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 ML₁ (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 anticonvulsant 6. 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 lab 7

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 Brukner 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. $^1$H NMR Spectra

$^1$H NMR spectral data of the Schiff base

$^1$H NMR spectral data of the Schiff base and their metal complexes is as shown in the table 1. $^1$H NMR spectrum of the Schiff base (L$_1$) shows singlet at 14.70 ppm, which can be attributed to the (–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 protons $^{10-11}$. Fig. 1 indicates the $^1$H NMR Spectra of the Schiff base L$_1$.

![Fig. 1. $^1$H NMR Spectra of Schiff base (L$_1$).](image)

$^1$H NMR spectrum of the [Co(L$_1$)$_2$] complex

In the $^1$H NMR spectrum of the [Co(L$_1$)$_2$] complex the signals due to OH protons is absent. Suggesting the deprotonation –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 9.38 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 protons $^{10-11}$. $^1$H NMR spectrum of the [Ni(L$_1$)$_2$] complex

In the $^1$H NMR spectrum of the [Ni(L$_1$)$_2$] complex the signals due to OH proton is absent. Suggesting the deprotonation –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 $^{12-14}$. 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 protons $^{10-11}$. $^1$H NMR spectrum of the [Cu(L$_1$)$_2$] complex

In the $^1$H NMR spectrum of the [Cu(L$_1$)$_2$] 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
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. Multiple signals in the region of 7.00-8.60 ppm are assigned to aromatic protons.

**\(^1\)H NMR spectrum of the [Zn(L\(_1\))\(_2\)] complex**

In the \(^1\)H NMR spectrum of the [Zn(L\(_1\))\(_2\)] 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. 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.

The representative \(^1\)H NMR Spectra of the compound [Zn(L\(_1\))\(_2\)] is as shown in the Fig.2.

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**3.2. Diffused Reflectance Spectra**

**Diffused reflectance spectrum of Schiff base L\(_1\)**

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. Fig 3 represents the Diffused Reflectance Spectra of the Schiff base L\(_1\).
Diffused reflectance spectrum of Schiff base [Co(L₁)₂]

The bands observed in the reflectance spectrum of the [Co(L₁)₂] complex of ligand shows absorption at 11723 cm⁻¹, 24154 cm⁻¹, 25906 cm⁻¹, 26525 cm⁻¹, 27932 cm⁻¹ and 35578 cm⁻¹ respectively which can be assigned to the transition $^4A_2(F) \rightarrow ^4T_1(F), ^4A_2(F) \rightarrow ^4T_1(P)$ and charge transfer bands. On the basis of paramagnetic nature and position of various d-d transition and charge transfer transition complex [Co(L₁)₂] may be assigned tetrahedral geometry. The representative Diffused Reflectance Spectra of the compound [Co(L₁)₂] is as shown in the Fig.4.

Diffused reflectance spectrum of [Ni(L₁)₂]

The bands observed in the reflectance spectrum of the [Ni(L₁)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.

**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.

**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.

| Compound  | $^1$H- OH | $^1$H CH=N | 7H Ar H |
|-----------|-----------|-----------|---------|
| L$_1$ C$_{14}$H$_{12}$N$_2$O$_4$ | 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 1.** $^1$H NMR spectral data of the Schiff base and their metal complexes.

| 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 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$_2$O$_4$
Reference: BaSO$_4$
Range: 190-900nm
Table 3. Diffused reflectance spectrum data of Co(II) Complex.

Complex: [Co(L$_1$)$_2$]
Molecular formula: C$_{28}$H$_{22}$N$_4$O$_8$. Co
Reference: BaSO$_4$
Range: 190-900 nm

| 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(L$_1$)$_2$]
Molecular formula: C$_{28}$H$_{22}$N$_4$O$_8$. Ni
Reference: BaSO$_4$
Range: 190-900 nm

| 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(L$_1$)$_2$]
Molecular formula: [C$_{28}$H$_{22}$N$_4$O$_8$]Cu
Reference: BaSO$_4$
Range: 190-900 nm

