Chapter 6

Chemistry of transition metal complexes derived from pyruvic acid Schiff bases having Isatin/triazole core
Hydrazones belong to a class of organic compounds with the structure R1R2C=NNH2. Hydrazones derived from the hydrazides are azomethines characterized by the presence of the triatomic group >C=N–N< and finds extensive applications in biological, clinical, analytical and various other fields. These are obtained by the condensation of various hydrazides with aldehydes or ketones. Hydrazones have attracted the attention of many workers since they are readily available, cheap and exhibit a varied spectrum of properties along with the structural flexibility.

A great deal of work has been done on hydrazones and their complexes. The ease of synthesis of hydrazones provides access to compounds with specifically tailored characteristics, widening the scope of their applications. Apart from these, they have interesting ligational properties due to the presence of several potential coordinating sites and possibility of tautomerism.

Schiff base hydrazones of pyruvic acid and their complexes with transition metals have provoked wide interest for their possession of a diverse spectrum of biological and pharmaceutical activities, such as anticancer, antitumour and antioxidative activities, as well as the inhibition of lipid peroxidation and so on. Also these compounds are known to be a versatile class of ligands capable of generating varied molecular architectures and coordination polyhedra. Thus considering the structural and pharmacological aspects of pyruvic acid hydrazones, here we report the synthesis and characterization of pyruvic acid Schiff bases having Isatin/ Triazole core.
Chapter 6

Section A

Synthesis and characterization of isatinyl-3-pyruvic acid hydrazone and its metal complexes
6A.1. INTRODUCTION

Oxindoles are the compounds found in mammalian body fluids and tissues, distributed all over the central nervous system. They have shown a broad range of biological activities, which comprise antibacterial, antifungal, anticonvulsant, antiviral, and antiproliferative activity [1]. A most important derivative of oxindoles viz., isatin (indole-2,3-dione; or 2,3-dioxoindoline; or indoline-2,3-dione) was discovered in the nineteenth century as an oxidation product of indigo [2] and it is probably the first example of tautomeric substance to be reported. Its tautomeric forms were formerly proposed in 1882, exhibiting two chemically dissimilar carbonyl groups, a lactam-carbonyl (α), and a keto-carbonyl (β), as shown in 6A.1 [3].

\[
\begin{align*}
\text{2,3-dioxoindoline} & \quad \text{2-hydroxy-indolin-3-one} \\
\end{align*}
\]

6A.1. Tautomeric forms of 1H-indole-2,3-dione.

Isatin, due to its cis α-dicarbonyl moiety, is a potentially good substrate for the synthesis of metal complexes, either alone or with other ligands. Their derivatives, mostly those substituted at β position, such as isatin-bishydrazones and isatin-3-imines bearing an extra heteroaromatic ring are also generally employed as ligands [4].

Additional interest in the synthesis of transition-metal complexes of isatin results from the presence of the carbonyl functions, which might themselves possess ligand properties towards other metals, leading to the formation of bi- and multimetallic coordination assemblies. A range of multimetallic structures based upon amide complexes have been reported [5]. The presence of two adjacent carbonyl groups in isatin, both of which could potentially act as ligands towards other metal centres, offers a new dimension in this area. We note that metal complexes of the related α, β-diketo ligands, oxalate [6] and oxamidate [7] are well known to form interesting coordination networks.
Manifestation of different pharmacological activities by the isatinyl derivatives, their metal complexes have gained biological relevance. Their antibacterial and antiproliferative or mutagenic properties were also investigated and a brief survey on the same is discussed in the following paragraphs.

Schiff bases of isatin were prepared by the reaction with amino acids or substituted hydrazines and were subsequently metallated with Ni(II), Fe(III) or Co(II) ions [8]. Zinc(II) and Hg(II) complexes of isatin-3-thiosemicarbazone were isolated and spectroscopically characterized [9]. Cu(II), Ni(II) and Co(II) complexes with pyridyl- and quinolyldihydrzones of isatin and N-methylisatin have also been prepared. In the case of the copper complex, spectroscopic results suggested a planar geometry [10].

Schiff base derived from the reaction of isatin and o-phenylenediamine and its Cu(II), Cr(III), Mn(II), Co(II), Ni(II), Zn(II), Cd(II) and Pb(II) complexes were reported. The ligand has coordinated in enolic form (6A.2) [11].

6A.2. Structures of different metal complexes with oxindole-derived ligands.

Co(II), Ni(II) and Cu(II) complexes of thiosemicarbazones, prepared by condensation of isatin or 1-methylisatin with the appropriate N(4)-substituted thiosemicarbazide, were studied by different spectral methods [12, 13]. The 3-thiosemicarbazones of isatin and their Cu(II) complexes were found to be active in the treatment of smallpox. The suggested mode of action of these compounds could involve the inhibition of virus growth through binding to copper ions, which are constituents of the virus.
Complexes of divalent Cu(II), Co(II), Ni(II) and Zn(II) ions with 3-salicylidenehydrazono-2-indolinone were isolated in the keto-form of the ligand, as shown in 6A.3 and exhibited antimicrobial activity against gram-positive and gram-negative organisms. This activity was enhanced compared to the proligand itself, especially against *Candida albicans*, and decreased in the metal order Zn > Cu > Co > Ni [14].

