

(RESEARCH ARTICLE)



Synthesis and characterization of Schiff base metal complexes derived from *Naphthofuran-2-Carbohydrazide* and *4-(methylthio)benzaldehyde*

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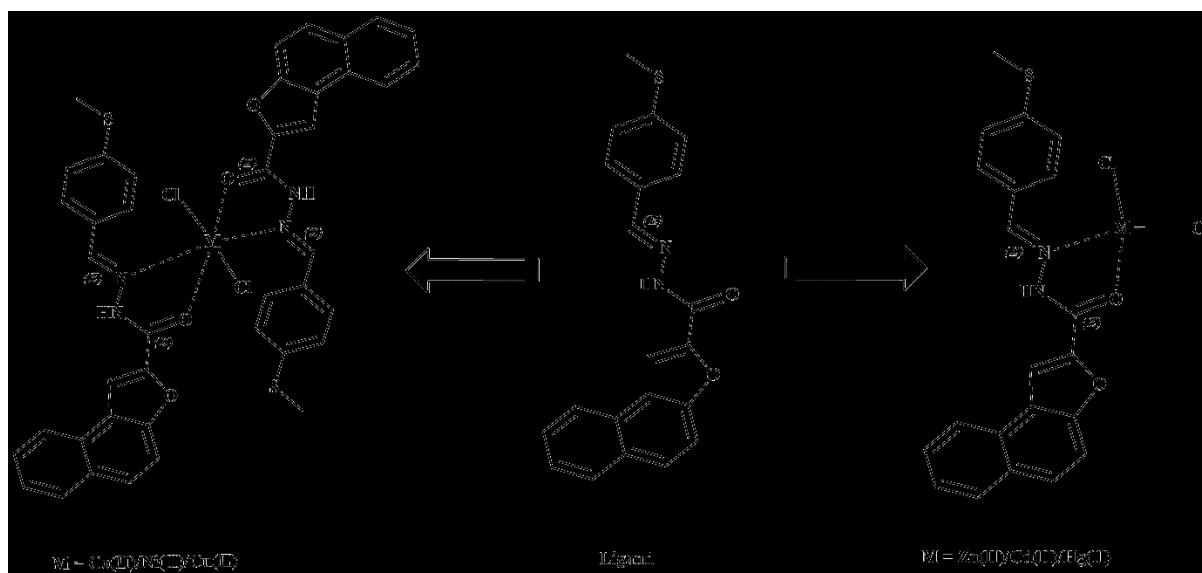
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Abstract:

The direct reaction of 4-(methylthio) benzaldehyde with Naphthofuran-2-carbohydrazide generated a new heterocyclic Schiff base ligand and its transition metal (II) complexes with the formula ML_2Cl_2 , where M= Co, Ni, Cu, Zn, Cd, and Hg. Analytical, Infrared, ¹HNMR, Mass, and UV-Visible spectral information have been used to perform a basic structural interpretation of the ligand and metal complexes.

Keywords: Schiff base; Naphthofuran; Metal complex; 4-(methylthio) benzaldehyde; Spectral studies.

Graphical abstract



1. Introduction

Among several naturally occurring compounds, naphthofuran derivatives are one of them. Several biological compounds that contain the naphthofuran ring have a broad range of biological effects, notably anthelmintic, anticonvulsant, and antipyretic effects.[1,2]. "Naphthofuran is one of many important molecules that, when condensed with other

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heterocyclic compounds, reveals superior biological and chemical activities." When we condensed them with metal ions, we observed this increased activity [3,4].

Schiff base and its metal complexes are important in a variety of sectors, particularly food, dye, catalysis, antimicrobials, and genetically modified crops, as well as biological activity exploration. "These molecules have remarkable pharmacological and biological characteristics, which may be ascribed to the Azomethine connection.[5,6] Hydrazone derivatives and their metal complexes are now well-known for their anticancer, antitumor, antioxidative, oxidative peroxidation inhibitor capabilities, among many other features.[7–9] When drugs are administered in the form of complexes, both toxicological and pharmacological properties may be modified. Transition metal that has already been investigated the most in this area and has shown to be effective in ailments such as tuberculosis, gastric ulcers, and rheumatoid arthritis.[10–12].

