and, therefore, affects the partitioning of a molecule into membranes and facilitates hydrophobic interactions of the molecule with specific binding sites on either receptor or enzymes. Because of its small size, fluorine has been used as a replacement for hydrogen in many biologically active molecules and the electronegativity of fluorine can have a substantial effect on the electron distribution, and on the basicity or acidity of neighboring groups, and can change the overall reactivity and stability of a molecule [25]. It has been observed that the introduction of a fluorine atom may act as a pharmacophore, enhancing the pharmacological properties of compounds compared with their non-fluorinated analogues [26].

The knowledge of the formation constant of complexes with drugs was useful to designate the appropriate from the drug and their effect with all other components of the blood stream as well as to measure the strength of metal ligand bonds [27]. Furthermore, it is useful to know, mode of the chelation of ligand toward metal and useful in theoretical problems as well as in the practical application of complexation. For the determination of the stability constant, various techniques are utilized, such as spectrophotometry, polarography, and potentiometry.

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pH-metric study is one of the best widely used technique because it has several distinction such as, it is simple and low cost technique, easy to operate, economic, and it is using to find the stability constant which is useful for the formation of a complex in solution [28]. Due to these valuable findings observed in the literature review and very less work observed on the complexation of 5-fluoro-2-hydroxyacetophenone, the present work was well planned and executed for the preparation of organic ligands through the condensation of 5-fluoro-2-hydroxyacetophenone with furan-2-carbohydrazide and thiophene-2-carbohydrazide, respectively. Complexation of newly synthesized organic ligand was carried out with transition metals (Co(II), Ni(II), and Cu(II)) to determine the order of stability constants using pH-metric technique at constant temperature $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ and at ionic strength of 0.1M KNO_3 , using 1,4-dioxane-water (60:40% V/V) system. Potentiometric titration curves of binary complexes were used in calculating the formation constant. The formation constant of the type of metal-Schiff base is calculated using Calvin-Bjerrum [29] and pH-metric titration technique as adopted by Irving-Rossotti [30,31].

2. EXPERIMENTAL

2.1. Materials

All the chemicals used were of A.R. grade, purchased from TCI and Thermo Fischer and used without any further purification. Other chemicals used were KOH, conc. HNO_3 and 1,4-dioxane. All the solutions were prepared in doubly distilled CO_2 free water and solutions of ligands were prepared in 1,4-dioxane. The stock solutions of metal ions Co(II), Ni(II), and Cu(II) were prepared from their nitrate salts and standardized using complexometric titration with the disodium salt of EDTA [32]. The carbonate-free KOH solution was standardized by a reported method [33]. Nitric acid was standardized with a standard KOH solution and the constant ionic strength was maintained with the inert electrolyte potassium nitrate (1M KNO_3). The pH measurements were recorded at $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ using combined electrode on Equiptronics pH meter with pH range 0–14. The melting points were recorded on a hot stage Veego (VMP-D) melting point apparatus. Elemental C, H, N, and S analysis were carried out on a Fison EA-1108 analyzer. The frontier infrared spectra (FT-IR) were recorded using a 8300 Shimadzu Spectrophotometer using potassium bromide (KBr) disc in the frequency range of $4000\text{--}400\text{ cm}^{-1}$. The ultraviolet-visible (UV) spectra were measured using a Shimadzu UV-Vis. 160 A-Ultra-violet Spectrophotometer in the range of 200–800 nm. The UV-Vis. spectra for the Schiff bases were recorded in DMF. The $^1\text{H-NMR}$ spectra were recorded on a NMR Spectrometer-300 MHz (Bruker) using deuterated $\text{d}_6\text{-DMSO}$ as the solvent and tetramethylsilane as the internal standard. Mass spectra were recorded on a Micromass UK PLATFORM II LC-MS spectrometer.

2.2. Experimental methods

2.2.1. Synthesis of 2-Hydroxy-5-fluoroacetophenone-furan-2-carbohydrazide (L_1)

L_1 was prepared by adding equimolar amounts of furan-2-carbohydrazide (1 mmol) and 2-hydroxy-5-fluoroacetophenone (1 mmol) in the presence of glacial acetic acid (2–3 drops) in absolute

methanol. The mixture was refluxed at 80°C for 6 h [34]. The progress of the reaction was monitored by TLC. At end of reaction, the mixture was cooled first at room temperature then poured into water with stirring. Yellowish crystalline product obtained was filtered and washed several times with cold methanol followed by crystallization and finally dried under vacuum. The yield was 78%. All analytical and physical data derived for synthesized ligand are given in Table 1. Elemental Analysis: Found (calculated) (%) $\text{C}_{13}\text{H}_{11}\text{FN}_2\text{O}_3$: C, 59.51 (59.54); H, 4.25 (4.23); F, 7.26 (7.24); N, 10.65 (10.68); O, 18.33 (18.30). $^1\text{H NMR}$ (DMSO-d_6 , δ -ppm): 12.95 (1H, s, Phenolic -OH); 11.24 (1H, s, imino NH); 7.99, 7.43 and 6.73 (3H, d, Furan); 7.49, 7.20 and 6.94 (3H, m, phenyl) and 2.46 (3H, s, methyl).