Different isatin-derivatives incorporating thiazole, thiadiazole, benzothiazole and p-toluene sulfonylhydrazide moieties as well as their corresponding Co(II), Cu(II), Ni(II) and Zn(II) complexes were prepared [15]. These compounds also showed good results as antibacterial and antifungal agents against different strains, and most of them had their activity enhanced on complexation.

Complexes of Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) with isatin-thiosemicarbazone were prepared (6A.3.), and the nickel complex was structurally characterized by X-ray crystallography. Investigations of cellular growth and apoptosis induction in the presence of these species indicated that the proligand and the corresponding Ni(II) and Cu(II) complexes can inhibit cell proliferation of human leukemia U937 cell lines. It was observed that the proligand and its Cu(II) complex were equally active, inhibiting the cellular growth by nearly 70% at 20 μg mL⁻¹. With the Ni(II) complex, an inhibition of only 30% was observed at 10 μg mL⁻¹; at higher concentration this complex was cytotoxic [16].

6A. 3. Isatin-β-thiosemicarbazone complexes active in the inhibition of cell proliferation.

![Complexes of divalent Cu(II), Co(II), Ni(II) and Zn(II) ions with 3-salicylidenehydrazono-2-indolinone.](image)
Chapter 6 A

Isatinyl-3-pyruvic acid hydrazone

The coordinating behavior of bis-isatinyl hydrazone prepared from the reaction of isatinyl monohydrazide with salicylaldehyde towards Cu(II) ion with different counter ions is reported [17]. Based on the electronic, spectral and magnetic moment values, a distorted square planar geometry was proposed for all the complexes.

Co(II), Ni(II), Cu(II) and Zn(II) complexes of 2-thiophenecarbonyl and isonicotinyl hydrazones of 3-(N-methyl)-isatin (6A.6.) were synthesized and structure of both the ligands and Ni(II) complexes were confirmed by single crystal X-ray diffraction studies. The compounds were screened for antimicrobial properties [18].

6A.6. 2-Thiophenecarbonyl and isonicotinyl hydrazones of N-methylisatin

Bis-isatinthiocarbonyldrazones and transition metal complexes were isolated by Satisha et al. [19]. The ligand acts as a monobasic, tridentate fashion ligand. The complexes along with the parent ligand were screened for antitumor activity against Ehrlish ascites carcinoma (EAC) in Swiss albino mice, the results of which shows an increase in the activity on complexation [19].

The various biological activities of pyruvic acid and isatin derived hydrazones and their metal complexes prompted us to prepare the novel ligand with isatin monohydrazone which might possess interesting pharmacological properties. Thus the present investigation throw light on synthesis and characterization of novel Schiff base Viz, Isatinyl-3-pyruvic acid hydrazone. The transition metal complexes (Co(II), Ni(II), Cu(II) and Zn(II)) of the hydrazone were prepared with a view towards evaluating their antimicrobial activities.
6A.2. EXPERIMENTAL

6A.2.1. Synthesis of Isatin monohydrazone

To a methanolic solution (20 mL) of isatin (0.147 g, 1 mmol), hydrazine hydrate (0.150 g, 3 mmol) was added with stirring. The resulting solution was refluxed for 3 h, and then cooled to room temperature, when an yellow solid separates (Scheme 6A.1). The solid was filtered, washed with ethanol and dried in air and recrystallised from methanol. The purity of the compound was checked by TLC on pre-coated silica gel plates.

Scheme 6A.1 Synthetic route for the preparation of isatin monohydrazone

6A.2.2. Synthesis of Isatinyl-3-pyruvic acid hydrazone (LIIH₂)

To a methanolic solution (20 mL) of isatin monohydrazone (0.161 g, 1 mmol), pyruvic acid (0.88 g, 1 mmol) was added and refluxed for 3 h, when yellowish-orange solid separates (Scheme 6A.2). The solid was filtered, washed with ethanol and dried in air and recrystallised from methanol. Yield: 72% and M.P.: 230 °C.

Scheme 6A.2 Synthetic route for the preparation of LIIH₂

6A.2.3. Synthesis of Co(II), Ni(II), Cu(II) and Zn(II) complexes of LIIH₂

To a 15 mL of an ethanolic solution of LIIH₂ (0.231 g, 1 mmol), 5 mL of ethanolic solution of equimolar quantity of corresponding metal salts (1 mmol) was added slowly with constant stirring. The pH of the solution is adjusted to 6-7 by
adding 2-3 drops of ammonia, and refluxed for about 1h. The precipitates thus obtained were filtered, washed repeatedly with ethanol and acetone and dried in air.

