



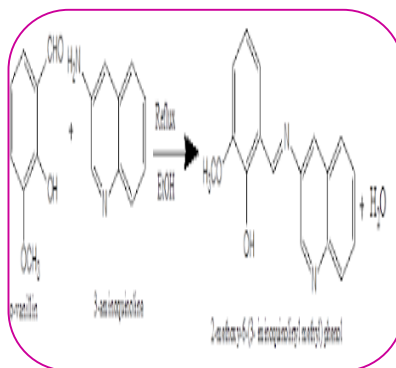
SYNTHESIS AND CHARACTERIZATION OF CO (II), NI (II) AND CU (II) COMPLEXES WITH 2-METHOXY-6-(6-IMINOQUINOLINYL METHYL) PHENOL

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ABSTRACT :

Condensation method was used to prepare a Schiff base from o-vanillin and 6-aminoquinoline in 1:1 molar ratio. The Schiff base metal complexes of Co (II), Ni (II) and Cu (II) were prepared using the metal salt and ligand in 1:2 ratio. The metal complexes were characterized by using elemental analysis, magnetic susceptibility, UV-Visible, and IR spectra. They



were also characterized by their thermo gravimetric analysis. The compositions of the Schiff base ligand (SB-3) and the metal complexes were established by elemental analysis which indicated a metal: ligand ratio of 1:2. The thermal and spectral studies indicated that ligand behaved as bidentate coordinating through phenolic oxygen and azomethine nitrogen

and formed octahedral metal complexes. The metal complexes revealed their general formula as $[ML_2(H_2O)_2]$ where $M=Co(II), Ni(II)$ or $Cu(II)$ and $L=$ deprotonated Schiff base ligand.

KEYWORDS : Synthesis, Schiff base, transition metal complexes, spectral characterization, octahedral geometry.

1.INTRODUCTION:

Schiff bases are ubiquitous in the field of co-ordination chemistry where they are used to prepare variety of metal complexes. These compounds contain an azomethine group ($-HC=N-$). These are also known as imines or anils. They are prepared by the condensation of primary amines with aldehydes or ketones, in good yields and high purity. Schiff bases containing co-ordination compounds have shown attractive properties and hence various applications in fields like biological, inorganic and analytical chemistry. Schiff bases can be synthesized by relatively simple procedures enabling us to design compounds which are structurally similar to some substances of biological origin [1-5].

It is well known that N and O atoms play a key role in the co-ordination of metals at the active sites of many metallic-biomolecules. Schiff base metal complexes have been widely studied because they have various properties like antibacterial, antifungal, anticancer, herbicidal, analytical etc. They find wide applications as catalysts in many synthetic and biological reactions. Besides, they can undergo bonding with metal ions in a variety of ways and the resulting compounds show varied activities. 6-aminoquinoline and o-vanillin are especially known for their antibacterial and antifungal activities and are thus used as synthetic precursors in pharmaceuticals. Considering the distinct biological activities of these compounds, we

herein put forth an account of the synthesis and characterization of ligand complexes of Co(II), Ni(II) and Cu(II) derived from 6-aminoquinoline and o-vanillin [6-8].

2. EXPERIMENTAL:

2.1 Apparatus:

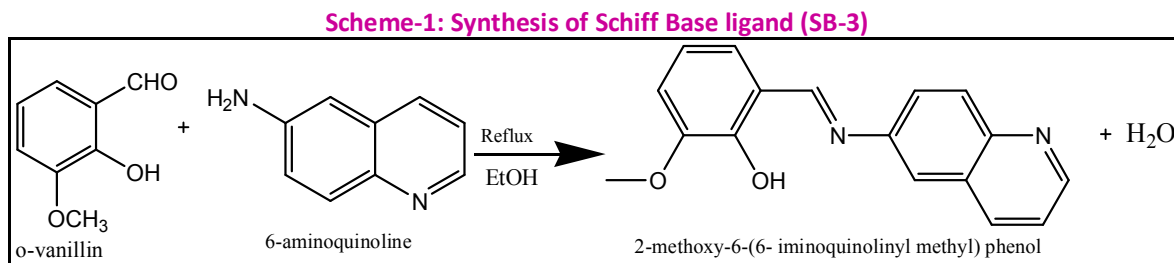
An UV-VIS-NIR-3600 recording spectrophotometer (Shimadzu, Japan) was used for the UV spectrum scanning and determination experiments. Bruker, Germany Model 3000 Hyperion Microscope with Vertex 80FTIR system range 400-4000 cm^{-1} (KBr discs) at SAIF, IIT, Bombay was used for IR spectral characterization of the Schiff base ligand and metal complexes. The thermogravimetric analysis of ligand and metal complexes was performed on Perkin-Elmer Diamond TG at SAIF, IIT, Bombay.