The synthesis of Cobalt, Nickel, Copper, Zinc, Cadmium, and Mercury complexes with Schiff base derivative from 4-(methylthio) benzaldehyde and Naphthofuran-2-carbohydrazide are discussed in this paper. Spectroscopic infrared, UV-Visible, ESR, mass spectral, and physical data were used to identify all of the synthesized compounds.

2. Experimental

All of the synthesis was conducted out with analytical reagent grade chemicals of the utmost purity commercially available. The basic component, naphthofuran-2-carbohydrazide, has been synthesized using a method reported in the literature. The metal and chloride content were determined using well-established techniques.[13] [14]

2.1. Synthesis of Schiff base ligand (4-(methylthio) benzylidene)naphtho[2,1-b] furan-2-carbohydrazide [L]

In absolute dry ethanol (30 mL), naphthofuran-2-carbohydrazide (0.1 Mol) and 4-(methylthio) benzaldehyde (0.1 mol) were refluxed for 8 hours on a water bath with a few drops of glacial acetic acid as a catalyst and occasional shaking to obtain needles of the ligand, the final crude product, which was separated as a yellowish crystalline solid, is collected and recrystallized from ethanol.

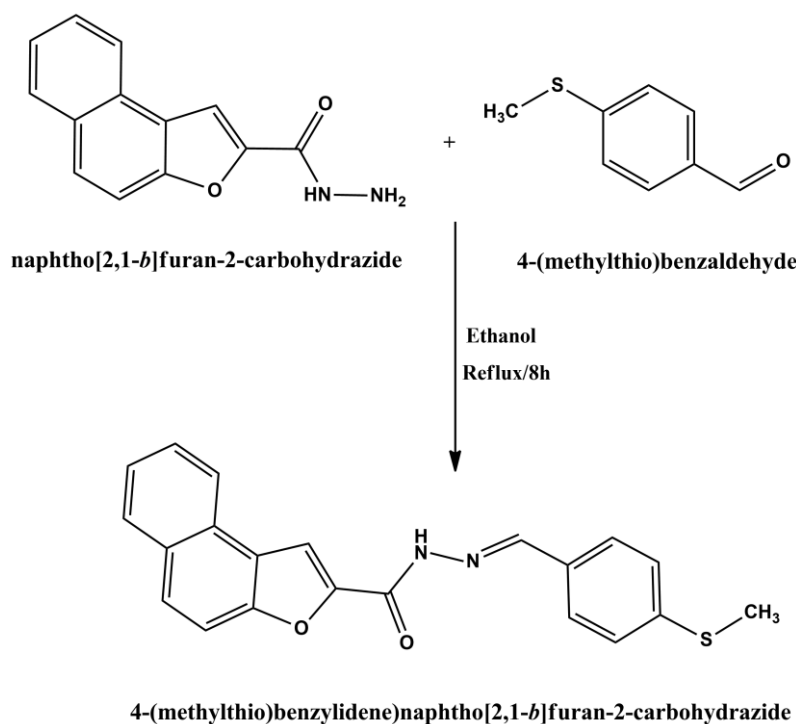


Figure 1 Synthesis of Ligand L

2.2. Preparation of metal complexes

In absolute ethanol, an accurately weighted metal chloride (0.01 mol) was introduced to Schiff base ligand (0.01 mol) (30 mL). This resulting mixture then was refluxed on the water bath for 4 hours, keeping the pH of the reaction mixture between 5 and 6, and then refluxed again for an hour. The crystals of the metal complexes that were separated filtered

off with Whatman filter paper No. 41 and washed several times with double distilled water, then alcohol, and eventually dried in a vacuum over fused calcium chloride.