2.2.2. Synthesis of 2-Hydroxy-5-fluoroacetophenone-thiophene-2-carbohydrazide (L_2)

L_2 was prepared by adding equimolar amounts of thiophene-2-carbohydrazide (1 mmol) and 2-hydroxy-5-fluoroacetophenone (1 mmol) in the presence of glacial acetic acid (2–3 drops) in absolute methanol. The mixture was refluxed at 80°C for 3 h. The progress of the reaction was monitored by TLC. At end of reaction, the reaction mixture was allowed to cool. Very pale yellow colored product obtained was filtered, washed several times with cold methanol followed by crystallization and finally dried under vacuum. The yield was 63%. All analytical and physical data derived for synthesized ligand are given in Table 1. Elemental Analysis: Found (calculated) (%) $\text{C}_{13}\text{H}_{11}\text{FN}_2\text{O}_2\text{S}$: C, 56.15 (56.11); H, 3.95 (3.98); F, 6.82 (6.83); N, 10.05 (10.07); O, 11.54 (11.50); S, 11.47 (11.52). $^1\text{H NMR}$ (DMSO-d_6 , δ -ppm): 13.00 (1H, s, Phenolic OH); 11.34 (1H, s, imino NH); 8.07, 7.94 and 7.20 (3H, d, Thiophene); 7.94, 7.48 and 6.94 (3H, m, phenyl) and 2.48 (3H, s, methyl).

2.3. Potentiometric apparatus and procedure

The pH measurements were recorded at $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ using combined electrode on equiptronics pH meter with pH range 0–14. Before and after each series of pH measurements started, a calibrated electrode was prepared using standard buffer solutions at pH 4.005, 6.850, and 9.180, and the temperature was fixed at $25^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$ by flowing water from a constant temperature water bath through the jacket. To measure the pH of the free hydrogen ion concentration $[\text{H}^+]$, the pH results were corrected by titrating an identified concentration of standard HCl solution with standard KOH solution using the same experimental conditions. Each of the investigated solutions was thermo stated at the 25°C temperature with accuracy of $\pm 0.5^{\circ}\text{C}$, and the solutions were left to stand at this temperature for about 15 min before titration.

For the evaluation of proton-ligand stability constant (pK_1^H) and metal-ligand stability constant ($\log K_1$) of binary systems, the following sets of solutions were prepared each with a total volume 50 mL and titrated against 0.2 M of standardized CO_2 -free KOH solution at constant ionic strength of 0.1 M KNO_3 and oxygen-free N_2 gas was bubbled through the mixture to keep an inert atmosphere under magnetic stirring.

- Set-1: HNO_3 (0.2M 5 mL) + KNO_3 (1M 9.0 mL) + D.D.W. (6.0 mL) + 30 mL 1,4-dioxane
- Set-2: HNO_3 (0.2M 5 mL) + KNO_3 (1M, 8.9 mL) + Ligand solution (0.02M 5mL) + D.D.W. (6.1 ml) + 25 mL 1,4-dioxane

Table 1: Physical data of synthesized compounds.

Compound code	MF	MW	Color	Elemental analysis (%)				MP ($^{\circ}\text{C}$)	Yield (%)
				C	H	N	S		
L_1	$\text{C}_{13}\text{H}_{11}\text{FN}_2\text{O}_3$	262.24	Yellow	59.51	4.25	6.31	9.25	179	78
L_2	$\text{C}_{13}\text{H}_{11}\text{FN}_2\text{O}_2\text{S}$	278.30	Pale Yellow	56.15	3.95	10.05	11.52	207	63



- Set-3: HNO₃ (0.2M 5 mL) + KNO₃ (1M 8.8 mL) + Ligand solution (0.02M 5 mL) + Metal nitrate Solution (0.02M 5 mL) + D.D.W. (1.2 mL) + 25 mL 1,4-dioxane.

For all investigated solutions, the Metal-ligand ratios in binary systems were kept 1:1.

Solutions prepared as given in above sets were titrated pH-metrically against 0.2 M KOH solution and the pH meter readings were recorded after each addition of alkali. The readings noted for 1,4-dioxane-water (60:40% V/V) system are corrected using Van Uitert and Hass relation [35]. The titration curves of pH versus volume of alkali added were plotted (Figures 1 and 2), Proton ligand (pK_1^H) and metal-ligand stability constant ($\log K_1$) were calculated by adopting the Irving and Rossotti technique [36]. In respect of Set-1, Set-2, and Set-3 titration curves are named as acid curve, ligand curve, and metal curve.