6A.3. RESULTS AND DISCUSSION

The condensation of isatin with hydrazine hydrate proceeds, as usual selectively on the carbonyl at β position in the isatin ring. Ligand was prepared by the condensation of isatin monohydrazone and pyruvic acid. The elemental analysis of the ligand is consistent with the molecular formula C₁₅N₄H₁₂O₂. The transition metal complexes of L₁₁H₂ are stable at room temperature and non-hygroscopic in nature. Complexes are insoluble in common organic solvents but soluble in coordinating solvents like DMF and DMSO. A formulation of these complexes has been done on the basis of elemental analysis and molar conductance. Analytical data of complexes is given in Table 6A.1.

6A.3.1. Molar conductance

Molar conductance values of the complexes measured in DMF (10⁻³ M solutions) adequately confirm the non-electrolytic nature of the complexes.

6A.3.2. Infrared studies

Infrared spectral data of the ligand and its complexes are presented in Table 6A.2 along with their assignments. In the free ligand sharp bands of medium intensity at 3393 and 3242 cm⁻¹ are due to symmetric stretching vibrations of -OH and -NH group [20]. The absorption bands characteristic of the ν(C=O) vibrations of isatinic and pyruvic acid fragments appear at 1740 cm⁻¹ [21] and 1722 cm⁻¹ [22] respectively and the absorption band at 1629 cm⁻¹ was assigned to azomethine ν(-C=N) stretching.

In the IR spectra of all the complexes, stretching frequency of lactam carbonyl of isatin disappears and new band appears at 1614-1618 cm⁻¹, which is due to ligation of carbonyl oxygen via enolisation and deprotonation [20]. The band due to ν(-OH) frequency has disappeared in the spectra of all the complexes indicating the coordination of hydroxyl oxygen after deprotonation. Moreover in the IR spectra, new absorption band at 1186-1189 cm⁻¹, were observed and assigned to the vibrations of
C-O-M bonds. These data indicates that the ligand is in enolic form in the complexes. This is also supported by the appearance of a new absorption band at 1278-1308 cm\(^{-1}\) due to \(\nu(C-O)\) stretching in all the complexes. The azomethine stretching frequency in all the complexes has shifted to lower frequencies, which indicates the involvement of the nitrogen atom of azomethine group in the coordination with metal ions.

6A.3.3. NMR spectral studies

The \(^1\)H NMR spectral assignments were done comparing with isatin monohydrazone and pyruvic acid. The numbering system for the assignments of protons is given in the Scheme 6A.3. Chemical shift assignments of \(^1\)H NMR and \(^{13}\)C NMR of \(\text{L}1\text{H}_2\) and its Zn(II) complex are given in Table 6A.3.

![Scheme 6A.3 Numbering scheme for \(\text{L}1\text{H}_2\)](image)

\(^1\)H NMR of \(\text{L}1\text{H}_2\) show singlets at 13.84 and 11.3 ppm integrating for one proton each assigned to N3H, and O1H respectively and both are D\(_2\)O exchangable. Four doublets at 6.89, 7.03, 7.40, 6.67 ppm each integrating for one proton were assigned to C(2)H, C(3)H, C(1)H, and C(4)H respectively. The -CH\(_3\) proton signal observed at ~2.17 ppm in ligand. The \(^{13}\)C NMR of \(\text{L}1\text{H}_2\) show eleven signals corresponding to the total number of carbon atoms present in the \(\text{L}1\text{H}_2\). Thus the \(^1\)H NMR and \(^{13}\)C NMR spectral studies prove the formation of ligand. Carbon signals due to carbonyl carbon C11, azomethine carbon C7, C9 and lactonyl carbon C8 are observed at 169.23, 137.04, 164.93 and 166.01 ppm respectively. Remaining aromatic carbons are observed in expected region. The \(^1\)H NMR and \(^{13}\)C NMR spectra of \(\text{L}1\text{H}_2\) are shown in Figures 6A.1, and 6A.2 respectively.
The $^1$H spectrum of Zn(II) complex is depicted in Figure 6A.3. The absorbance for signals due to N3H, and O1H in $^1$H NMR spectrum of Zn(II) complex indicates the deprotonation of N3H, and O1H protons via enolisation and supports the coordination of ligand in the enol form. No considerable change was observed in the chemical shifts of aromatic protons. The -CH$_3$ proton signal observed at ~2.17 ppm in ligand shifts down field due to the involvement of adjacent azomethine nitrogen >C=N in bonding with the Zn(II) ion.

6A.3.4. Electronic spectral studies

The electronic absorption spectrum of ligand exhibit strong bands at around 303, 360 and 410 nm respectively assignable to $\pi \rightarrow \pi^*$, n$\rightarrow \pi^*$ transitions associated with azomethine linkage [24, 25]. All the complexes show $\pi \rightarrow \pi^*$ transition in the range 350-390 nm. In addition, they also display bands in the region 420-450 nm in case of Co(II), Ni(II), Cu(II) and Zn(II) complexes respectively and were assigned to ligand to metal charge transfer transitions (LMCT). A broad band around 790-820 nm appearing as an envelope in the Cu(II) complex, was assigned to $^2$E$g \rightarrow ^2$T$_{2g}$ transition which reveals the octahedral geometry [23, 24, 25]. Ni(II) complex exhibits an absorption at 872 nm was due to $^3$A$_{2g} \rightarrow ^3$T$_{2g}$ ($v_1$). The bands near 560 and 425 nm were assigned to $^3$A$_{2g} \rightarrow ^3$T$_{1g}$ ($v_2$) and $^3$A$_{2g} \rightarrow ^3$T$_{1g}$ (P) ($v_3$) respectively, indicating an octahedral geometry around Ni(II) ion [23, 24, 26]. The low intensities of the d-d bands compared to intra-ligand and metal to ligand charge transfer absorptions in DMSO solution prevent an accurate assignment for the Co(II) complex. The electronic spectra of representative compounds are depicted in the Figure 6A.4 and the electronic spectral data are given in Table 6A.4.

