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SYNTHESIS AND SPECTRAL STUDIES OF CO (II), NI (II) AND CU (II) COMPLEXES WITH 2–METHOXY-6-(5-IMINOQUINOLINYL METHYL) PHENOL

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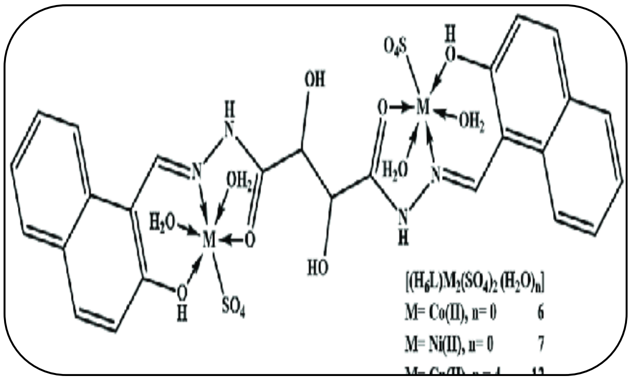
ABSTRACT:

A Schiff base ligand was synthesized by condensation of o-vanillin with 5-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 ligand was characterised by elemental analysis, UV-Visible, IR, NMR and mass spectra. 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 and the metal complexes were established by elemental analysis which indicated a metal: ligand ratio of 1:2.Magnetic, 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$_2$O)$_2$] where M=Co(II),Ni(II) or Cu(II) and L=deprotonated Schiff base ligand.



KEYWORDS: *Synthesis, Schiff baseligand ,transition metal complexes, spectral characterization , thermal studies.*

INTRODUCTION

Schiff bases reported by scientistHugo Schiff play an important role in co-ordination chemistry. 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, resulting into the formation of a new C=N bond. Schiff bases derived from aromatic aldehydes and amines have a wide variety of applications in various fields likebiological, inorganic and analytical chemistry. Schiff bases can be synthesizedby 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 [4]. Schiff bases form stable metal complexes with many transition metals. They 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. 5-aminoquinoline and o-vanillin are especially known for theirantibacterial and antifungal activities and are thus used as synthetic precursors in pharmaceuticals.In continuation of earlier work, a Schiff base derived from 5-aminoquinoline and o-vanillin was used to synthesizeitsCo(II), Ni(II) and Cu(II) complexes. Considering the distinct biological activities of these compounds hereinput forth an account of the synthesis and characterization of ligand and its complexes [6-9].

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, Bombaywas used for IR spectral characterization of the Schiff base ligand and metal complexes. The thermogravimetric analysis ofligand and metal complexes was performed on Perkin-Elmer Diamond TG at SAIF, IIT, and Bombay.

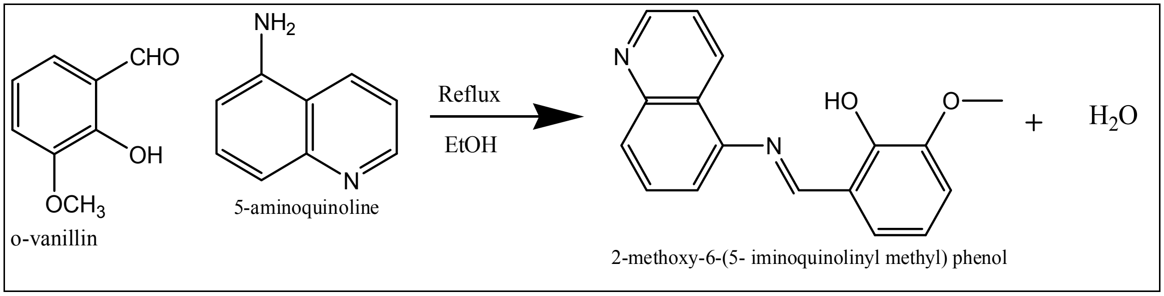
2.2 Reagents:

Sigma- Aldrich o-vanillin, 5-aminoquinoline, and Standard Qualigens (SQ) hydrated Cobalt (II) chloride; Nickel (II) chloride and Copper (II) chloride were used for synthesis. The solvents ethanol, DMSO etc. was used.