2.3. Physical data

Using traditional KBr pellet techniques, the IR spectra of the ligand and its metal complexes were collected. On an Elico-SL-164 double-beam spectrophotometer, ultraviolet-visible spectra of Cobalt(II), Nickel(II), and Copper(II) complexes were recorded in the range of 200-900 nm using DMF (10^{-3} M) as a solvent. At IIT Bombay, the Copper (II) complex's ESR spectrum was scanned (India). A dip-type conductivity cell with a platinum electrode was used to test molar conductivity on an Elico CM-180 Conductivity Bridge in dimethylformamide (10^{-3} M) solvent. Magnetic susceptibility studies were done on a Gouy balance at room temperature utilizing Hg $[\text{Co}(\text{NCS})_4]$ as the calibrant.

3. Spectral Studies

3.1. Infrared spectral analysis

The IR frequency study of the ligand and its metal complexes reveals a strong band at 1686 cm^{-1} which is assigned to the $\nu(\text{C}=\text{O})$ stretch of the amide functional group, that further undergoes a negative shift by $21 - 46\text{ cm}^{-1}$ in the complexes, indicating the carbonyl group's involvement in coordination[15,16]. The $(\text{C}=\text{N}-)$ stretching vibrations of the azomethine substituents in the free ligand developed a high to medium intensity band at 1614 cm^{-1} ; this band shows a negative shift in the spectra of metal complexes, signifying that its azomethine group plays a significant role in metal ion coordination[8,17]. The band at 1205 cm^{-1} is attributed to $\nu(\text{C}-\text{O}-\text{C})$ stretch of an aryl ring in free ligand[18] this band stays consistent upon complexation with a metal ion, indicating that the furan ring oxygen is not engaged in bond formation. In all-metal complexes, non-ligand bands in the range of $558-533\text{ cm}^{-1}$, $450-436\text{ cm}^{-1}$ and $392-354\text{ cm}^{-1}$ have been characterized as $\nu(\text{M}-\text{O})$, $(\text{M}-\text{N})$ and $(\text{M}-\text{Cl})$ stretching oscillations[19–21]. All the above values indicate that the ligand plays a role as a bidentate, with the azomethine nitrogen atom behaving as a donor site and the carbonyl oxygen atom acting as an acceptor site.

Table 1 Data on Schiff base (L) and its metal complexes, including elemental analysis, molar conductance, and magnetic susceptibility

Molecular formula	Mol. Wt	M.P.°C	Yield (%)	Elemental analysis (%) Found/(Calculated)					μ_{eff} B.M.	Λ_{M} ohm ⁻¹ cm ² mole ⁻¹
				C	H	N	M	Cl		
Ligand (L) [C ₂₁ H ₁₆ N ₂ O ₂ S]	360.09	225	65	69.62 (69.98)	4.12 (4.47)	07.13 (7.77)	--	--	--	--
[Co(C ₂₁ H ₁₆ N ₂ O ₂ S) ₂ Cl ₂]	850.00	> 300	65	59.02 (59.30)	3.56 (3.79)	6.44 (6.59)	6.88 (6.93)	8.10 (8.34)	4.86	16.54
[Ni(C ₂₁ H ₁₆ N ₂ O ₂ S) ₂ Cl ₂]	850.46	289	60	54.02 (52.32)	3.70 (3.79)	6.52 (6.59)	6.90 (6.90)	8.42 (8.34)	2.89	17.23
[Cu(C ₂₁ H ₁₆ N ₂ O ₂ S) ₂ Cl ₂]	855.31	>300	65	58.76 (58.98)	3.57 (3.77)	6.47 (6.55)	7.42 (7.43)	8.13 (8.29)	1.87	15.22
[Zn(C ₂₁ H ₁₆ N ₂ O ₂ S) Cl ₂]	496.71	280	56	50.62 (50.78)	3.15 (3.25)	5.17 (5.64)	12.93 (13.16)	14.04 (14.27)	-----	14.56
[Cd(C ₂₁ H ₁₆ N ₂ O ₂ S) Cl ₂]	543.75	291	66	46.22 (46.39)	2.89 (2.97)	5.05 (5.15)	20.44 (20.67)	12.92 (13.04)	-----	15.23
[Hg(C ₂₁ H ₁₆ N ₂ O ₂ S) Cl ₂]	631.92	>300	70	39.84 (39.91)	2.45 (2.55)	4.23 (4.43)	31.57 (31.74)	11.04 (11.22)	-----	16.54