2.2 Reagents:

All chemicals and reagents used were of AR grade or higher grades. o-vanillin and 6-aminoquinoline were purchased from Sigma-Aldrich. Cobalt (II) chloride, Nickel (II) chloride and Copper (II) chloride were used for synthesis are used of Standard Qualigens (SQ) AR grade chemicals. The solvents absolute ethanol, DMSO etc. was used.

2.3 Synthesis of Schiff base ligand (SB-3)

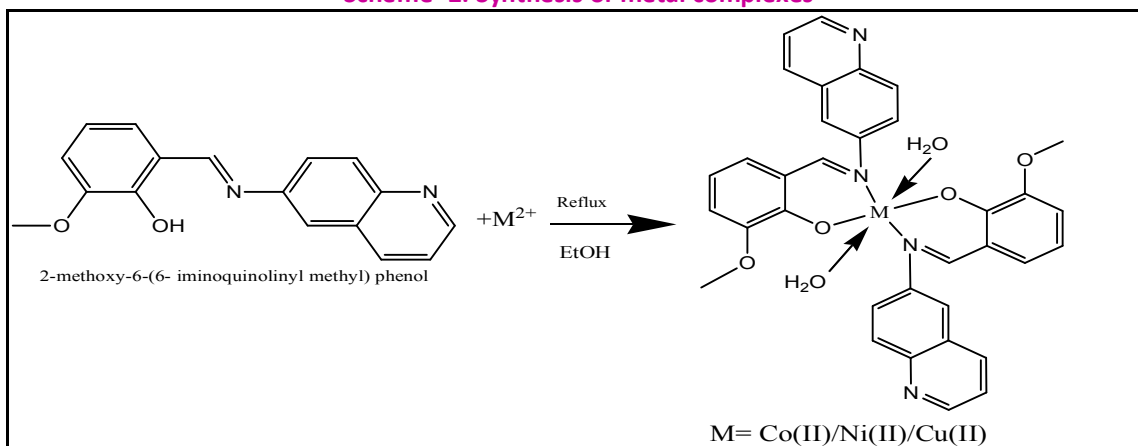
20 mmol (3.04g) of o-vanillin is dissolved in absolute ethanol. Then it was added dropwise into 20 mmol (2.88g) of ethanolic solution of 6-aminoquinoline. Then the mixture was refluxed for 2 hours then cooled and filtered [6-7]. The formation of ligand was visualized by change in colour of the solution. Intense orange colored crystals of Schiff base SB-3 were formed (yield 90%, 5 g). The crystals were washed with anhydrous diethylether and dried over anhydrous CaCl_2 [9-15]. The synthesis of Schiff base ligand (SB-3) is shown in Scheme-1



2.4 Synthesis of Schiff base transition metal complexes:

20 mmol of Schiff base (SB-3) was dissolved in ethanol (30ml) and added to 10 mmol ethanolic solution (20ml) of metal (II) chloride salt. The metal-ligand molar ratio taken was 1:2. The mixture was refluxed for 3 hours. On cooling, a crystalline metal complex was obtained. It was filtered, recrystallized from ethanol and dried in desiccator over anhydrous CaCl_2 . The Co(II), Ni(II) and Cu(II) metal complexes of Schiff base (SB-3) were prepared by above general method using salts $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ [9-18]. The preparation of metal complexes is shown in Scheme -2

Scheme -2: Synthesis of metal complexes



Schiff base (SB-3) and its Co (II), Ni (II) and Cu (II) complexes synthesized were stable at room temperature and soluble in common solvents like DMSO, methanol etc. The synthesized ligand and the metal complexes were characterized by elemental analysis. The geometry of the synthesized compounds has been elucidated on the basis of their elemental and spectral studies.