3. RESULTS AND DISCUSSION

3.1. Characterization of ligands

Two new Schiff base compounds were synthesized by condensation of 5-fluoro-2-hydroxyacetophenone with furan-2-carbohydrazide and thiophene-2-carbohydrazide respectively, in 1:1 molar ratio using anhydrous absolute methanol as solvent. These reactions are

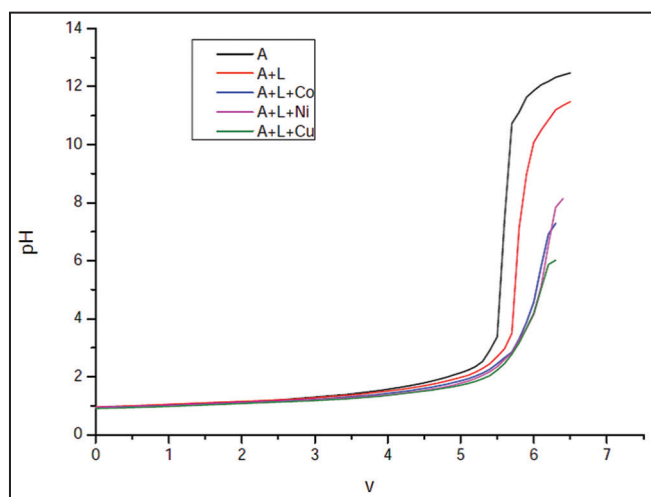


Figure 1: pH metric titration curve of L₂.

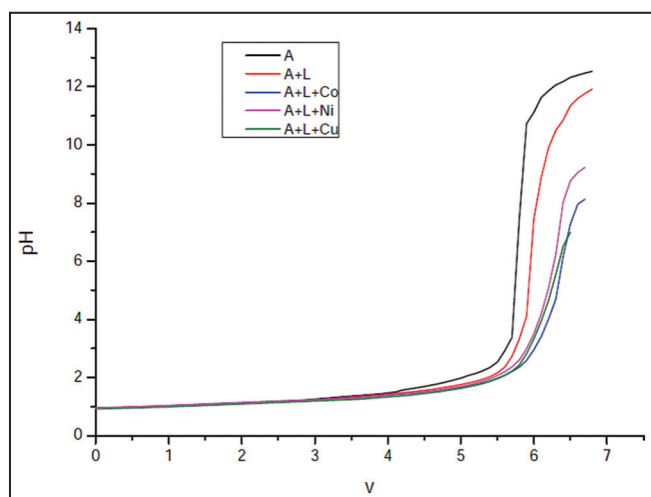


Figure 2: pH metric titration curve of L₁.

indicated in Scheme 1. The reactions were found to be quite facile and could be completed after reflux for 6–8 h. All the compounds were intensely colored solids. They are soluble in common organic solvents. The purity of the Schiff bases was checked by TLC using silica gel-G as adsorbent. Schiff bases L₁ and L₂ gave a sharp melting point indicating the isolation of pure compounds. The micro-elemental analysis for C, H, N, and S, melting point as well as the molecular weight of the ligands are given in Table 1. An outline of the proposed structure for Schiff bases are depicted in Scheme 1. The structure of synthesized Schiff bases L₁ and L₂ were established by IR, ¹H NMR, mass spectrometry, and CHN(S) analysis.

3.1.1. FT-IR spectra

The IR spectra of the ligands show characteristic bands at 1661, 1645 cm⁻¹ due to $\nu(\text{C}=\text{O})$ of hydrazinic group in the L₁ and L₂, respectively. The very strong and sharp bands located at 1586 and 1610 cm⁻¹ are assigned to the $\nu(\text{C}=\text{N})$ stretching vibrations of azomethine of the ligands L₁ and L₂, respectively. Bands at 3129 and 3121 cm⁻¹ were assigned to the $\nu(\text{N}-\text{H})$ stretching group of hydrazinic for ligands L₁ and L₂, respectively [37]. A peak at 3220 cm⁻¹ in the IR spectrum of the ligands corresponds to the phenolic -OH group. Bands at 1100 and 1113 cm⁻¹ can be assigned to $\nu(\text{N}-\text{N})$ of hydrazide moiety of ligand L₁ and L₂, respectively [38] (Supporting information, Figures 3 and 4).

3.1.2. ¹H NMR

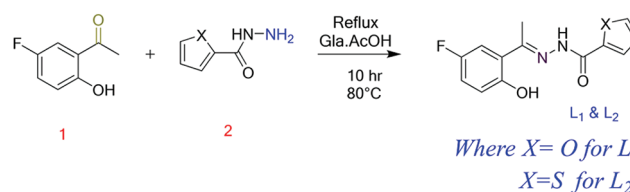
The ¹H NMR spectra of the ligands in d₆.DMSO showed peaks at 6.73–7.99 and 7.20–8.07 δ ppm (parts per million) assigned to protons of furan, and thiophene ring for L₁ and L₂, respectively. Sharp peaks at 12.95 and 13.00 δ ppm were assigned to O–H of phenolic groups for L₁ and L₂, respectively. Peaks at chemical shifts 11.24 and 11.34 δ ppm were assigned to N–H of hydrazinic groups for L₁ and L₂, respectively. Peaks at 6.94–7.49 and 6.94–7.94 δ ppm assigned to protons of phenyl ring for L₁ and L₂, respectively. The methyl group protons appear as a singlet at 2.46–2.48 δ ppm (See supporting information, Figures 5 and 6).