3.2. Magnetic Properties

Magnetic susceptibility data at Standard Temperature and Pressure (STP) demonstrate the paramagnetic behavior of the cobalt, nickel, and copper metal complexes in the applied magnetic field. The magnetic moment of the cobalt metal complex is 4.86 B.M., implying octahedral geometry. This value for nickel complex is 2.859 B.M., which is slightly greater than a spin-only value (2.83 B.M.), demonstrating an octahedral structural environment[22–24]. The copper complex displays a magnetic moment value of about 1.87 indicating a deformed octahedral geometry [25].

3.3. Electronic spectral studies

The electronic spectra of Cobalt, Nickel, and Copper complexes were measured at room temperature in a DMF (10^{-3} M) solvent. The band can be seen at 16900 cm^{-1} and 21112 cm^{-1} in the cobalt complex. In an octahedral environment, these two bands pertain to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3) transitions. Because of the instrument's limited range, the lowermost band ν_1 $12382\text{--}16602\text{ cm}^{-1}$ is calculated using a band fitting procedure [26][27].

Table 2 Infrared frequencies of Schiff base (L) and its metal complexes

Molecular formula	$\nu(\text{CO})$	$\nu(\text{C=N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
(L*) $[\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S}]$	1686	1614	----	----	----
$[\text{Co}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})_2\text{Cl}_2]$	1620	1592	533	450	392
$[\text{Ni}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})_2\text{Cl}_2]$	1665	1590	551	441	366
$[\text{Cu}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})_2\text{Cl}_2]$	1620	1592	553	442	650
$[\text{Zn}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})\text{Cl}_2]$	1660	1594	555	436	370
$[\text{Cd}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})\text{Cl}_2]$	1663	1589	558	446	367
$[\text{Hg}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})\text{Cl}_2]$	1662	1595	551	438	354

*L= Ligand

Table 3 Electronic spectral bands and ligand field parameters of metal complexes in DMF (10^{-3}M) solution

Metal complexes	Transitions in cm^{-1}			Dq (cm^{-1})	B' (cm^{-1})	β	$\beta\%$	ν_2 / ν_1	LFSE (K.cal)
	ν_1^*	ν_2	ν_3						
$[\text{Co}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})_2\text{Cl}_2]$	7866	16900	21112	903.45	961	0.989	1.026	2.148	15.49
$[\text{Ni}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})_2\text{Cl}_2]$	9402	15312	25702	940.16	853.94	0.8211	17.89	1.63	32.23
$[\text{Cu}(\text{C}_{21}\text{H}_{16}\text{N}_2\text{O}_2\text{S})_2\text{Cl}_2]$		12382-16602		1449.2	----	----	----	----	24.84

*Calculated values

The band's broadness is mainly used to define three transitions ${}^2B_{1g}(F) \rightarrow {}^2A_{2g}(\nu_1)$, ${}^2B_{1g}(F) \rightarrow {}^2B_{2g}(\nu_2)$, and ${}^2B_{1g}(F) \rightarrow {}^2E_{2g}(\nu_3)$ which have similar energy levels and only contribute to one broad distorted band [28]. The ligand field parameters such as Racah inter-electronic repulsion parameter (B), ligand field splitting energy (10 Dq), covalency factor (β), and ligand field stabilization energy(LFSE) all seem to have a significant effect on the complex's octahedral geometry [20]. The 'B' values for the complex were significantly lower than those for the free ion, indicating orbital overlap and d-orbital delocalization. The β values found are less than unity, indicating that the metal-ligand bonds have a significant amount of covalent character. The β values for the Nickel complex have lower values than the Cobalt complex, indicating that the metal-ligand bond has more covalency[29].

