

¹H NMR, Diffused Reflectance, Thermal studies, ESR And Anti microbial Activities Of Schiff Base Derived From 5- Nitro Salicylaldehyde and p-Anisidine

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ABSTRACT

Transition metal complexes of the type ML_1 [Where M= Co(II),Ni(II),Cu(II) and Zn(II), L= Schiff base of 5^{nitro}-salicylaldehyde and p- anisidine were characterized by using ¹H NMR ,TGA, Diffused reflectance and ESR spectroscopy. On the basis of above studies Co(II), Ni(II) shows tetrahedral structure, Cu(II) and Zn(II) shows square planar structure.

Keywords: ¹H NMR; 5-nitrosalicylaldehyde; TGA; Square planar complex

1. INTRODUCTION

The co-ordination behaviour and synthesis of Schiff base has received much attention in recent years¹⁻³ because of their enormous uses. Mononuclear complexes derived from Schiff proved to be valuable catalysts in various organic reactions, especially in enantio selective transformation.⁴ Different Schiff bases and their metal complexes find applications in tuberculosis⁵ and as anticonvulsant⁶. Schiff base of 5- Nitro-Salicylaldehyde, P- Anisidine and its metal complexes of Co(II),Ni(II),Cu(II) and Zn(II) with their characterization by using elemental analysis , UV-Visible, IR, X- Ray diffraction were already reported by this lab⁷

In this paper we are reporting further investigation of the Schiff base and its metal complexes by using ¹H NMR ,TGA, Diffused reflectance and ESR spectroscopy.

2. EXPERIMENTAL

¹H NMR Spectra were recorded on a Bruker Act 300(300 Mz) spectrophotometer at I.I.T Bombay, Diffused reflectance spectra were recorded at Department Of Chemistry University Of Mumbai , ESR spectra was recorded at IIT Bombay and TGA analysis at B.A.R.C. Trombay, Mumbai, .Biological studies were carried out at Nicholas Piramal India ,Ltd., Goregaon, Mumbai.

3. RESULT AND DISCUSSION

3.1. ^1H NMR Spectra

^1H NMR spectral data of the Schiff base

^1H NMR spectral data of the Schiff base and their metal complexes is as shown in the table1.

^1H NMR spectrum of the Schiff base (L_1) shows singlet at 14.70 ppm, which can be attributed to the ($-\text{OH}$) proton, while singlet at 9.20 ppm was observed due to azomethine proton^{8,9}. Multiple signals in the region of 7.00- 8.60 ppm are assigned to aromatic protons¹⁰⁻¹¹. Fig.1 indicates the ^1H NMR Spectra of the Schiff base L_1 .

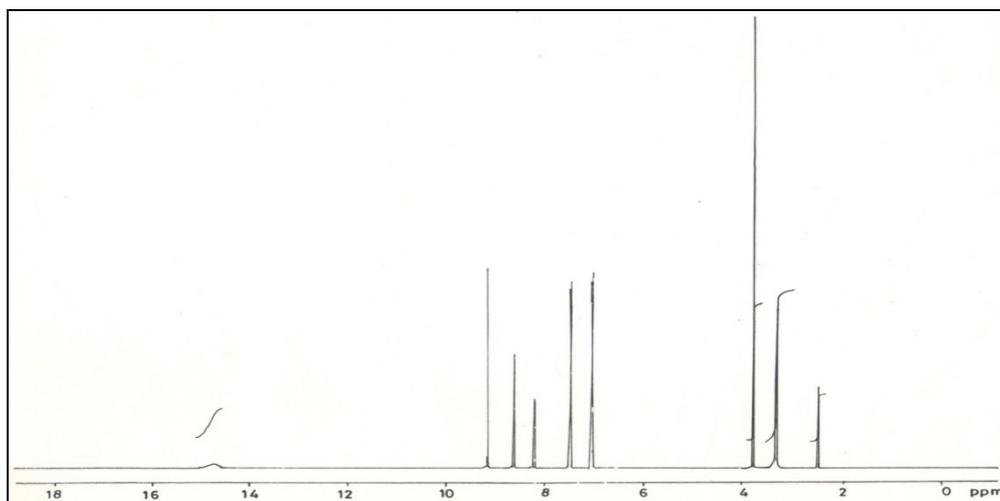


Fig.1. ^1H NMR Spectra of Schiff base (L_1).