3.1.3. Mass spectra

The mass spectra of the ligands were also consistent with the proposed structural formula. The mass spectrum of L₁ and L₂ showed several peaks corresponding to successive fragmentations of the molecule. Peak detected at m/z 261.1 and 277.10 (M^+) represents the molecular ion peak of the ligands L₁ and L₂, respectively. Other distinct peaks were observed in the spectrum, assigned to the fragments (See supporting information, Figures 7 and 8).

3.1.4. Electronic spectra

The electronic spectral analysis of L₁ and L₂ ligands was carried out in DMF (10⁻⁴ M) at room temperature ranging from 200 to 800 nm (Figure 9) and the data are shown in Table 2. The spectra of the ligands exhibit two main absorption bands in the range of 301.84–288.49 nm might be attributed to $\pi \rightarrow \pi^*$ transitions of the chromophore (-C=N-NH-CO-), and the second band in the range of 337.54–335.79 nm might be attributed to the $n \rightarrow \pi^*$ transitions resulting from azomethine and carbonyl groups [39].



Scheme 1: Synthesis of ligand L₁ and L₂.

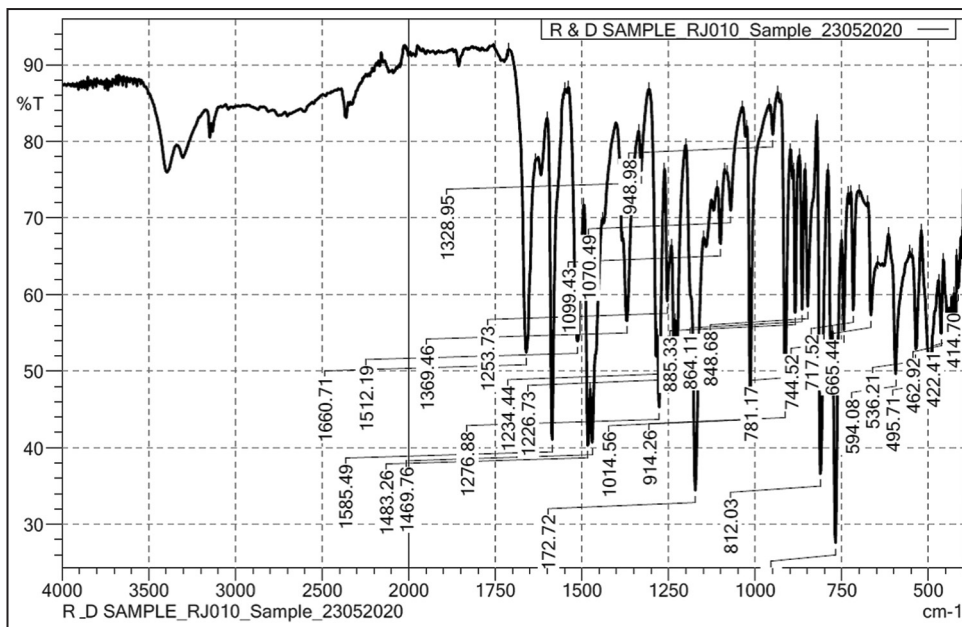


Figure 3: IR spectrum of L₁.

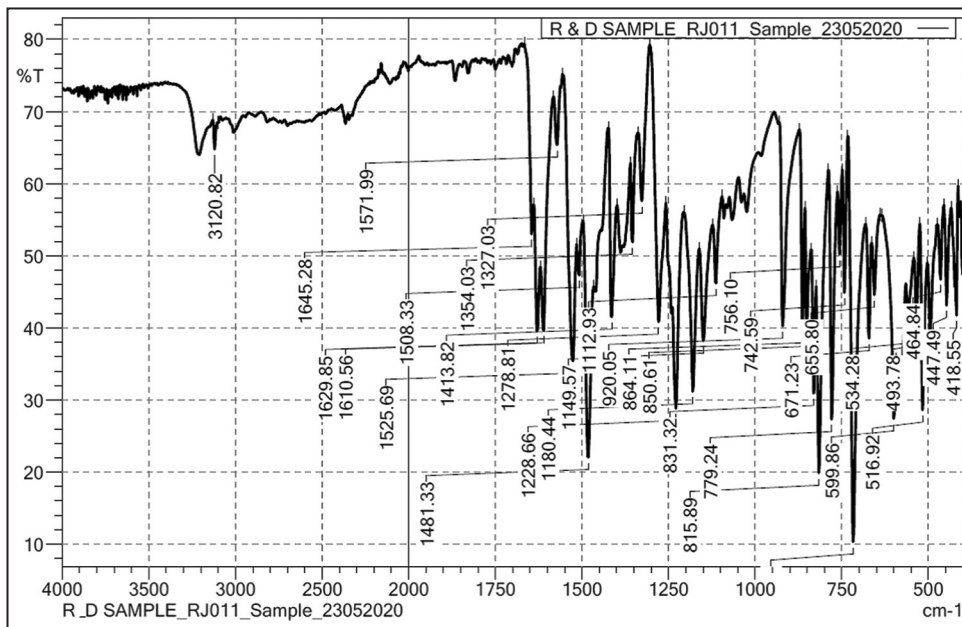


Figure 4: IR spectrum of L₁.