6A.3.5. Magnetic properties

Magnetic moments of paramagnetic complexes were recorded in order to obtain the structural information of these complexes. The corrected magnetic moments at room temperature for diamagnetism are given in Table 6A.1. The magnetic moment of Co(II) complex is 4.77 BM which is greater than the spin-only value (3.46 BM) indicates the high-spin state of the complex and an octahedral geometry [27]. The magnetic moment observed for Ni(II) complex is 3.42 BM,
consistent with octahedral geometry [25]. The magnetic moment value for Cu(II) complex is well within the range corresponding to spin-only value for one unpaired electron with an octahedral geometry and indicating no metal-metal interaction.

**6A.3.6. EPR spectral studies**

The EPR spectra of the polycrystalline sample of Cu(II) complex (Figure 6A.5) at room temperature (300 K) and liquid nitrogen temperature (77 K) exhibit isotropic, intense broad signal with $g_{iso}$ values 2.09, 2.02 respectively.

**6A.3.7. FAB mass spectral studies**

The FAB mass spectra of [Ni(L11)(H2O)3] and [Cu(L11)(H2O)3] complexes show peaks with m/z values 341 and 346 corresponding to the molecular weight of the respective complexes. These values are in good agreement with the proposed composition for the complexes. FAB mass spectra of both complexes are shown in Figures 6A.6 and 6A.7 respectively.

**6A.3.8. Cyclic voltammetric studies**

In the voltammogram of the [Cu(L11)(H2O)3] complex, cathodic peak is observed in the range $E_{pc} = 0.102$ to $0.345$ V evidences the reduction of metallic species, Cu(II)$\rightarrow$Cu(I). The reverse scan shows anodic peak with potential in the range, $E_{pa} = 0.45$ to $0.61$ V corresponding to Cu(I)$\rightarrow$Cu(II) oxidations (Figure 6A.8). The separation between anodic and cathodic peak potentials $E_p = E_{pa} - E_{pc}$ for the complex is found to be $300$ mV $> 60$ mV and the ratio of cathodic to anodic peak currents, $I_{pc}/I_{pa}$ is $\sim 1.13$. This indicates the single electron quasi-reversible nature of the assigned redox process [28].

The voltammogram of the [Ni(L11)(H2O)3] complex (Figure 6A.9) shows only one irreversible oxidation peak in the region 0.502 to 0.310 V assignable to Ni(II)/Ni(III). For an irreversible oxidation process, the number of electron transferred per molecule (n) could be calculated from the following equation [29].

$$|E_{pa} - E_{pc/2}| = 1.857RT/(1-\alpha)nF$$
where $E_{pa}$ is the potential of the oxidation peak, $E_{pa/2}$ the half peak potential of oxidation peak, $\alpha$, the electron transfer coefficient (generally, $0.3 < \alpha < 0.7$), F Faraday constant ($96,487 \text{ C mol}^{-1}$), R universal gas constant ($8.314 \text{ J K}^{-1}\text{mol}^{-1}$), T Kelvin temperature. From the voltammogram of $[\text{Ni(L11)}_2]$ complex, the value of $|E_{pa} - E_{pa/2}|$ was determined to be 0.082 V. According to the above equation, the number of electron transferred was then calculated to be 1.163 when $\alpha$ was assumed as 0.5, which suggest the involvement of one electron per molecule.

6A.3.7. Thermal studies

Co(II), Ni(II) and Cu(II) complexes are taken as representatives of the series for thermal studies. Themograms of these complexes are shown in Figures 6A.10, 6A.11 and 6A.12 respectively.

Co(II) and Ni(II) complexes show weight losses of 15.40% (Calc 15.78%) and 15.59% (Calc 15.79 %) around 190-280 °C corresponding to the loss of three coordinated water molecules. The corresponding DTA peak at 200 °C in the spectrum signifies the endothermic process. In the second stage, decomposition corresponds to a mass loss of 67.11 % (67.54 % cal.) and 68.12 % (67.55 % cal.) respectively, in the range 250 to 700 °C shows the loss of the ligand. The plateau obtained after heating the complexes above 900 °C corresponds to the formation of stable metal oxides. The thermogram of $[\text{Cu(L11)(H_2O)}_3]$ complex exhibit several thermal events. Weight loss of 15.98 % (cal 15.57 %) in 160-230 °C corresponds to three coordinated water molecules. The corresponding DTA peak at 190 °C in the complex signifies the endothermic process. Further decomposition of 66.81 % (66.32 %) above 250 °C corresponds to the loss of the ligand. The plateau obtained after heating the complex above 700 °C corresponds to the formation of stable CuO.