2.3 Synthesis of Schiff base ligand (SB-2)

20 mmol (3.04g) of o-vanillin is dissolved in absolute ethanol. Then it was added dropwiseinto20mmol (2.88g) of ethanolic solution of 5-aminoquinoline. The mixture was refluxed for 2hours then cooled and filtered [10-15]. Intense yelloworange colored crystals of Schiff base SB-2 were formed (yield 90%, 5.0 g). The crystals were washed with cold ethanol and anhydrous diethylether and dried over anhydrous$CaCl_2$. The synthesis of Schiff base ligand (SB-2) is shown in Scheme-1

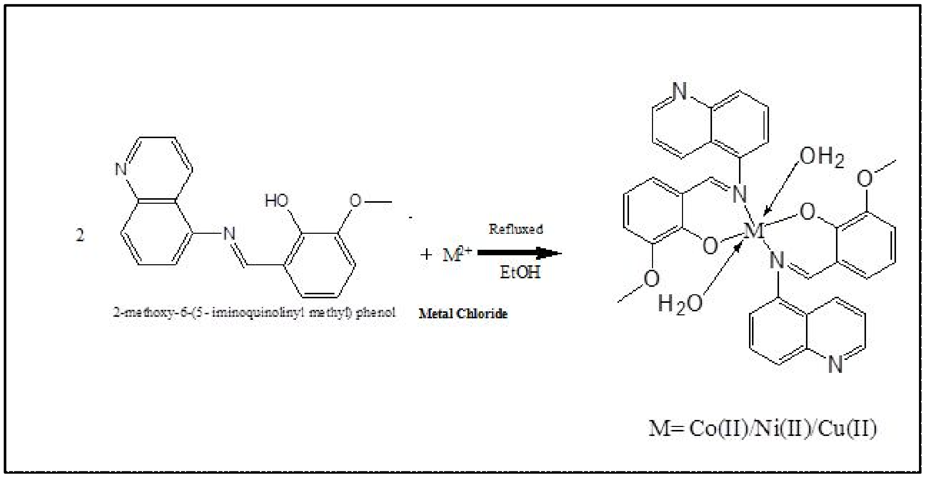
Scheme-1: Synthesis of Schiff Base ligand (SB-2)



2.4 Synthesis of Schiff base transition metal complexes:

20 mmol of Schiff base (SB-2) 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-2) were prepared by above general method using salts $CoCl_2.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$. The preparation of metal complexes is shown in Scheme -2

Scheme -2: Synthesis of metal complexes



Schiff base (SB-2) 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.[16-21] 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-2) and its metal complexes is found in good agreement with the proposed structure of ligand and the metal complexes. The data being listed in Table-1

Table-1: Analytical and Physicochemical data of Schiff base (SB-2) and its metal complexes

Comp.	Molecular formula	M. p. (°C)	Mol. Weight	Color	% Observed (Theoretical)			
					C%	H%	N%	M%
SB-2	$C_{17}H_{14}O_2N_2$	162	278	Yellow Orange	72.46 (73.38)	4.83 (5.03)	9.94 (10.07)	-
SB-2-Co	$C_{34}H_{26}O_4N_4Co.(H_2O)_2$	>350	648.93	Dark Pink	61.95 (62.8)	4.81 (4.62)	8.45 (8.62)	8.92 (9.08)
SB-2-Ni	$C_{34}H_{26}O_4N_4Ni.(H_2O)_2$	>350	648.69	Dark Green	62.54 (62.89)	4.81 (4.62)	8.89 (8.63)	8.91 (9.04)
SB-2-Cu	$C_{34}H_{26}O_4N_4Cu.(H_2O)_2$	>350	653.55	Grey	62.19 (62.4)	4.89 (4.59)	8.51 (8.65)	9.43 (9.72)

3.2 UV Spectral Analysis:

The UV spectrum of Schiff base ligand SB-2 is exhibiting two intense bands at 272 nm and337 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 642 nm and 535 nm 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 at1082 nm, 682 nm and 441 nm 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 590 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.[12-22]The UV spectra of Schiff base SB-2 and its metal complexes are represented in Figure-1.