Table 2: Proton-ligand stability constant of Schiff.

Compound	Log pK ₁ ^H	pK ₁ ^H
L ₁	3.364	2.313×10 ³
L ₂	3.7078	5.102×10 ³

3.2. Potentiometric studies

When metal forms a series of steps complexes with the ligand a general decrease in Stability constant is usually found. Measuring for the solution equilibria of the studied Co (II), Ni (II) and Cu (II) hydrazone ligand complexes cannot be investigated in aqueous solution because of the nature of the involved compounds and to obtain homogenous solution. The 1,4-dioxane-water (60:40% V/V) solution mixture was selected as a solvent due to the studied ligands and its metal complexes

are soluble forming stable solutions. In all the systems, the ionic strength was kept constant at 0.1 mol dm⁻³ by addition of KNO₃ as supporting electrolyte. On addition of KOH deprotonation of the investigated ligands occurs and representation of the protonation constants in stability study expressed in terms of proton-ligand stability constant or protonation constants was given by equation 1 and 2. The protonation constants of hydrazone ligands are given in Table 3. The potentiometric titration was carried out keeping 1:1 metal to ligand ratio. In this present study, the formation constants were determined by Calvin-Bjerrum pH-metric titration technique as adopted by Irving-Rossotti, through titration of the ligands with the metal ions at a constant ionic strength 0.1 M KNO₃ at 25°C ± 0.5°C. Evaluated values of formation constants show the behavior of ligands and their interaction with metal ion in solution. The formation constants are depending on experimental conditions of solvent system, 60:40% V/V 1,4-dioxane-water system at 25°C ± 0.5°C. In the present work, metal nitrates of Co (II), Cu (II), and

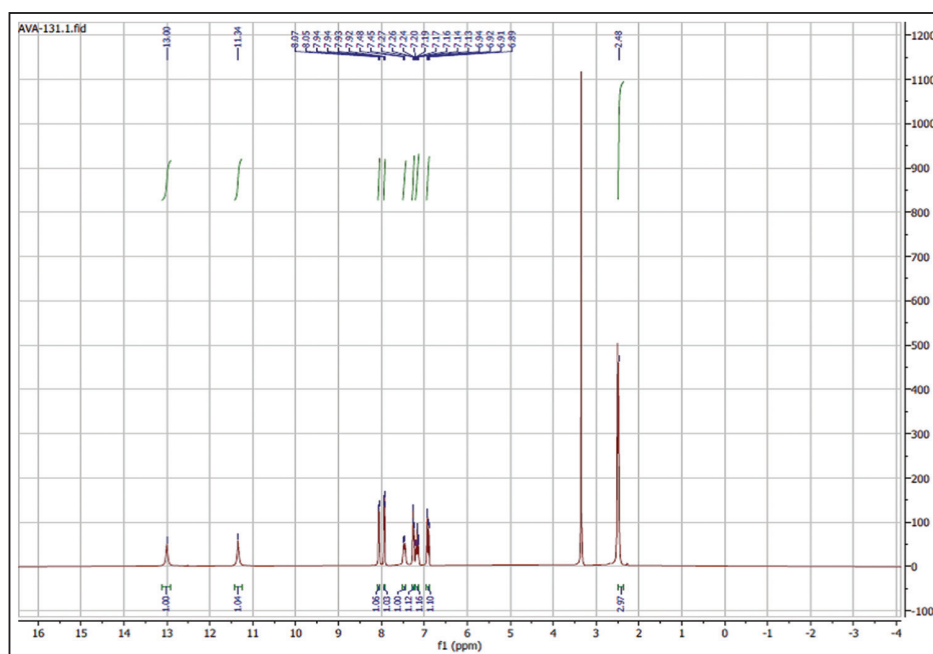


Figure 5: ¹H NMR spectrum of L₁.