6A.4. CONCLUSIONS

This chapter presents the synthesis of isatinyl-3-pyruvic acid hydrazone and its transition metal complexes and are well established from elemental analysis, molar conductivity, IR, NMR, electronic, mass spectral and thermal studies.
Spectral studies reveal that the ligand gets coordinated through nitrogen of the hydrazide fragment and lactum oxygen via deprotonation. The ligand behaves as dibasic tridentate donor (ONO) yielding six coordinated transition metal complexes with octahedral geometry around the central metal ion. The mode of coordination in complexes is presented in Figure 6A.13.

![Proposed structure for complexes](image)

\[
M = \text{Co(II), Ni(II), Cu(II), Zn(II)}
\]

**Figure 6A.13. Proposed structure for complexes**

**Note:** The newly synthesized ligand \(L11H_2\) along with its complexes has been screened for the antimicrobial studies. The details of the activity are discussed in Chapter 7C.
### Table 6A.1. Analytical, conductance and magnetic moment data for the ligand L11H₂ and its complexes

<table>
<thead>
<tr>
<th>Code</th>
<th>Empirical formula</th>
<th>Elemental analysis (%)</th>
<th>Conductance</th>
<th>Magnetic Moment</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>found</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>calculated</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L11H₂</td>
<td>L11H₂</td>
<td>57.17 (57.14)</td>
<td>3.89 (3.92)</td>
<td>18.18 (18.17)</td>
</tr>
<tr>
<td>C45</td>
<td>[Co(L11) (H₂O)₃]</td>
<td>38.63 (38.61)</td>
<td>3.85 (3.83)</td>
<td>12.27 (12.29)</td>
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<tr>
<td>C46</td>
<td>[Ni(L11) (H₂O)₃]</td>
<td>38.64 (38.64)</td>
<td>3.86 (3.83)</td>
<td>12.31 (12.29)</td>
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<td>C47</td>
<td>[Cu(L11) (H₂O)₃]</td>
<td>38.13 (38.10)</td>
<td>3.80 (3.78)</td>
<td>12.16 (12.12)</td>
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<td>C48</td>
<td>[Zn(L11) (H₂O)₃]</td>
<td>37.89 (37.90)</td>
<td>3.76 (3.76)</td>
<td>12.09 (12.05)</td>
</tr>
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</table>

*Ω⁻¹ cm² mol⁻¹, Dia = Diamagnetic, Values in parenthesis are calculated values.

### Table 6A.2. IR spectral data of the L11H₂ and its complexes (cm⁻¹)

<table>
<thead>
<tr>
<th>Compd</th>
<th>ν(NH)</th>
<th>ν(OH)</th>
<th>ν(C=O)</th>
<th>ν(C=N)</th>
<th>ν(OH) Water</th>
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</thead>
<tbody>
<tr>
<td>L11H₂</td>
<td>3242m</td>
<td>3393m</td>
<td>1722s</td>
<td>1740s</td>
<td>---</td>
</tr>
<tr>
<td>C45</td>
<td>---</td>
<td>---</td>
<td>1723s</td>
<td>---</td>
<td>1619s 3376b</td>
</tr>
<tr>
<td>C46</td>
<td>---</td>
<td>---</td>
<td>1720s</td>
<td>---</td>
<td>1615s 3423b</td>
</tr>
<tr>
<td>C47</td>
<td>---</td>
<td>---</td>
<td>1719s</td>
<td>---</td>
<td>1619s 3421b</td>
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<tr>
<td>C48</td>
<td>---</td>
<td>---</td>
<td>1718s</td>
<td>---</td>
<td>1614s 3394b</td>
</tr>
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</table>

*b = broad, m = medium, s = strong.*
Table 6A.3. NMR spectral data of L11H₂ and its Zn(II) complex (ppm)

<table>
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<tr>
<th>Position</th>
<th>L1H</th>
<th>Zn(II) complex</th>
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<tr>
<td></td>
<td>^H NMR</td>
<td>^13C NMR</td>
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<tr>
<td>O1</td>
<td>13.77 (s, 1H)</td>
<td>—</td>
</tr>
<tr>
<td>N3</td>
<td>11.04 (s, 1H)</td>
<td>—</td>
</tr>
<tr>
<td>C1</td>
<td>7.40</td>
<td>129.98</td>
</tr>
<tr>
<td>C2</td>
<td>6.89</td>
<td>122.96</td>
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<td>C3</td>
<td>7.08</td>
<td>132.09</td>
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<tr>
<td>C4</td>
<td>7.61</td>
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<td>C5</td>
<td>—</td>
<td>148.06</td>
</tr>
<tr>
<td>C6</td>
<td>—</td>
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</tr>
<tr>
<td>C7</td>
<td>—</td>
<td>137.04</td>
</tr>
<tr>
<td>C8</td>
<td>—</td>
<td>166.01</td>
</tr>
<tr>
<td>C9</td>
<td>2.17 (s, 3H)</td>
<td>164.93</td>
</tr>
<tr>
<td>C10</td>
<td>—</td>
<td>16.61</td>
</tr>
<tr>
<td>C11</td>
<td>—</td>
<td>169.23</td>
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Table 6A.4. Electronic spectral data of L11H₂ & its complexes (nm)