^1H NMR spectrum of the $[\text{Co}(L_1)_2]$ complex

In the ^1H NMR spectrum of the $[\text{Co}(L_1)_2]$ complex the signals due to OH protons is absent, Suggesting the deprotonation $-\text{OH}$ group attached to benzene ring in the Schiff base. This confirms the coordination of the ligand to the metal ion through phenolic oxygen atom¹²⁻¹³. The singlet due to azomethine proton at 9.20 ppm is deshielded and appears at 9.38 ppm indicates that azomethine group is coordinated to Co(II) ion through nitrogen atom. Multiple signals in the region of 7.00- 8.60 ppm are assigned to aromatic protons¹⁰⁻¹¹.

^1H NMR spectrum of the $[\text{Ni}(L_1)_2]$ complex

In the ^1H NMR spectrum of the $[\text{Ni}(L_1)_2]$ complex the signals due to OH proton is absent. Suggesting the deprotonation $-\text{OH}$ group attached to benzene ring in the Schiff base. This confirms the coordination of the ligand to the metal ion through phenolic oxygen atom¹²⁻¹⁴. The singlet due to azomethine proton at 9.20 ppm is deshielded and appears at 9.60 ppm indicates that azomethine group is coordinated to Ni(II) ion through nitrogen atom. Multiple signals in the region of 7.00- 8.60 ppm are assigned to aromatic protons¹⁰⁻¹¹.

^1H NMR spectrum of the $[\text{Cu}(L_1)_2]$ complex

In the ^1H NMR spectrum of the $[\text{Cu}(L_1)_2]$ complex the signals due to OH protons is absent. Suggesting the deprotonation of $-\text{OH}$ group attached to benzene ring in the Schiff base. This confirms the coordination of the ligand to the metal ion through phenolic oxygen atom

¹⁴⁻¹⁶. The singlet due to azomethine proton at 9.20 ppm is deshielded and appears at 9.40 ppm indicates that azomethine group is coordinated to Cu(II) ion through nitrogen atom ¹⁷⁻¹⁸. Multiple signals in the region of 7.00- 8.60 ppm are assigned to aromatic protons ¹⁰⁻¹¹.

¹H NMR spectrum of the [Zn(L₁)₂] complex

In the ¹H NMR spectrum of the [Zn(L₁)₂] complex the signals due to OH protons is absent, Suggesting the deprotonation of –OH group attached to benzene ring in the Schiff base. This confirms the coordination of the ligand to the metal ion through phenolic oxygen atom ¹²⁻¹³. The singlet due to azomethine proton at 9.20 ppm is deshielded and appears at 9.40 ppm indicates that azomethine group is coordinated to Zn(II) ion through nitrogen atom ¹⁹. The representative ¹H NMR Spectra of the compound [Zn(L₁)₂] is as shown in the Fig.2.

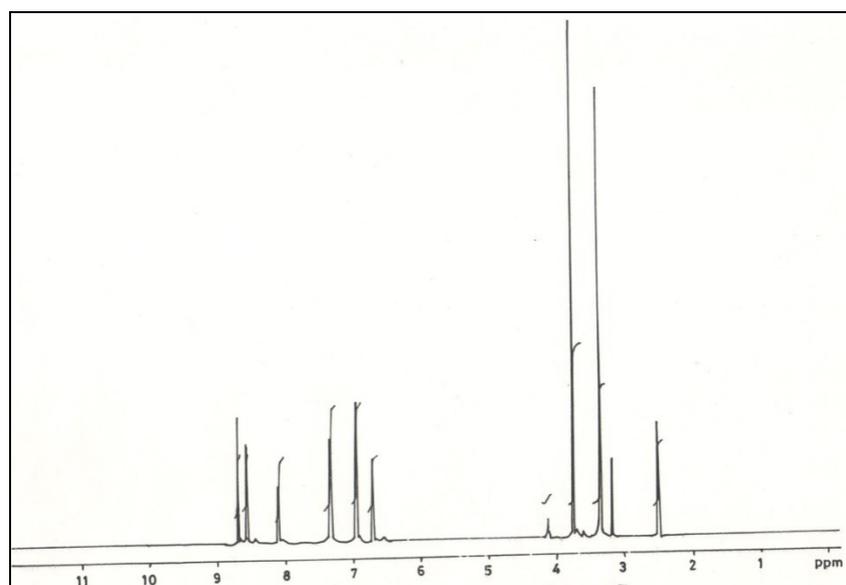


Fig.2. ¹H NMR Spectra of the compound [Zn(L₁)₂].