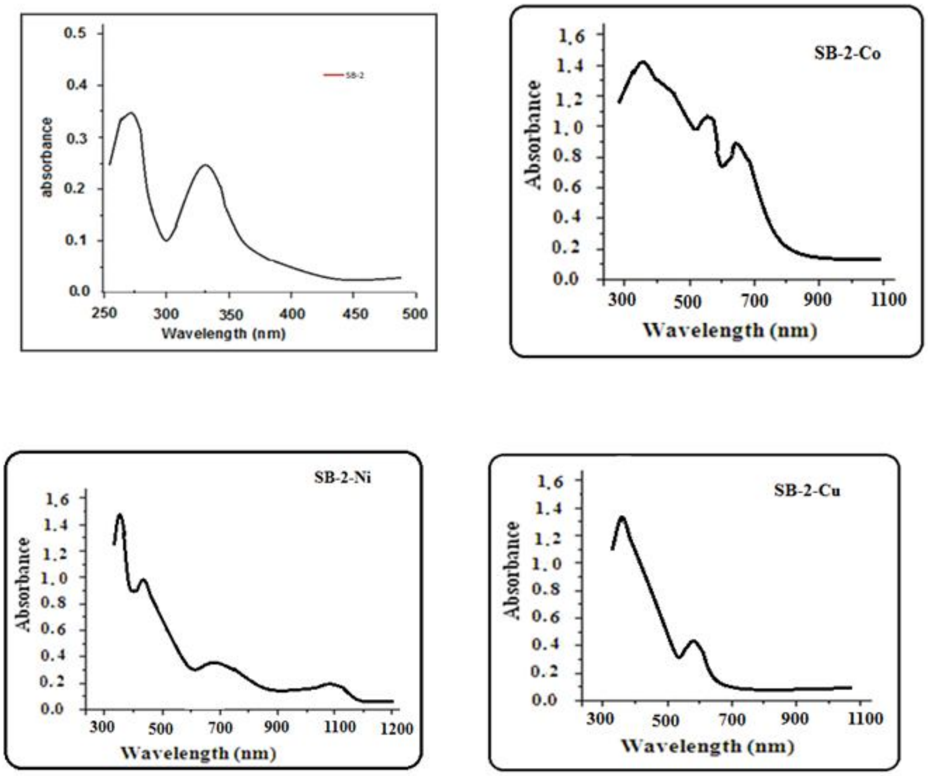


Figure-1: The UV spectra Schiff base and metal complexes

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 4.85 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 of Co (II) complex under study indicates that, it has an octahedral configuration. The Ni(II) complex showed magnetic moment of 3.01 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 1.92 BM which indicated its octahedral configuration[22-25].

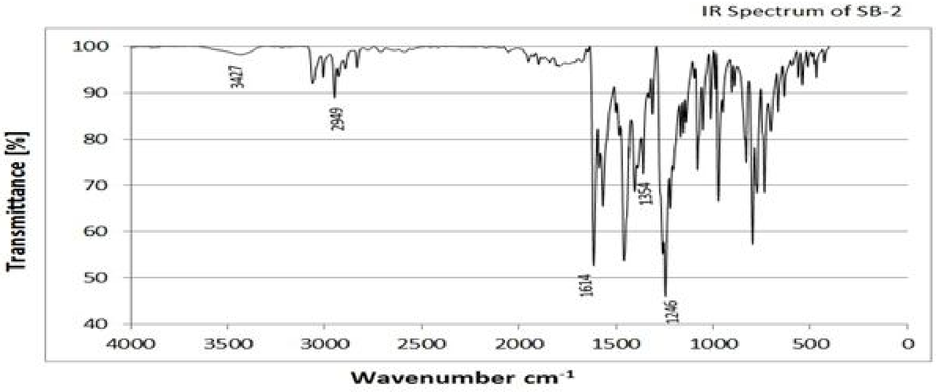
3.4 FTIR Spectral Analysis:

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-2) and its Co(II),Ni(II) and Cu(II) metal complexes are presented in Table-2 and FTIR spectra of these compounds are represented in Figure-2.