<table>
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<th>Code</th>
<th>Compound</th>
<th>Amax (nm)</th>
<th>Geometry assigned</th>
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<tr>
<td>L11H₂</td>
<td>L11H₂</td>
<td>267, 303 and 350</td>
<td>—</td>
</tr>
<tr>
<td>C45</td>
<td>[Co(L11)(H₂O)₃]</td>
<td>308, 367, 420, 550 and 830</td>
<td>octahedral</td>
</tr>
<tr>
<td>C46</td>
<td>[Ni(L11)(H₂O)₃]</td>
<td>307, 339, 430, 560 and 872</td>
<td>octahedral</td>
</tr>
<tr>
<td>C47</td>
<td>[Cu(L11)(H₂O)₃]</td>
<td>310, 360, 456 and 676</td>
<td>octahedral</td>
</tr>
<tr>
<td>C48</td>
<td>[Zn(L11)(H₂O)₃]</td>
<td>306, 367 and 396</td>
<td>octahedral</td>
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</tbody>
</table>
Isatinyl-3-pyruvic acid hydrazone

Figure 6A.1. $^1$H NMR spectrum of L11H$_2$

Figure 6A.2. $^{13}$C NMR spectrum of L11H$_2$

Figure 6A.3. $^1$H NMR spectrum of [Zn(L11) (H$_2$O)$_3$].
Figure 6A.4. Electronic spectra of (a) L1H2, (b) [Co(L11) (H2O)3] (c) [Ni(L11) (H2O)3] and (d) [Cu(L11) (H2O)3].

Figure 6A.5. EPR spectrum of [Cu(L11) (H2O)3]
Chapter 6 A

Isatinyl-3-pyruvic acid hydrazone

Figure 6A.6. Mass spectrum of [Ni(L11)(H2O)3]

Figure 6A.7. Mass spectrum of [Cu(L11)(H2O)3]

(a)  
(b)
**Figure 6A.8.** Cyclic voltammograms of $[\text{Cu(L1)}(\text{H}_2\text{O})_3]$ at the scan rate

(a) 50 mV s$^{-1}$ (b) 100 mV s$^{-1}$

**Figure 6A.9.** Cyclic voltammograms of $[\text{Ni(L1)}(\text{H}_2\text{O})_3]$ at the scan rate

(a) 50 mV s$^{-1}$ (b) 100 mV s$^{-1}$

**Figure 6A.10.** Thermogram of $[\text{Co(L1)}(\text{H}_2\text{O})_3]$
Figure 6A.11. Thermogram of [Ni(L11)(H2O)3]

Figure 6A.12. Thermogram of [Cu(L11)(H2O)3]
References

18. M. C. Rodríguez-Argüelles, S. Mosquera-Vázquez, P. Touro'n-Touceda, J. S.
Chapter 6 A

Isatinyl-3-pyruvic acid hydrazone


Chapter 6

Section B

Construction and spectro-analytical characterization of transition metal complexes of triazolo-pyruvic acid Schiff bases


**Chapter 6 B
Triazolo-pyruvic acid Schiff bases**

6B.1. INTRODUCTION

Hydrazone ligands containing 1, 2, 4-triazole nucleus have attracted great and growing interest in chemistry and biology for many years due to their facile synthesis and wide applications [1-3]. 1, 2, 4-Triazole derivatives have shown variety of interesting biological actions, including antibacterial, anticonvulsant, antimicrobial, anticancer, antitubercular and antifungal activities [4-7]. These diversified applications are at least in part a consequence of the numerous approaches that are available for the insertion of specific functionalities into the 1,2,4-triazole nucleus. The alterations in chemical structure of substituted 1, 2, 4-triazoles strongly change their activities and affect their interaction with cells, thereby leading to different biological effects [8].

3-Amino-1, 2, 4-triazole has been reported as being a carcinogenic reagent, but its ring has shown a well known anti-microbial effect. It has been proved that the incorporation of this molecule into the biologically active azomethine linkage (—CH=N—) produces compounds with high pharmacological activity [9].

An exhaustive survey of literature reveals that a lot of work has been done on the complexes of 1, 2, 4-triazoles with various metals [10, 11]. The chemistry of 1,2,4-triazoles has been reviewed by Kroger *et. al.* [12]. The tridentate Schiff bases with heterocyclic amine [6B.1] containing ONS sequence have been tried for complexation with transition metals such as Cu(II), Ni(II), Co(II), Zn(II) & Cd(II). The dimeric complexes of Cu(II) with sub normal magnetic moments are reported.