3.2. Diffused Reflectance Spectra

Diffused reflectance spectrum of Schiff base L₁

Diffused reflectance spectrum is very important analytical tool for the diagnosis of various d-d transition and charge transfer spectra. The bands observed in the reflectance spectrum appears at 11481 cm⁻¹, 26525 cm⁻¹, 27472 cm⁻¹, 30303 cm⁻¹ and 39215 cm⁻¹ which may be assigned to n→π*, π→π* and σ→σ*. The position of these bands can be utilized for calculating shift in the corresponding position in the respective spectra of the metal complexes ²⁰⁻²¹. Fig 3 represents the Diffused Reflectance Spectra of the Schiff base L₁.

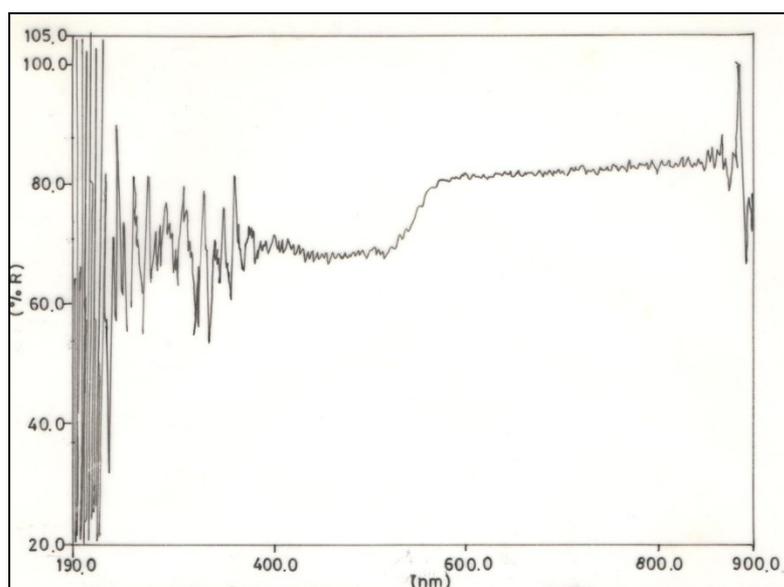


Fig.3. Diffused reflectance spectrum of the Schiff base L1.

Diffused reflectance spectrum of Schiff base $[\text{Co}(\text{L}_1)_2]$

The bands observed in the reflectance spectrum of the $[\text{Co}(\text{L}_1)_2]$ complex of ligand shows absorption at 11723 cm^{-1} , 24154 cm^{-1} , 25906 cm^{-1} , 26525 cm^{-1} , 27932 cm^{-1} and 35587 cm^{-1} respectively which can be assigned to the transition ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$, ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$ and charge transfer bands. On the basis of paramagnetic nature and position of various d-d transition and charge transfer transition complex $[\text{Co}(\text{L}_1)_2]$ may be assigned tetrahedral geometry^{22,23,24,25}. The representative Diffused Reflectance Spectra of the compound $[\text{Co}(\text{L}_1)_2]$ is as shown in the Fig.4.