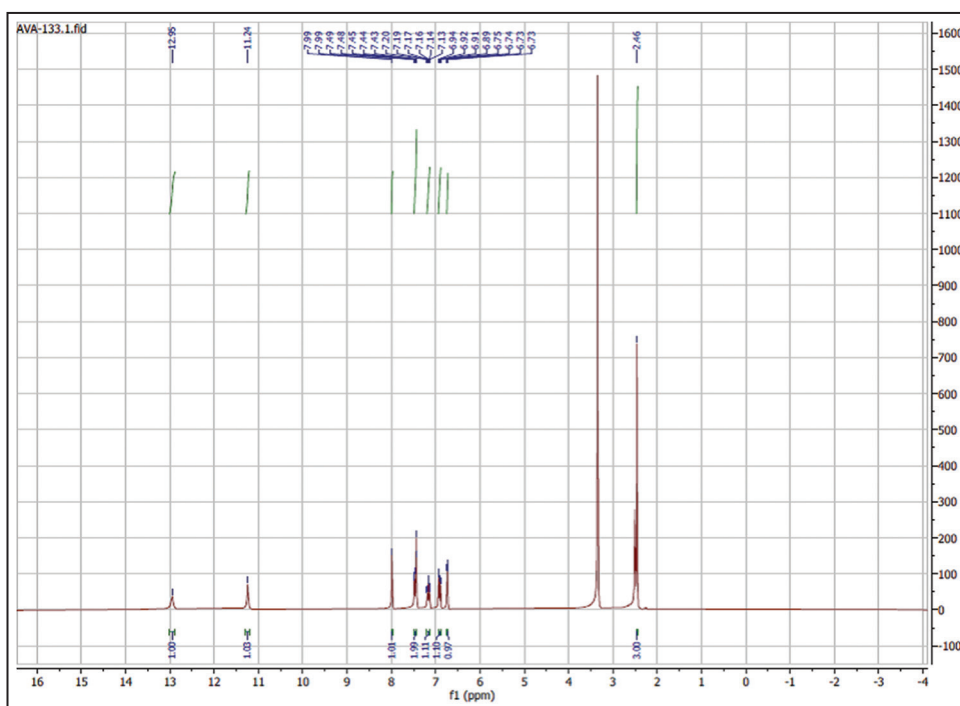


Figure 6: ¹H NMR spectrum of L₂.

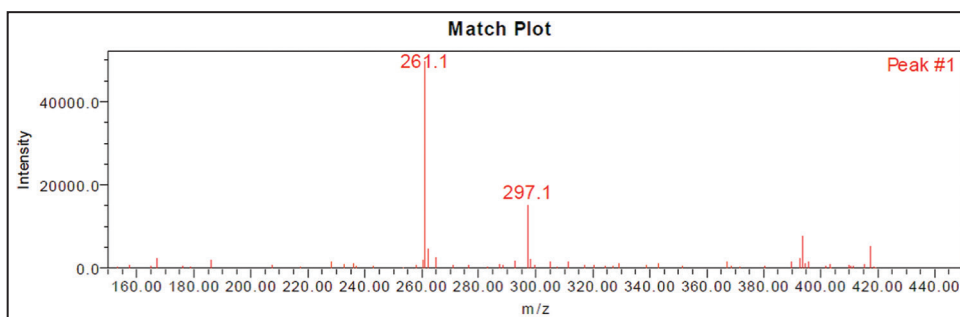


Figure 7: Mass spectrum of L₁.

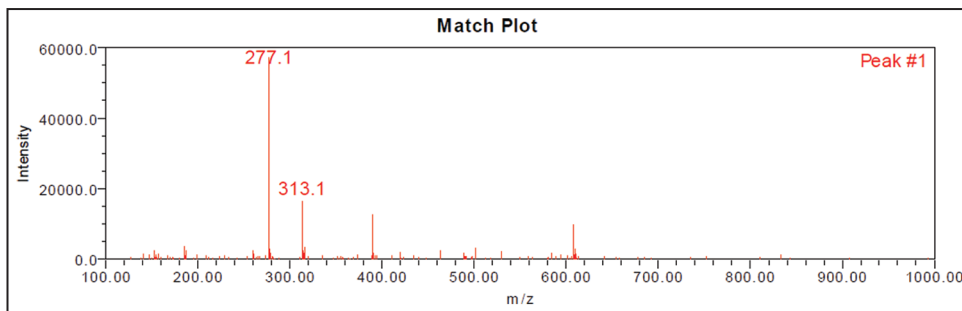


Figure 8: Mass spectrum of L₂.

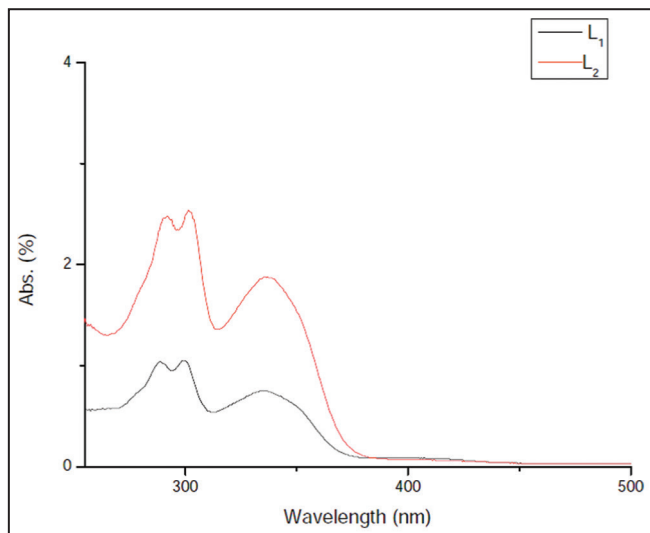


Figure 9: UV-Vis. Spectra of L₁ and L₂.