![Diagram](image)

**6B.1**

Pannu *et. al.* [13], have reported Mg(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), & Hg(II) complexes of 4n-buty1-4H-1,2,4-trizoles in which the ligand shows bidentate behaviour except in case of Cd(II), & Hg(II).
Garag et. al., [14], have reported the complexes of Co(II), Ni(II) & Cu(II) with a 4-amine-3-hydrazino-1,2,4-triazole hydrochloride [6B.2] and have assigned the high spin distorted octahedral geometry.

![Triazolo-pyruvic acid Schiff bases](image)

**6B.2.** M=Co(II), Ni(II), & Cu(II).

Mishra et. al., [15], have reported the Co(II), Ni(II), Cu(II) & Zn(II) complexes with 3-amino-5-(a/b) pyridyl-1,2,4-triazoles. Literature also records the complexes of same bivalent metal ions with 4-salicylaldiammino-3-mercapto-5-phenyl-1,2,4-triazole.

Cr(III), Fe(III) and Ru(III) complexes of 3-methyl-4-benzylidineimino-5-mercapto-1,2,4-triazole are reported in the literature. These trivalent metal ion complexes have been characterised by magnetic and spectral studies and were assigned the low spine octahedral geometries.

Kaushik et. al., [16] and Satpathy et. al., [17], has used triazoles as ligands for complexation of bivalent metal ions. The ligands as well as the complexes were tested for their toxicity against two fungi, Fusarium oxysporium and helminthosporium oryzae by horsfall method. The Co(II) exhibited more fungal-toxicity.

Electrochemical properties of ruthenium(III) complexes with triazole derivatives have been studied by Fennena et. al.,[18]. Literature also records the X-ray studies of zinc(II) chloride complexes with 4-ammino-3,5-dimethyl-1,2,4-triazole.

Ginzburg et. al., [19], have synthesised the Cu(II) complexes of 3-ammino-5-carboxy-1,2,4-triazole and they have been characterized by ESR spectra. Varma et. al., [20], have reported the Cu(II) complexes of 4-ammino-3-hydrazino-5-mercapto-1,2,4-triazole. Revankar and Mahale [21], have studied the Co(II), Ni(II) & Cu(II)
Chapter 6B  

Triazolo-pyruvic acid Schiff bases

complexes with 3-methylsulphhydryl-4-ammino-5-mercapto-1,2,4-triazole and have assigned octahedral configuration on the basis of magnetic and spectral data they have also been evaluated for their antibacterial and antifungal activities.

Recently Mustafa Kamil Said et. al., [22], have reported iron(III) complexes with 4-ammino-3-mercaptop-5-phenyl 1,2,4-triazole and have assigned high spin octahedral type configuration. The complexes have also been evaluated for their antibacterial, antifungal and antitumor activities. Antitumor activity of iron(III) complex was tested with P388 lymphocytic leukaemia test system in the mice. P388 cells were maintained in RPMI-1640 medium supplemented with 5% fetal calf serum and kanamycin (100 mg/ml).

Sinha and co-workers [23] have reported the Co(II), Ni(II) and Cu(II) complexes with 4-ammino-3,5-dimercapto 5-phenyl-1,2,4-triazole and have assigned octahedral geometry for Co(II), Ni(II) & Cu(II) complexes on the basis of magnetic and spectral data.

3-Substituted-4-amino-5-mercapto-1,2,4-triazoles were synthesised and characterised by Hosur et. al.,[24]. They studied the antibacterial, antifungal, antiinflammation and anticonvulsant activities. Results showed that the compounds were much potent towards herbicidal activities.

A series of new Schiff base hydrazones were synthesized by condensation reaction of 4-amino-3-(4-pyridine)-5-mercapto-1,2,4-triazole with various aldehydes and/or dialdehydes [6B.3] by H. Khanmohammadi et. al. [25]. The structure of the prepared compounds was confirmed by means of ¹H NMR, ¹³C NMR, UV–Vis, IR and elemental analyses. All the prepared compounds were assayed for antibacterial (Escherichia coli and Staphylococcus aureus) and antifungal (Candida albicans) activities by disc diffusion method. The results indicate that the compounds containing 4-Cl, 4-Me, 4-MeO, 2, 4-di-Cl and 2-OH substituted phenyl moiety, respectively, showed good inhibition against S. aureus as compare to standard drugs. The structures the compounds have also been theoretically studied by ab initio Hartree–Fock (HF) methods.
A series of metal complexes of Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized with newly biologically active ligands prepared by the condensation of 4-amino-5-mercapto-3-methyl-S-triazole, 4-amino-3-ethyl-5-mercapto-S-triazole with 2-acetylpyridine. The structures of the complexes have been proposed by elemental analysis, spectroscopic data and magnetic measurements. The authors discussed the analytical application of the prepared compounds for spectrophotometric micro determination of Co(II). Some radiochemical studies were also presented by Issa et al. [26].

Starting from these premises this section presents the synthesis and characterization of transition metal complexes Co(II), Ni(II), Cu(II) and Zn(II) of two new Schiff bases obtained by condensing 4-Amino-3-methyl-1,2,4-triazole-5-thione and 4-Amino-3-ethyl-1,2,4-triazole-5-thione with pyruvic acid. The transition metal(II) complexes of these two hydrazones were prepared with a view towards evaluating their antimicrobial activities.