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

Assignments	SB-2	SB-2-Co	SB-2-Ni	SB-2-Cu
ν(Hydrogen bonded O-H)	3427	-	-	-
ν(Coordinated water)	-	3330	3325	3322
ν (C=N)	1614	1592	1590	1595
ν (Ar-O)	1246	1267	1271	1273
ν (C-N)	1361	1370	1372	1380
ν ($O-CH_3$)	2929	2930	2929	2931
ν (H_2O rocking)	-	820	857	861
ν (M-O)	-	554	554	555
ν (M-N)	-	437	435	438

The broad peak observed at 3427 cm^{-1}in the IR spectra of Schiff base ligand assigned to ν(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 ν(Ar-O) towards higher frequency, indicating the coordination of phenolate oxygen to metal ion. The ν(C=N) vibration of the Schiff base ligand (SB-2) occursat 1614 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 ν(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 $O-CH_3$ bonds for ligand and complexes are almost same, indicating the nonparticipation of methoxy oxygen in coordination. The new bands in IR spectra of complexes in the regions 554-555 cm^{-1} and 435-438 cm^{-1} are ascribed to ν(M-O) and ν(M-N) vibrations respectively.In the IR spectra of complexes appearance of a new broad band in the region 3300-3320 cm^{-1}corresponding to the stretching frequency of ν(O-H) of H_2O indicated the presence of coordinated water. It is further confirmed by the appearance of non-ligand band in complexes in the region 820-861 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 [20-33].