| 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(L₁₂)] | Molecular formula: C₂₈H₂₂N₄O₈.Zn | Reference: BaSO₄ | Range: 190-900nm |
|--------------------|----------------------------------|------------------|------------------|
| Wave length (nm)   | Wave number (cm⁻¹)               | Intensity I/I₀   |
| 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(L₁₂)]  | C₂₈H₂₂N₄O₈.Co (600.93)               | 87.53(87.50)     | 12.46(12.50)  |
| [Ni(L₁₂)]  | C₂₈H₂₂N₄O₈.Ni (600.69)              | 87.53(87.50)     | 12.46(12.50)  |
| [Cu(L₁₂)]  | C₂₈H₂₂N₄O₈.Cu (605.55)              | 86.86(86.73)     | 13.13(13.27)  |
| [Zn(L₁₂)]  | C₂₈H₂₂N₄O₈.Zn (607.39)              | 86.73(86.60)     | 13.26(13.40)  |

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

| Compound | Conc. Mg/ ml | ZONE SIZE IN MM |
|----------|--------------|-----------------|
|          |              | Candida Albicans | Candida krusei | Aspergillus fumigatus | Staphylococcus aureus |
| Ligand (L₁) | 5.0          | ---             | ---            | ---                   | ---                   |
|          | 2.5          | ---             | ---            | ---                   | ---                   |
### 3.3. Thermal studies

**Thermal decomposition studies of Cobalt(II) Complexes**

The thermogram of [Co(L\(_1\))\(_2\)] shows that the complex starts decomposing at the temperature corresponding to 400\(^\circ\)C. Till this point there is no weight loss, horizontal nature of the curve up to 400\(^\circ\)C indicate absence of coordinated water molecule. After this [Co(L\(_1\))\(_2\)] complex shows sharp decrease in weight indicating decomposition of organic content of the metal complex, this loss and decomposition continue up to the temperature 600\(^\circ\)C. 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 oxide \((\text{CoO})\). 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(L\(_1\))\(_2\)] complex and Schiff base L\(_1\) 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(L\(_1\))\(_2\)] shows that the complex starts decomposing at the temperature corresponding to 300\(^\circ\)C. Till this point there is no weight loss, horizontal nature of the curve up to 300\(^\circ\)C indicate absence of coordinated water molecule. After this [Ni(L\(_1\))\(_2\)] complex shows sharp decrease in weight indicating decomposition of organic content of the metal complex, this loss and decomposition continue up to the temperature 410\(^\circ\)C. The

| Complex       | Temperature (\(^\circ\)C) | Weight Loss (\%) |
|---------------|---------------------------|-----------------|
| [Co(L\(_1\))\(_2\)] | 5.0 | 13  |
|               | 2.5 | 11  |
|               | 1.25 | 11  |
| [Ni(L\(_1\))\(_2\)] | 5.0 | 12  |
|               | 2.5 | 11  |
|               | 1.25 | 11  |
| [Cu(L\(_1\))\(_2\)] | 5.0 | 12  |
|               | 2.5 | 11  |
|               | 1.25 | 11  |
| [Zn(L\(_1\))\(_2\)] | 5.0 | 13  |
|               | 2.5 | 14  |
|               | 1.25 | 14  |
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 \([\text{Ni}(L_1)_2]\) 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 \([\text{Ni}(L_1)_2]\).

**Fig.5. TGA Curve of the compound \([\text{Ni}(L_1)_2]\).**

**Thermal decomposition studies of Copper (II) Complexes.**

The thermogram of \([\text{Cu}(L_1)_2]\)shows that the complex shows decomposition at 300\(^0\)C. After this Organic content of the metal complex is removed during this loss, decomposition continue up to the temperature 500\(^0\)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 \([\text{Cu}(L_1)_2]\) 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 \([\text{Zn}(L_1)_2]\)shows that the complex shows decomposition at 330\(^0\)C. After this Organic content of the metal complex is removed during this loss, decomposition continue up to the temperature 800\(^0\)C. The percentage weight loss of organic content 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 [Zn(L1)2] metal complex and Schiff base L1 is bidentate ligand with O:N donor 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 [Cu(L1)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 [2Cu(L)2]. The solid state ESR spectrum of [2Cu(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.\textsuperscript{38,39,40}. Fig.6 represents the ESR Spectra of the compound [Cu(L1)2].

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

Fig. 6. ESR Spectra of the compound [Cu(L1)2].
3.5. Biological Studies of Schiff Base L\textsubscript{1} 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 same with 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.\textsuperscript{12,41,42}

4. CONCLUSION

On the basis of \textsuperscript{1}H 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.

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

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