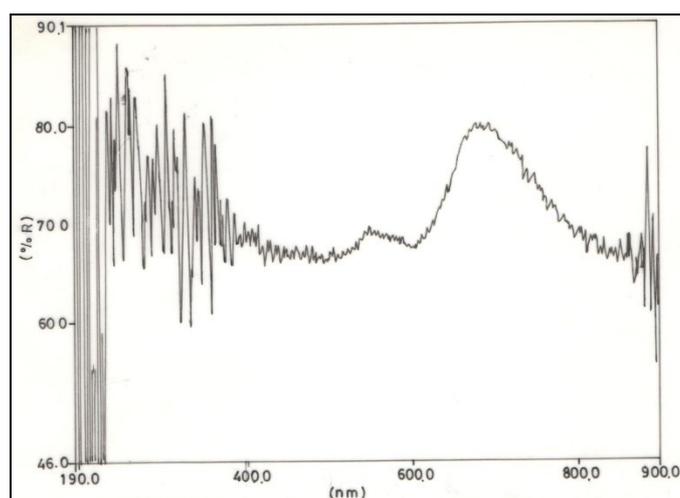


Fig.4. Diffused Reflectance Spectra of the compound $[\text{Co}(\text{L}_1)_2]$.

Diffused reflectance spectrum of $[\text{Ni}(\text{L}_1)_2]$

The bands observed in the reflectance spectrum of the $[\text{Ni}(\text{L}_1)_2]$ complex of ligand shows absorption at 11481 cm^{-1} , 26525 cm^{-1} , 27472 cm^{-1} , 30303 cm^{-1} and 39215 cm^{-1} respectively

which can be assigned to the transition ${}^3T_{2g}(F) \rightarrow {}^3T_{1g}(P)$, ${}^3T_{1g}(F) \rightarrow {}^3A_{2g}(F)$ and charge transfer band. On the basis of paramagnetic nature and position of various d-d transition and charge transfer transition complex $[Ni(L_1)_2]$ may be assigned tetrahedral geometry.^{22,23,24,25}

Diffused reflectance spectrum of $[Cu(L_1)_2]$

The bands observed in the reflectance spectrum of the $[Cu(L_1)_2]$ complex of the ligand shows absorption at 11806 cm^{-1} , 26385 cm^{-1} , 28818 cm^{-1} , 30769 cm^{-1} and 32573 cm^{-1} respectively which can be assigned to the transition ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2E_g$ and charge transfer band respectively. On the basis of paramagnetic nature and position of various d-d transition and charge transfer transition complex $[Cu(L_1)_2]$ may be assigned to square planar structure.²⁶⁻³²

Diffused reflectance spectrum of $[Zn(L_1)_2]$

The Diffused reflectance spectrum of the $[Zn(L_1)_2]$ complex of shows absorption at 11737 cm^{-1} , 26525 cm^{-1} , 28571 cm^{-1} , 34129 cm^{-1} , 37593 cm^{-1} respectively.

Table 1. 1H NMR spectral data of the Schiff base and their metal complexes.

Compound	1H - OH	1H CH=N	7H Ar H
L_1 $C_{14}H_{12}N_2O_4$	14.70	9.20	8.60- 7.00
$[Co(L_1)_2]$	---	9.38	7.90- 6.20
$[Ni(L_1)_2]$	---	9.60	8.60- 7.00
$[Cu(L_1)_2]$	---	9.40	8.69- 6.64
$[Zn(L_1)_2]$	---	9.40	8.62- 6.70

Table 2. Diffused reflectance spectrum of Schiff base L_1 .

Ligand: -4[[[2-hydroxy-5-Nitrophenyl]methylene]-amino]-Anisole

Molecular formula: $C_{14}H_{12}N_2O_4$

Reference: $BaSO_4$

Range: 190-900nm

Wave length (nm)	Wave number (cm^{-1})	Intensity I/I_0
872	11467	84.38
425	23529	70.42
375	26666	73.66
359	27855	81.86
288	34722	77.24

Table 3. Diffused reflectance spectrum data of Co(II) Complex.**Complex:** [Co(L₁)₂]**Molecular formula:** C₂₈H₂₂N₄O₈. Co**Reference:** BaSO₄**Range:** 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
853	11723	67.91
414	24154	70.18
386	25906	71.26
377	26525	72.55
358	27932	81.13
281	35587	77.04

Table 4. Diffused reflectance spectrum data of Ni(II) Complex.**Complex:** [Ni(L₁)₂]**Molecular formula:** C₂₈H₂₂N₄O₈. Ni**Reference:** BaSO₄**Range:** 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
871	11481	75.67
377	26525	15.32
364	27472	20.37
303	30303	21.64
255	39215	22.65