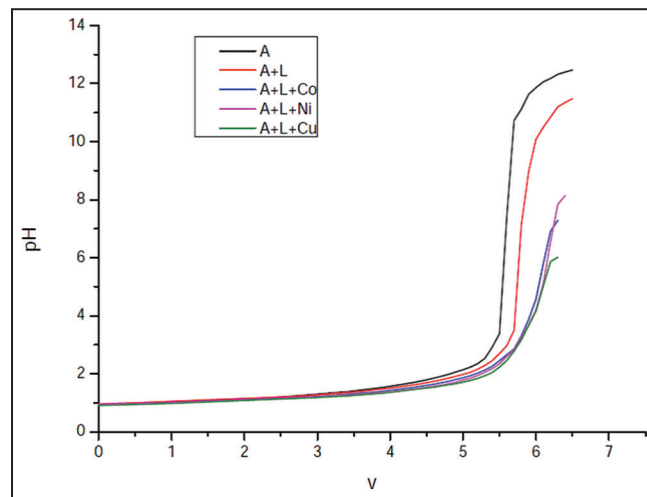


Figure 10: Plot of pH against log ($\bar{n}H/(1-\bar{n}H)$) of L₁.

Ni (II) are used to minimize the interference of anion complexing. The discussion of $\log K_f$ values is fully restricted in the studies of systems at constant ionic strength ($\mu = 0.1M KNO_3$). Irving-Rossotti explained that the titration curve of a metal complex is directly calculated from the pH-meter reading without any knowledge of hydrogen ion concentration or activity. Ph-metry data can be converted into formation constant using a computational method as given by Irving and Rossotti. The titration curves were obtained by the pH values plotted against the volume of alkali as given in Figures 1 and 2 for L₁ and L₂. An examination of the titration curves indicates that the metal-titration curve is depressed below the reagent titration curve and a distinct color appears at pH value and it is the reason for complex formation in solution. The stability constants are calculated between pH range 2.5–4.4 where precipitation is not observed for any system and metal hydroxides can also not be precipitated. The highest values of \bar{n} obtained were about 0.7 indicating the formation of 1:1 complex in solution. Metal-ligand complex formation occurred at lower pH than that of metal ion hydrolysis.

3.2.1. Proton-ligand stability constant

The hydrazone ligands act as a base and the basicity of the ligands is one of the important factors which is helpful in deciding the stability of the resulting complex. Hence, if other factors are same the stability is proportional to the proton-ligand stability constant (pK_f^H). The titration curves show that there is one sharp jump indicative of one neutralization equilibrium corresponding to the liberated proton of the OH group of the acetophenone moiety. The proton-ligand formation curves are obtained on plotting pH against \bar{n}_H . The value of proton ligand stability has been obtained by linear plot of log [$\bar{n}_H/(1-\bar{n}_H)$] versus pH, as given in Figures 10 and 11. The average numbers of protons associated with the ligand (\bar{n}_H) at different values were

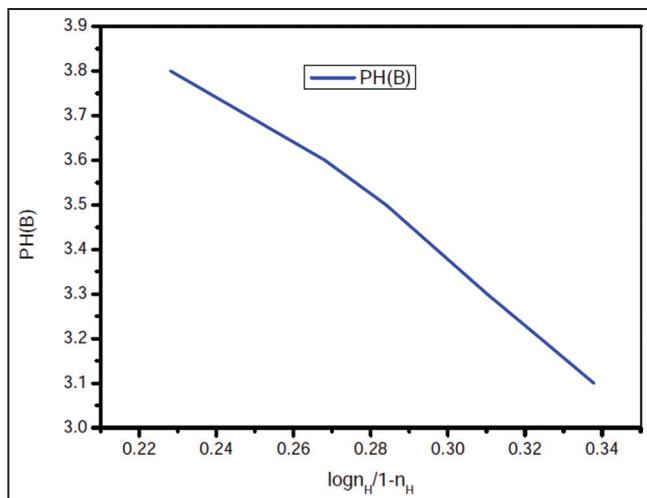


Figure 11: Plot of pH against log ($\bar{n}H/(1-\bar{n}H)$) of L₂.

calculated from the horizontal difference between acid curve and reagent curves using Irving and Rossotti equations. Derived values of proton-ligand stability constant by equation 2 are given in Table 2. From the data of $\log pK_f^H$, the order of proton-ligand stability constant is L₂ > L₁. The principle affecting factors for proton-ligand stability constant are inductive effect and electrostatic effect.