3. RESULTS AND DISCUSSION:

3.1 Analytical and Physicochemical data:

The stoichiometry of ligand and their metal complexes is confirmed by the elemental analysis. The analytical and physicochemical data of Schiff base (SB-3) and its metal complexes is found in good agreement with the proposed structure of ligand and the metal complexes[19-20]. The data being listed in Table-1

Table-1: Analytical and Physicochemical data of Schiff base (SB-3) and its metal complexes

Comp.	Molecular formula	m. p. (°C)	Mol. Weight	Color	% Observed (Theoretical)			
					C%	H%	N%	M%
SB-3	C ₁₇ H ₁₄ O ₂ N ₂	90	278	Orange	72.82 (73.38)	4.85 (5.03)	9.99 (10.07)	-
SB-3-Co	C ₃₄ H ₂₆ O ₄ N ₄ Co.(H ₂ O) ₂	>350	648.93	Dark Pink	62.10 (62.87)	4.71 (4.62)	8.23 (8.62)	9.01 (9.08)
SB-3-Ni	C ₃₄ H ₂₆ O ₄ N ₄ Ni.(H ₂ O) ₂	>350	648.69	Dark Green	62.41 (62.89)	4.91 (4.62)	8.81 (8.63)	8.89 (9.04)
SB-3-Cu	C ₃₄ H ₂₆ O ₄ N ₄ Cu.(H ₂ O) ₂	>350	653.55	Grey	62.31 (62.42)	4.71 (4.59)	8.351 (8.658)	9.32 (9.72)

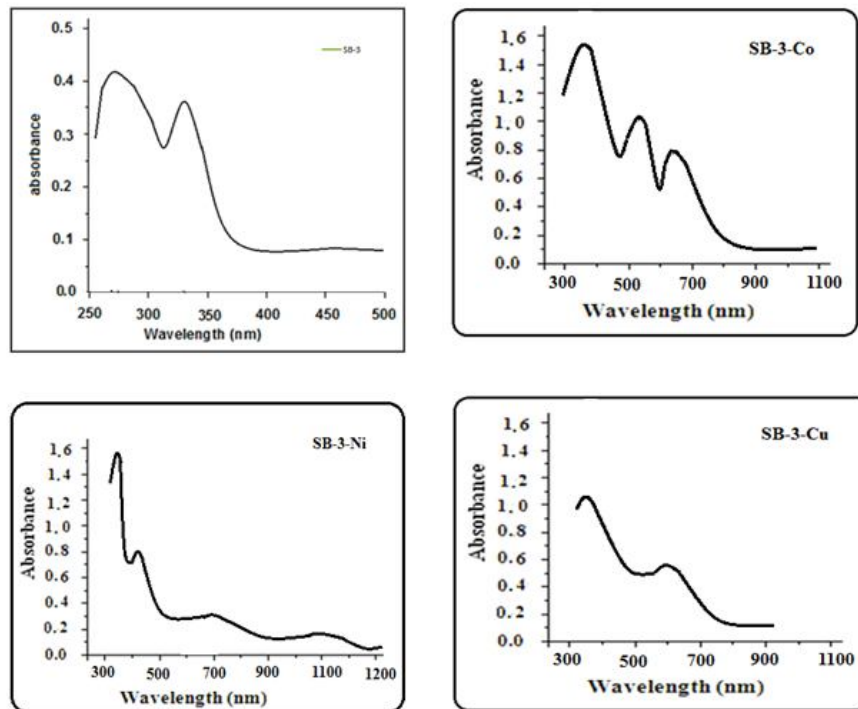
3.2 UV Spectral Analysis:

The UV spectrum of Schiff base ligand SB-3 is exhibiting two intense bands at 270 nm and 335 nm which can be assigned respectively to $\pi \rightarrow \pi^*$ transition within aromatic moiety and $n \rightarrow \pi^*$ transition of azomethine group of ligand. In the spectra of complexes, the bands due to azomethine group are shifted to higher frequency indicating that azomethine nitrogen atom is involved in coordination to the metal ion.