Table 5. Diffused reflectance spectrum data of Cu(II) Complex.**Complex:** [Cu(L₁)₂]**Molecular formula:** [C₂₈H₂₂N₄O₈]Cu**Reference:** BaSO₄**Range:** 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
847	11806	74.34
379	26385	15.00
347	28818	20.03
325	30769	22.82
307	32573	23.07

Table 6. Diffused reflectance spectrum data of Zn(II) Complex.**Complex:** [Zn(L₁)₂]**Molecular formula:** C₂₈H₂₂N₄O₈.Zn**Reference:** BaSO₄**Range:** 190-900nm

Wave length (nm)	Wave number (cm ⁻¹)	Intensity I/I ₀
852	11737	84.61
377	26525	39.64
350	28571	46.32
293	34129	43.19
266	37593	51.83

Table 7. Thermo gravimetric Analysis Data Of Complexes.

[Compound] Molecular formula (Molecular Weight)	Thermal Analysis,	Obs(Theor.)%
	Organic Content	Metal Oxide Content
[Co(L ₁) ₂] C ₂₈ H ₂₂ N ₄ O ₈ .Co (600.93)	87.53(87.50)	12.46(12.50)
[Ni(L ₁) ₂] C ₂₈ H ₂₂ N ₄ O ₈ .Ni (600.69)	87.53(87.50)	12.46(12.50)
[Cu(L ₁) ₂] C ₂₈ H ₂₂ N ₄ O ₈ .Cu (605.55)	86.86(86.73)	13.13(13.27)
[Zn(L ₁) ₂] C ₂₈ H ₂₂ N ₄ O ₈ .Zn (607.39)	86.73(86.60)	13.26(13.40)

Table 8. Antifungal and Antibacterial Studies of Schiff Base And Its Metal Complexes.

Compound	Conc. Mg/ ml	ZONE SIZE IN MM			
		<i>Candida Albicans</i>	<i>Candida krusei</i>	<i>Aspergillus fumigatus</i>	<i>Staphylococcus aureus</i>
Ligand (L ₁)	5.0	---	---	---	---
	2.5	---	---	---	---

	1.25	---	---	---	---
[Co(L ₁) ₂]	5.0	13	14	15	13
	2.5	13	11	12	12
	1.25	12	11	12	11
[Ni(L ₁) ₂]	5.0	12	13	10	---
	2.5	09	11	09	---
	1.25	09	11	09	---
[Cu(L ₁) ₂]	5.0	09	12	10	---
	2.5	09	11	09	---
	1.25	09	11	09	---
[Zn(L ₁) ₂]	5.0	13	15	12	25
	2.5	13	14	11	24
	1.25	13	14	11	21

3.3. Thermal studies

Thermal decomposition studies of Cobalt(II) Complexes

The thermogram of [Co(L₁)₂] shows that the complex starts decomposing at the temperature corresponding to 400⁰C. Till this point there is no weight loss, horizontal nature of the curve up to 400⁰C indicate absence of coordinated water molecule. After this [Co(L₁)₂] complex shows sharp decrease in weight indicating decomposition of organic content of the metal complex, this loss and decomposition continue upto the temperature 600⁰C. The percentage weight loss of organic content from the Co(II) complex was found to be 87.53% which matches with the theoretical value (87.50%). After this the weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable residual metal oxide³³⁻³⁴(CoO). The percentage weight loss of the residual oxide was found to be 12.46% which is very close (12.50%).

Thermal analysis further confirms our finding that coordinated water molecule is absent in [Co(L₁)₂] complex and Schiff base L₁ is bidentate ligand with O:N donar sequence and complex is having tetrahedral geometry.

Thermal decomposition studies of Nickel (II) Complexes

The thermogram of [Ni(L₁)₂] shows that the complex starts decomposing at the temperature corresponding to 300⁰C. Till this point there is no weight loss, horizontal nature of the curve upto 300⁰C indicate absence of coordinated water molecule. After this [Ni(L₁)₂] complex shows sharp decrease in weight indicating decomposition of organic content of the metal complex, this loss and decomposition continue up to the temperature 410⁰C. The

percentage weight loss of organic content from the Ni(II) complex was found to be 87.53% which matches with the theoretical value(87.50%). After this the weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable residual metal oxide ³³⁻³⁴(NiO). The percentage weight loss of the residual oxide was found to be 12.46% which is very close (12.50%).