3.4. ${}^1\text{H}$ NMR spectral analysis

The ${}^1\text{H}$ NMR spectra of the Schiff base and Zn complex were recorded in $\text{DMSO-}d_6$ (Figure-2). The signal at (12.10) (s, 1H) is assigned to the amide proton ($-\text{CONH}-$) of Schiff base L, while the signal at (8.42) (s, 1H) is assigned to the azomethine proton ($-\text{N}=\text{CH}-$). Protons of amide and azomethine shift to lower values in the proton NMR spectra of the Metal (II) complex. All of these indicators point to the formation of the compounds.

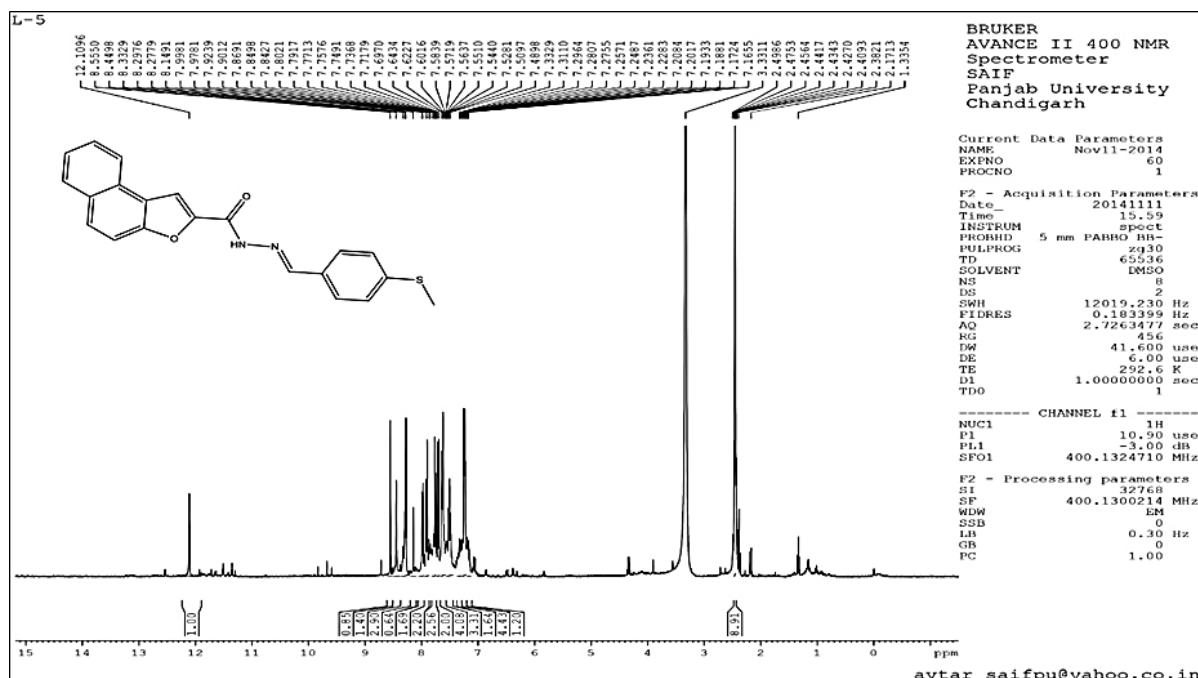


Figure 2 ¹H NMR Spectrum of Ligand L

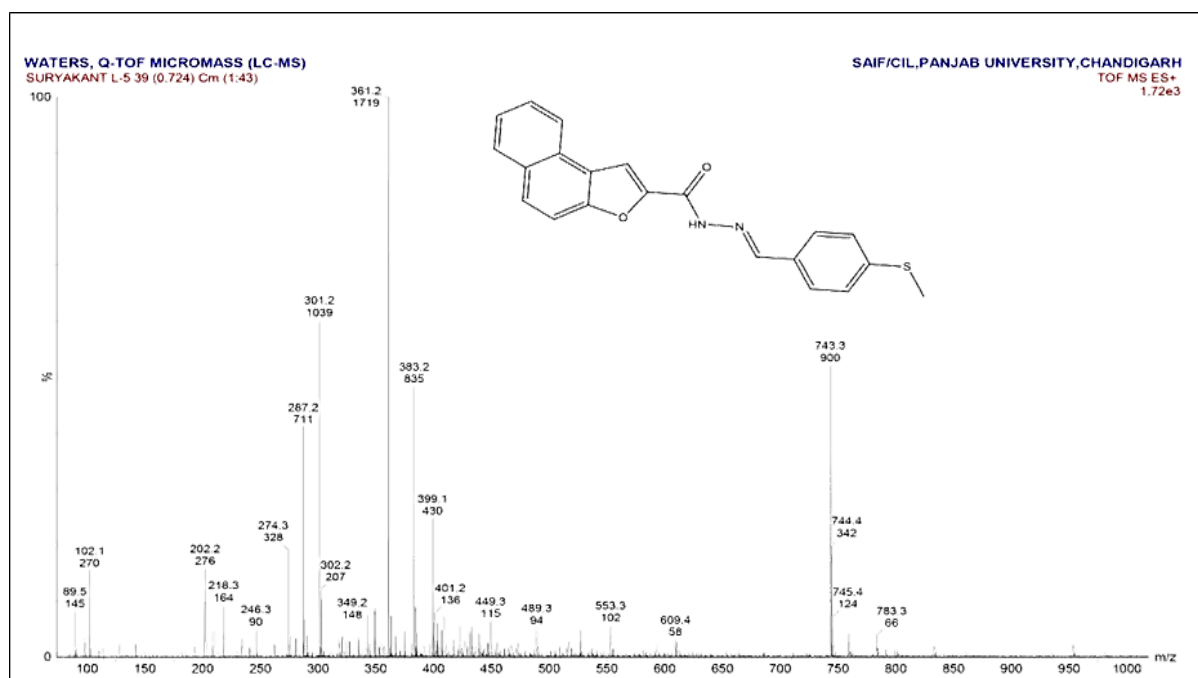


Figure 3 ¹Mass Spectra of the ligand (L)

3.5. Mass spectral analysis

The LC-MS mass spectra of ligand (L) (Figure-3) revealed a molecular ion peak at m/z 361, which is slightly higher than the actual molecular weight of a Schiff base ligand, showing the predicted structure.

3.6. ESR Spectra of Copper complex

(Figure-4). 2.2947 And 2.0731, respectively, were found to be the g and g values. 2.8514 was found to be the g_{av} . The spectra show irregular bands with $g_{\parallel} > g_{\perp} > 2.00277$, implying that the unpaired electrons are mostly in the $d_{x^2 - y^2}$ orbital, with d_z^2 mixing being possible due to its low symmetry [30]. $G = (g_{\parallel} - 2.00277) / (g_{\perp} - 2.00277) = 4.2$, which is significantly higher than 4, stating that solid-state communication is constrained [31]