In the present investigation, the electronic spectra of Co(II) complex showed two absorptions bands associated with d-d transitions at 627nm and 527nm due to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3) transitions respectively. The electronic spectra of Ni(II) complex exhibited three bands associated with d-d transitions at 1074nm, 680nm and 438nm assignable to transitions ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) respectively. The electronic spectrum of Cu(II) complex showed one low intensity

broad absorption band due to d-d transition at 595 nm assigned to ${}^2E_g \rightarrow {}^2T_{2g}$ (ν_2). These observed d-d transitions for metal complexes are consistent with octahedral geometry of Co(II), Ni(II) and Cu(II) metal complexes of Schiff base ligand [21-25]. The UV spectra of Schiff base ligand and its Co(II), Ni(II) and Cu(II) metal complexes are represented in Figure-1.

Figure-1: The UV spectra Schiff base and metal complexes



3.3 Magnetic Susceptibility studies of complexes:

The magnetic moments obtained at room temperature for the metal complexes indicate paramagnetism. The Co(II) complex showed the magnetic moment of 4.81 BM. The spin free octahedral complexes of Co(II) are reported to exhibit magnetic moment in the range of 4.70 to 5.20 BM. Hence the observed moment 4.94 B.M. of Co(II) complex under study indicates that, it has an octahedral configuration. The Ni(II) complex showed magnetic moment of 3.12 BM. This value of magnetic moment is within the range of 2.7 to 3.3 BM, reported for octahedral Ni(II) complexes thereby suggesting octahedral geometry for Ni(II) complex under study. For octahedral Cu(II) complexes, the magnetic moment values are expected to be in the range 1.80 to 2.20 BM. The Cu(II) complex under study exhibited magnetic moment of 1.83 BM which indicated its octahedral configuration [22-27].

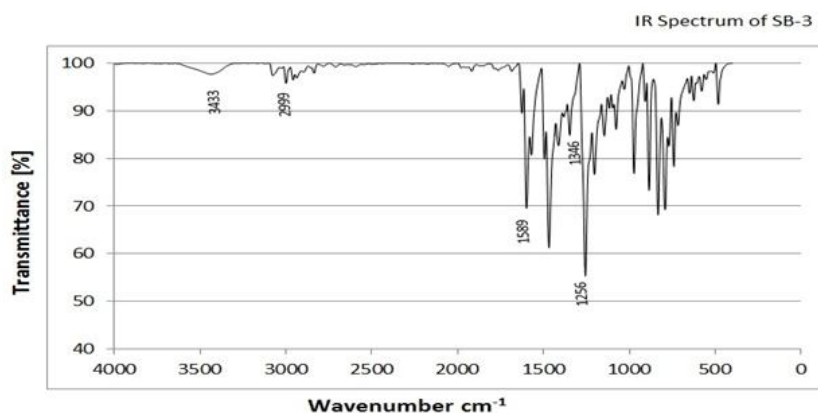
3.4 FTIR Spectral Analysis:

The IR spectra of complexes are compared with those of ligand in order to determine the coordination sites that may be involved in chelation. The prominent FTIR data with the assignments of bond frequencies of Schiff base ligand (SB-1) and its Co(II), Ni(II) and Cu(II) metal complexes are presented in Table-2 and their FTIR spectra are reported in Figure-3.

Table-2:FTIR Spectral data (cm⁻¹) of Schiff base ligand and its metal complexes

Assignments	SB-3	SB-3-Co	SB-3-Ni	SB-3-Cu
v(Hydrogen bonded O-H)	3433	-	-	-
v(Coordinated water)	-	3339	3330	3330
v (C=N)	1589	1575	1572	1574
v (Ar-O)	1256	1280	1282	1288
v (C-N)	1346	1389	1394	1387
v (O-CH ₃)	2999	2992	2992	2985
v (H ₂ O rocking)	-	831	857	835
v (M-O)	-	549	554	555
v (M-N)	-	436	435	437