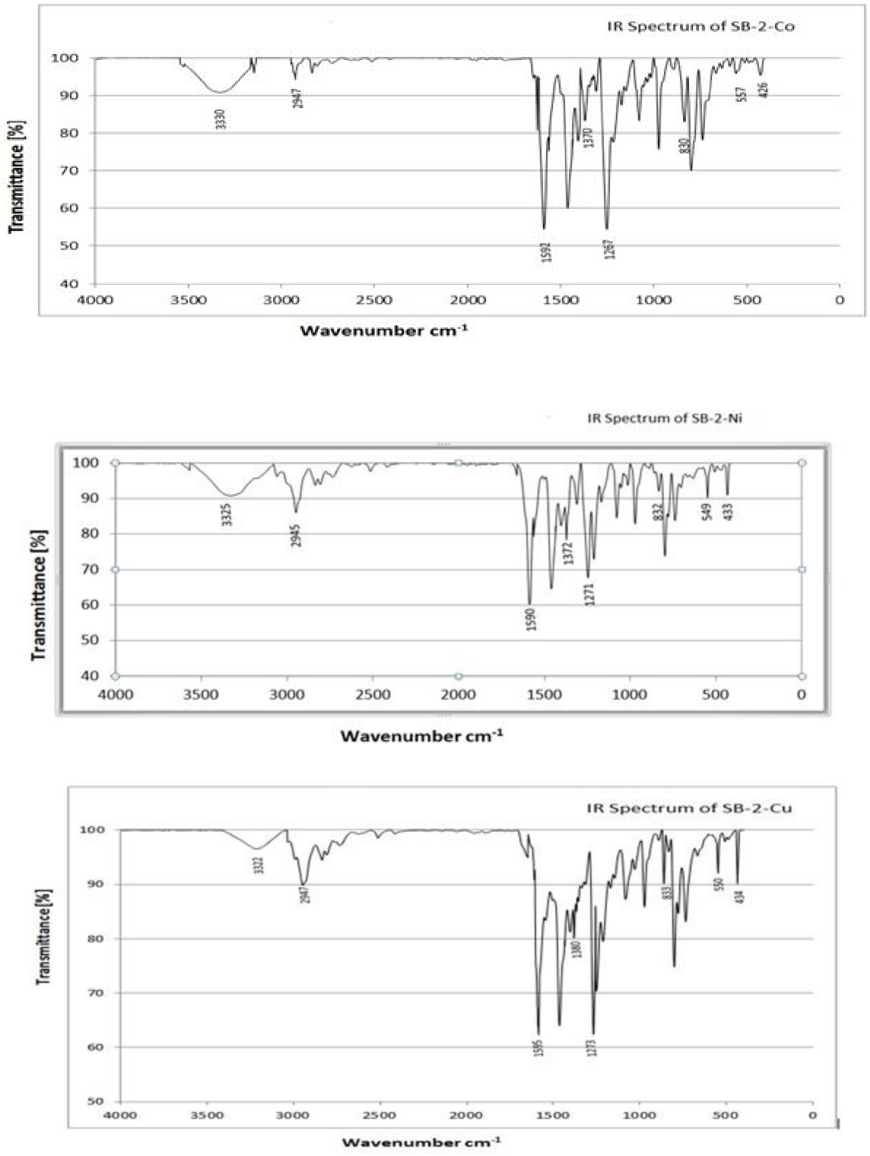


Figure-2: FTIR spectra of Schiff base-2 and its metal complexes

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 metal complexes ofSchiff base -2 is reported in Table-3.The thermograms of complexesare shown in Figure-3

Table-3: Thermal data of metal complexes

Complex	Temperature (°C)	Loss of molecule	Percentage weight loss	
			Calculated	Observed
SB-2 Co	220°C-260°C	$2H_2O$	5.54	5.71
	260°C-560°C	Org. moiety	85.37	76.43
	>560°C	CoO	11.54	11.42
SB-2 Ni	140°C-260°C	$2H_2O$	5.54	5.00
	260°C-540°C	Org. moiety	85.40	78.43
	>540°C	NiO	11.51	11.42
SB-2Cu	150°C-250°C	$2H_2O$	5.50	5.71
	250°C-560°C	Org. moiety	84.76	78.68
	>560°C	CuO	12.17	10.00

In case of Co(II) complex observed weight loss of 5.71% between temperature range 220°C-260°C indicated the presence of two molecules of coordinated water (calculated 5.54%). The anhydrous compound further decomposed rapidly between 260°C-560°C with 76.43% weight loss corresponding to decomposition of organic moiety of the complex (calculated 85.37%) leading to the formation of 11.42% stable residue of cobalt oxide (calculated 11.54%) above 560°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 [15-25].