Thermal analysis further confirms our finding that coordinated water molecule is absent in $[\text{Ni}(\text{L}_1)_2]$ complex and Schiff base L_1 is bidentate ligand with O:N donar sequence and complex is having tetrahedral geometry. Fig.5 represents the TGA Curve of the compound $[\text{Ni}(\text{L}_1)_2]$.

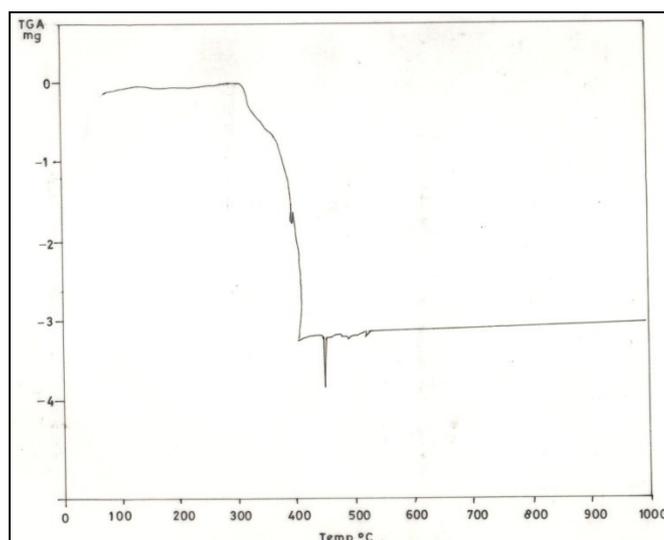


Fig.5. TGA Curve of the compound $[\text{Ni}(\text{L}_1)_2]$.

Thermal decomposition studies of Copper (II) Complexes

The thermogram of $[\text{Cu}(\text{L}_1)_2]$ shows that the complex shows decomposition at 300°C . After this Organic content of the metal complex is removed during this loss, decomposition continue up to the temperature 500°C . The percentage weight loss of organic content from the Cu (II) complex was found to be 86.86% which matches with theoretical value(86.73%). After this, weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable residual metal oxide ³⁵⁻³⁶(CuO). The percentage weight of the residual metal oxide was found to be 13.13% which matches with theoretical value (13.26%). Thermal analysis further confirms our finding that coordinated water molecule is absent in the of $[\text{Cu}(\text{L}_1)_2]$ metal complex and Schiff base L_1 is bidentate ligand with O:N donar sequence and complex is having square planar geometry.

Thermal decomposition studies of Zinc (II) Complexes.

The thermogram of $[\text{Zn}(\text{L}_1)_2]$ shows that the complex shows decomposition at 330°C . After this Organic content of the metal complex is removed during this loss, decomposition continue up to the temperature 800°C . The percentage weight loss of organic content from from the Zn(II) complex was found to be 86.86% which matches with theoretical value(86.73%). After this weight of the complex remains constant and the horizontal nature of the curve indicates the presence of thermally stable residual metal oxide ³⁵⁻³⁶(ZnO). The percentage weight of the

residual metal oxide was found to be 13.13% which matches with theoretical value(13.26%). Thermal analysis further confirms our finding that coordinated water molecule is absent in the $[\text{Zn}(\text{L}_1)_2]$ metal complex and Schiff base L_1 is bidentate ligand with O:N donar sequence and complex is having square planar geometry

3.4. ESR spectral studies of copper (II) complex

This technique is used to detect the presence of unpaired electron in a metal cluster. The x- band ESR Spectrum of $[\text{Cu}(\text{L}_1)_2]$ complex exhibit a single line resulting the interaction of unpaired electron present in the Cu(II) complex. The table reveals that g_{\perp} factor is found to be 1.9350, while g_{\parallel} factor is found to be 1.8549. The g_{\parallel} value is less than 2.3 which suggest existence sufficient co-valency in the $[\text{2Cu}(\text{L}_2)]$. The solid state ESR spectrum of $[\text{2Cu}(\text{L}_2)]$ complex at room temperature yielded a broad signal with $g_{\text{avg}} = 1.9083$, indicating unpaired electron lie in $d^{x^2-y^2}$ orbital of Cu(II) complex.^{38,39,40} Fig.6 represents the ESR Spectra of the compound $[\text{Cu}(\text{L}_1)_2]$.