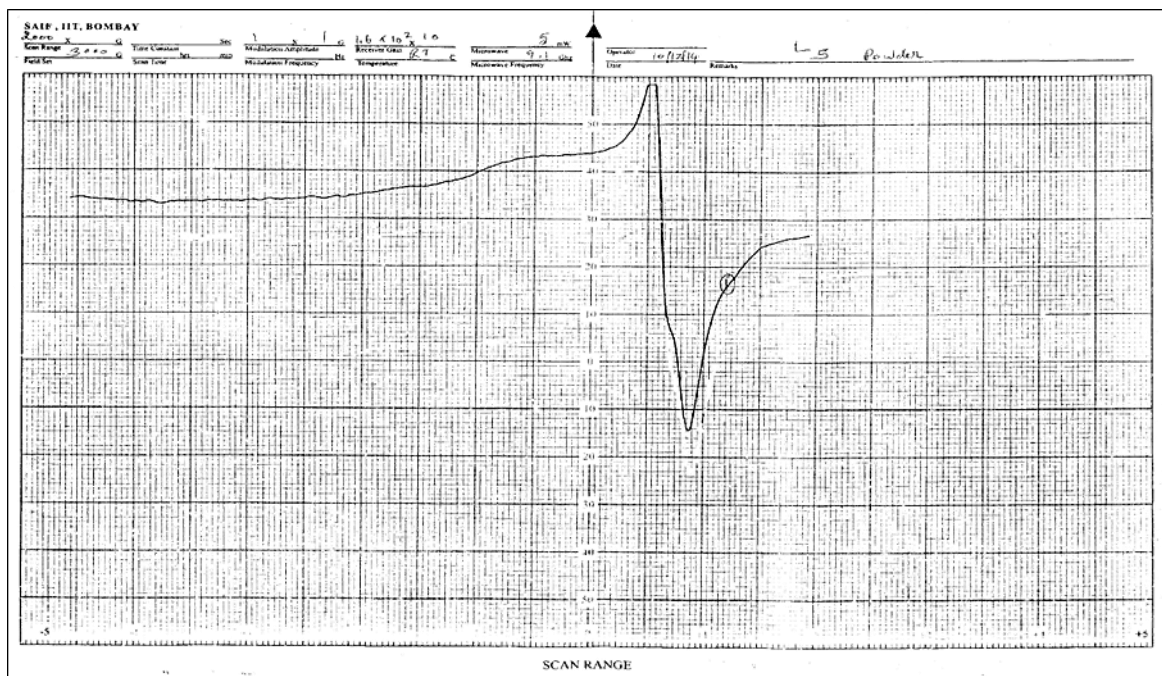


Figure 4 EPR spectrum of Copper complex

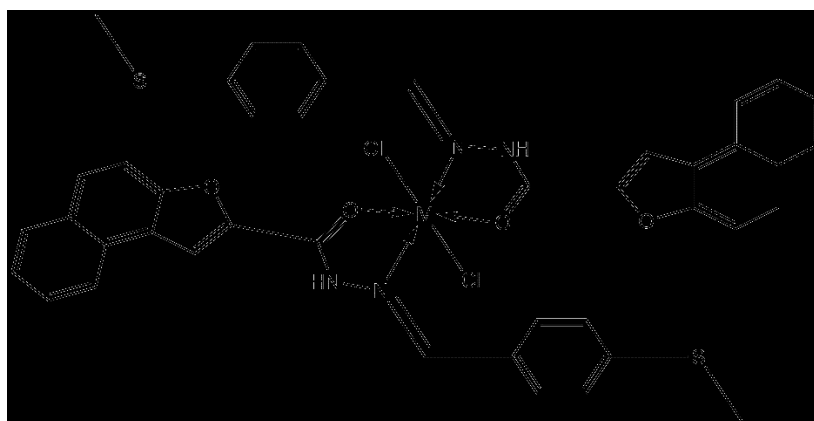


Figure 5 Suggested structure of Co (II), Ni (II), or Cu (II) metal complexes Where M = Co (II), Ni (II), or Cu (II)

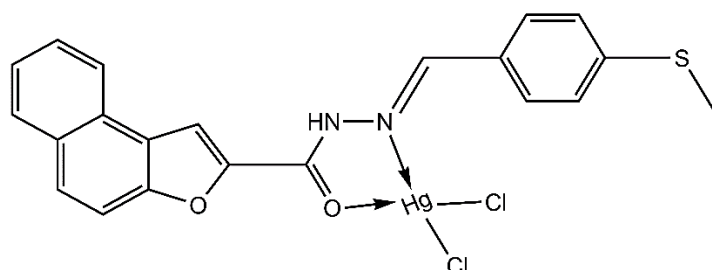


Figure 6 Suggested structure of Zn (II), Cd (II), or Hg (II) metal complexes. Where M = Zn (II), Cd (II), or Hg (II)

4. Conclusion

The Schiff base ligand (L) is a neutral bidentate ligand that's been synthesized. The metal ion is coordinated by the azomethine group's amide oxygen and nitrogen. Analytical data, spectral and magnetic studies all support the metal's

bonding to the ligand. We established octahedral molecular arrangements for Cobalt (II), Nickel(II), and Copper(II) and tetrahedral geometry to Zinc(II), Cadmium(II), and Mercury(II) complexes.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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