$$\bar{n}_H = Y + [(V''-V') (N^{\circ}+E^{\circ})/(V^{\circ}+V')TL^{\circ}] \quad (1)$$

$$\log pK_f^H = B + \log [\bar{n}_H/(1-\bar{n}_H)] \quad (2)$$

where: V', V'' are the volumes of alkali required to reach the same pH in the acid and acid + ligand titration curves, respectively, V^o and

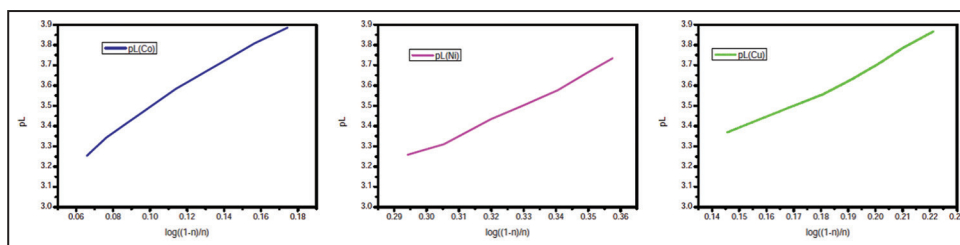


Figure 12: Plot of $\log \bar{n}/1 - \bar{n}$ against pL^- for L_1 with metals.

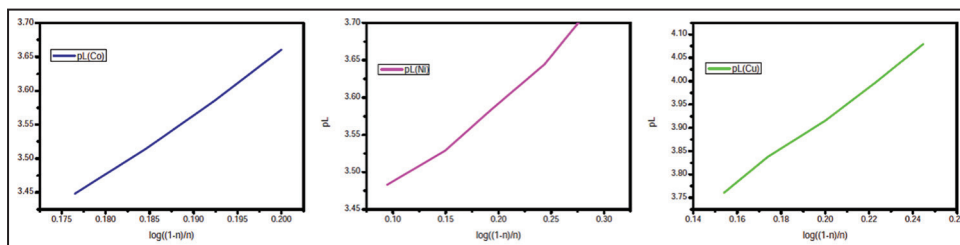


Figure 13: Plot of $\log \bar{n}/1 - \bar{n}$ against pL^- for L_2 with metals.

Table 3: Metal-ligand stability constants for binary (M-Schiff base) complex system.

Compound	Log K_f		
	Co	Ni	Cu
L_1	3.4864	3.1683	3.4414
L_2	3.3639	3.4624	3.7189

T_L^o are the initial volume of mixtures and initial concentration of the ligand, respectively, N^o and E^o are the concentration of base and initial concentration of acid in the mixture, respectively, Y is the number of dissociable protons from ligand and B is the pH meter readings.

3.2.2. Metal-ligand stability constant

In this present work, the point-wise calculation method is used to calculate the metal-ligand stability constant. The metal-ligand formation curves were obtained on plotting free ligand exponent (pL) against average number of ligands attached per metal ion (\bar{n}). The value of Metal-ligand stability constant ($\log K_f$) has been obtained by extrapolating the linear plot of $\log (\bar{n}/1 - \bar{n})$ against pL^- as given below in Figures 12 and 13. An assessment of the titration curves indicates that the metal titration curve is dislodge from the ligand titration curve. The end points of the titration of the three solutions increase in the order acid < ligand < complex curves. This is characteristic of the formation of the complexes. The values of metal ligand stability constant ($\log K_f$) are collected in Table 3. The values of \bar{n} were found to be between 0 and 1, indicating the formation of 1:1 complex in solution. From the data of $\log K_f$, the order of the stability constants of the formed complexes observed in L_1 is $Co > Cu > Ni$ and in L_2 is $Cu > Ni > Co$.

The \bar{n} values and the values of free ligand exponent, pL are determined using these equations:

$$\bar{n} = \frac{(V^m - V^m[N^o + TL^o(Y - \bar{n}H)])}{(V^o + V^m)\bar{n}HT^o_M} \quad (3)$$

$$pL = \log 10 \left[\frac{\sum_{j=0}^J \beta \frac{H}{j} \frac{1}{(anti \log B)^j}}{T^o_L - nT^o_M} \times \frac{V^o - V^m}{V^o} \right] \quad (4)$$

where, \bar{n} is average number of ligands bound per metal ion, T^o_M is initial total metal ion concentration and V^m and V^m are volumes of alkali required to attain the same pH in the (acid + ligand) and (acid + metal + ligand) curves, respectively, β_j^H is the overall proton ligand stability constant and the other terms have their same meaning as mentioned above.

4. CONCLUSION

Fluorinated Schiff bases have been successfully synthesized and characterized. Elemental analysis results agreed with predicted formulae. In the present article, the proton-ligand and metal-ligand stability constants of binary complexes of Schiff bases with different metal ions were calculated using potentiometric methods in 60:40% (V/V) 1,4-dioxane-water mixture at constant temperature $25^\circ C \pm 0.5^\circ C$ and at ionic strength of 0.1 M KNO_3 . To determine the stability constant of binary complexes in solution, point-wise calculation method was used. The order of stability of the formed binary complexes in solution was analyzed.

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