Table 9. ESR Spectral Data Of Cu(II) Complex.

Complex	g_{\perp}	g_{\parallel}	g_{avg}	G (Axial Symmetry Parameter)	μ_{eff} (B.M.) From ESR	μ_{eff} (B.M.) From Gouy Method
$2\text{Cu}(\text{L}_2)$	1.9535	1.8271	1.9114	3.7182	1.655	1.870

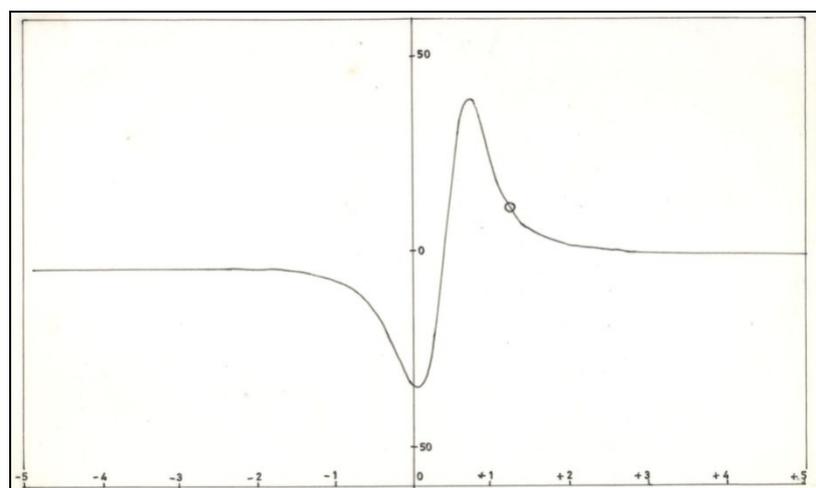


Fig. 6. ESR Spectra of the compound $[\text{Cu}(\text{L}_1)_2]$.

3.5. Biological Studies of Schiff Base L₁ And Co(II),Ni(II),Cu(II) and Zn(II) Metal Complexes

The concentration used for testing 5.0mg/ml, 2.5mg/ml and 1.25mg/ml in DMF. The results from the table reveals that the ligand is inactive towards all the fungi as well as bacterial strains. All the metal complexes were found to have excellent fungi toxic properties even after decreasing concentration of metal complex in the test sample, activity almost remains samewith slight decrease. Thus we can conclude that at low concentration metal complexes are most active against fungal and bacterial strains as desirable. In general metal complexes are more active than their parent ligand and hence may serve as vehicle for activation of the ligand as principle cytotoxic species.^{12,41,42.}

4. CONCLUSION

On the basis of ¹H NMR, Diffused reflectance data and Thermo gravimetric studies , Co(II),Ni(II) shows tetrahedral structure where as Cu(II) and Zn(II) exhibits square planar structure.

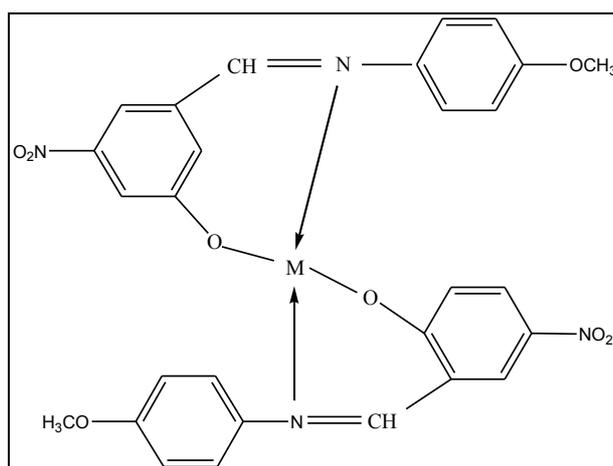


Fig.7. Where , M=Co(II), Ni(II) Tetrahedral complexes and Cu(II) and Zn(II) square planar complexes.

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