The broad peak observed at 3433 cm⁻¹ in the IR spectra of Schiff base ligand assigned to v(O-H), was found to be disappeared in all the complexes, thereby indicating deprotonation and formation of metal-oxygen bond. This is further supported by the shifting of phenolic v(Ar-O) towards higher frequency, indicating the coordination of phenolate oxygen to metal ion. The v(C=N) vibration of the Schiff base ligand (SB-3) occurs at 1589 cm⁻¹, which is shifted to a lower frequency of the complexes, indicating the involvement of azomethine nitrogen in chelation with the metal ion. The observed increase in magnitude of v(C-N) on complexation may be attributed to increase in double bond character of aryl azomethine C-N bond. It is due to π electron delocalization from the metal ion to the nitrogen atom and resonance interaction with the benzene ring. However the stretching frequencies of Methoxy O-CH₃ bonds for ligand and complexes are almost same, indicating the nonparticipation of methoxy oxygen in coordination. The new bands in IR spectra of complexes 547-555 cm⁻¹ and 429-437 cm⁻¹ are ascribed to v(M-O) and v(M-N) vibrations respectively. In the IR spectra of complexes appearance of a new broad band in the region 3330-3339 cm⁻¹ corresponding to the stretching frequency of v(O-H) of H₂O indicated the presence of coordinated water. It is further confirmed by the appearance of non-ligand band in complexes in the region 835-837 cm⁻¹ assignable to rocking mode of water. Presence of two molecules of coordinated water in molecules of metal complexes is further confirmed by their thermogravimetric analysis. From the above observations, it can be concluded that the ligand behaves as bidentate coordinating through deprotonated phenolic oxygen and azomethine nitrogen [15-30].



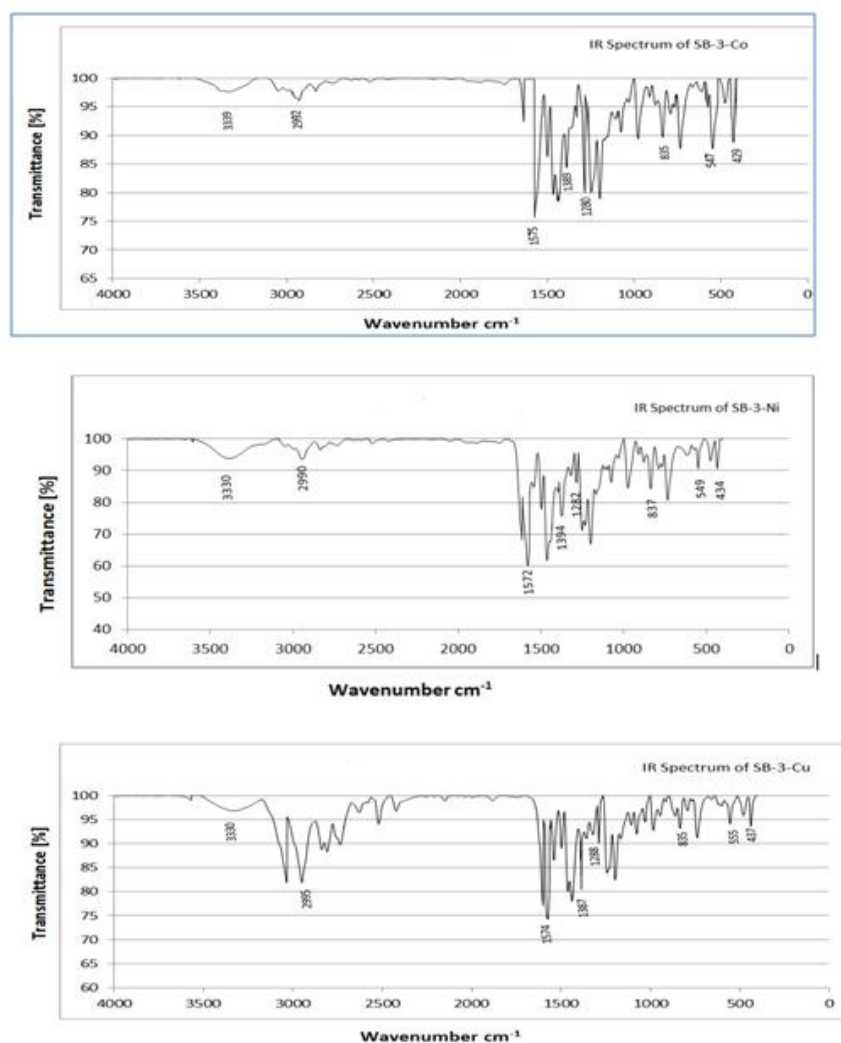


Figure-3: FTIR spectra of Schiff base and metal complexes

3.5 Thermal decomposition studies of metal complexes:

Thermal decomposition studies of metal complexes have been undertaken to know the presence or absence of coordinated water molecules. Thermal decomposition data of Schiff base and its metal complexes is reported in Table-3. The thermogram of Co(II) complex is shown in Figure-4.