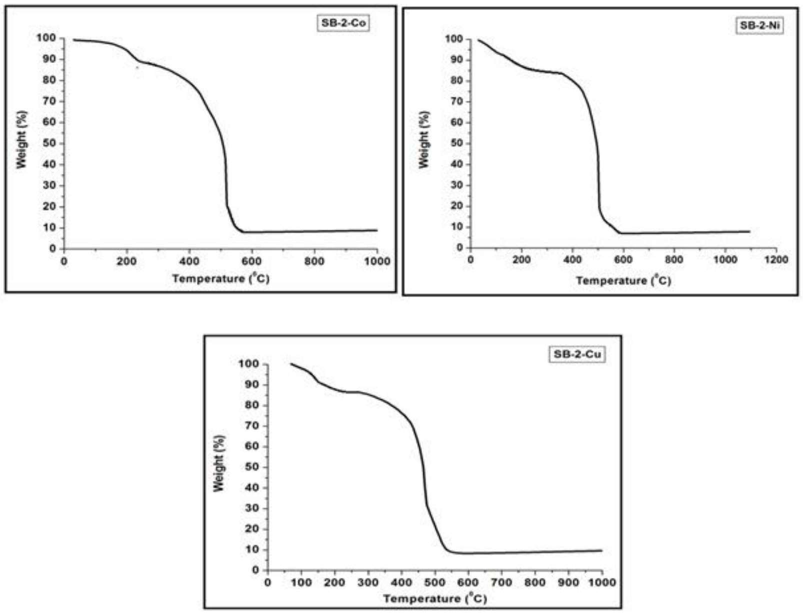


Figure-3 : Thermograms of metal complexes

3.6 H^1 NMR Spectroscopic Studies:

The H^1 NMR Spectrum of the Schiff base (SB-2) Shows D_2O exchangeable broad singlet at 13.664ppm integrating for one proton is assigned to –OH. The H^1 NMR spectrum of Schiff base shows multiplet in the range 6.958-9.002 ppm due to aromatic protons. The -N=CH- proton of Schiff baseexhibits singlet at 9.006ppm. The H^1 NMR spectrum of Schiff base is shown in Figure-4.

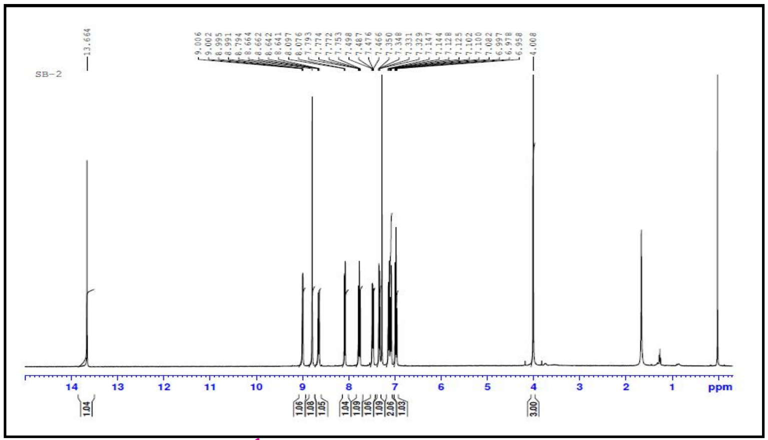


Figure-4 : H^1 NMR spectra of Schiff Base (SB-2)

3.7 Mass spectroscopic Studies:

The mass spectrum of Schiff base (SB-2) was recorded. It shows parent peak due to molecular ion (M^+). The proposed molecular formula of Schiff base was confirmed by comparing its molecular formula weight with m/z value. The molecular ion peak with m/z = 279.3, corresponds with the proposed molecular formula of Schiff base. In addition, the mass spectrum exhibited peaks assignable to various fragments arising from the thermal cleavage of the compound have been observed[26-33].The mass spectrum of Schiff base is shown in Figure-5.

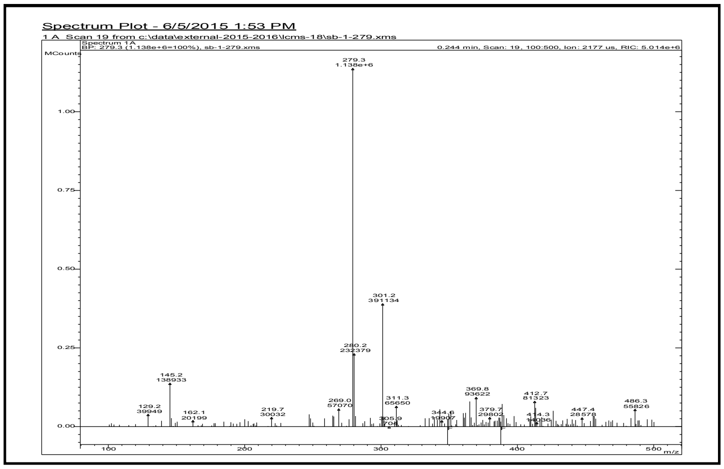


Figure- 5 : Mass spectrum of Schiff base (SB-2)

4. ACKNOWLEDGEMENT:

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