Table-3: Thermal data of metal complexes

Sr.No.	Complex	Temperature (°C)	Loss of molecule	Percentage weight loss	
				Calculated	Observed
1.	SB-3 Co	200°C-260°C	2H ₂ O	5.54	5.71
		260°C-600°C	Org. moiety	85.37	83.56
		>600°C	CoO	11.54	7.14
2	SB-3 Ni	150°C-240°C	2H ₂ O	5.54	5.00
		240°C-550°C	Org. moiety	85.40	77.81
		>550°C	NiO	11.51	11.42
3	SB-3 Cu	160°C-230°C	2H ₂ O	5.50	5.71

	230°C-520°C	Org. moiety	84.76	84
	>520°C	CuO	12.17	12

In case of Co(II) complex a weight loss of 5.33% between temperature range 150°C-250°C indicated the presence of two molecules of coordinated water (calculated 5.54%). The anhydrous compound further decomposed rapidly between 250°C-610°C with 83.23% weight loss corresponding to decomposition of organic moiety of the complex (calculated 85.37%) leading to the formation of 11.43% stable residue of cobalt oxide (calculated 11.54%) above 610°C. All the complexes are found to follow two step decomposition pattern. In the first step there is loss of two molecules of coordinated water and in the second step there is oxidative decomposition of organic part of the ligand leading to the formation of stable residue of metal oxide. Thermal studies supported the octahedral structure of all the metal complexes indicating presence of two coordinated water molecules[25-32].

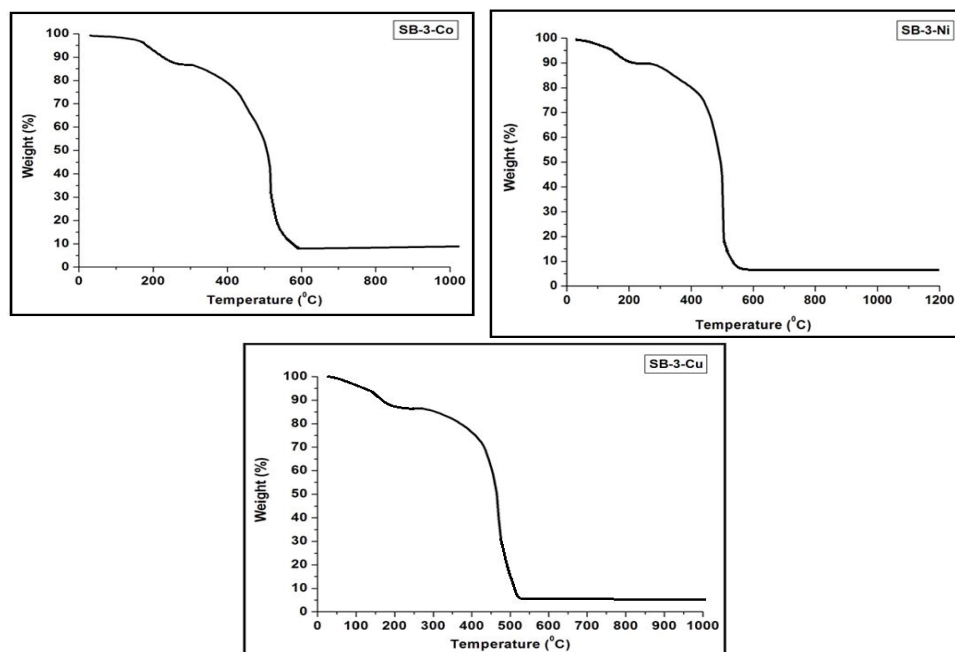


Figure-4: Thermograms of metal complexes

3.6 ^1H NMR Spectroscopic Studies:

The ^1H NMR Spectrum of the Schiff base (SB-3) Shows D_2O exchangeable broad singlet at 13.554ppm integrating for one proton is assigned to $-\text{OH}$. The ^1H NMR spectrum of Schiff base shows multiplet in the range 6.932-8.937 ppm due to aromatic protons. The $-\text{N}=\text{CH}-$ proton of Schiff base exhibits singlet in the region 8.941ppm[15-30]. The ^1H NMR spectrum of Schiff base is shown in Figure-5.

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