6B.2. EXPERIMENTAL

6B.2.1. Synthesis of 4-amino-3-methyl-1,2,4-triazole-5-thione (AMTT) and 4-amino-3-ethyl-1,2,4-triazole-5-thione (AETT)

4-Amino-3-methyl-1,2,4-triazole-5-thione and 4-amino-3-ethyl-1,2,4-triazole-5-thione were prepared as per the reported method [27]. A mixture of 10 g of thiocarbohydrazide in 30 mL glacial acetic acid for (AMTT)/propanoic acid for (AETT) was heated under reflux for 4 h. The resulting clear solution was allowed to
stand overnight in a capped round bottom flask. During this time the product crystallized as a coarse off-white crust on the sides of the flask. The solid was collected by suction filtration, washed thoroughly with distilled water to remove residual acid and air dried (M.P.: 138-140 °C and 149-152 °C respectively, Yield 80%).

6B.2.2. General procedure for the preparation of ligands L12H and L13H.

**L12H:** 2-(3-methyl-5-thioxo-1H-1,2,4-triazol-4(5H)-ylimino)propanoic acid  
**L13H:** 2-(3-ethyl-5-thioxo-1H-1,2,4-triazol-4(5H)-ylimino)propanoic acid

Hot solution of triazole (0.01 M, 1.30 g (AMTT) and 1.44 g (AETT)) in 25 mL of methanol was treated with the methanolic solution of pyruvic acid (0.012 M, 1.562 g). The mixture was stirred and refluxed for 6-7 h on a steam bath in presence of catalytic amount of conc. HCl (1 mL). The solid product separated was filtered, washed with methanol and dried over anhydrous CaCl₂. The reaction pathway is represented in Scheme 6B.1.

![Scheme 6B.1. Schematic representation of preparation of ligands.](image)

6B.2.3. General procedure for the preparation of complexes

Metal(II) chloride \{CoCl₂·6H₂O (0.237 g, 0.01 M), NiCl₂·6H₂O (0.237 g, 0.01 M), CuCl₂·2H₂O (0.170 g, 0.01 M) and ZnCl₂ (0.136 g, 0.01 M)\} in methanol was added with stirring to 25 mL of methanolic solution (0.01 M) of the ligand \{**L12H**, 0.20 g and **L13H**, 0.214 g\}. The mixture was then refluxed for 2 h on water bath and thus obtained complexes were filtered, washed repeatedly with hot methanol and dried over anhydrous CaCl₂.
6B.3. RESULTS AND DISCUSSION

The compounds obtained in the present study were amorphous and non-hygroscopic. The metal complexes were easily soluble in DMSO and DMF, sparingly soluble in ethanol and methanol, whereas insoluble in chlorinated hydrocarbons. The composition and coordination geometry of these complexes have been established based on elemental analyses, IR, NMR, mass spectral analyses. All the experimental results were in well agreement with the molecular formulae suggested for the compounds. The elemental analysis data of the ligands and their complexes along with molar conductivity and magnetic moment values are compiled in Table 6B.1.

6B.3.1. Molar conductivity measurements

The molar conductance values of the complexes measured at room temperature in DMSO solution with 10⁻³ mol dm⁻³ concentration are in the range 13.3 to 16.8 ohm⁻¹cm²mol⁻¹, (Table 6B.1.) indicating non-electrolytic nature for the complexes [28].

6B.3.2. Infrared spectral studies

The IR spectra of the free ligands show a band of medium intensity around 3236-3256 cm⁻¹ which is assigned to ν(N-H). The absence of any band in the region 2400-2600 cm⁻¹, due to ν(SH) in L12H and L13H confirms that the ligands exist in the thioketo form. The sharp band around 1640 and 1637 cm⁻¹ assigned to ν(C=N) in the free ligands, and have shifted to lower frequency region in the spectra of the complexes, suggesting coordination of azomethine nitrogen to the metal. The broad ν(O-H) band at ~3436 cm⁻¹ in the free ligands is absent in the spectra of all the complexes, suggesting the ceprotonation of the phenolic oxygen on coordination. The vibrational couplings amor.g thioamide group are distributed in the region around 1550, 1450, 1320 and 975 cm⁻¹. In all the complexes, the signal due to ν(N-H) are retained and thioamide bands which have major contribution of ν(C=S) have undergone considerable reduction in intensity. This supports the thio-keto mode [29] of coordination of sulphur to metal ions. The low frequency bands in the 500-465 cm⁻¹
1 and 440-410 cm\(^{-1}\) region are tentatively assigned to \(\nu(M-N)\) and \(\nu(M-S)\) respectively. All the complexes exhibit broad peak in the region \(\sim3400\) cm\(^{-1}\) suggesting the presence of coordinated water molecules. The IR spectral data is presented in Table 6B.2.

6B.3.3. NMR Spectral studies

The proton NMR data for the ligands and their zinc complexes were recorded in DMSO \(d_6\). The spectral data of both the ligands and their zinc complexes are in good agreement with the proposed structures. In the spectrum of \(L_{12}H\), signals around 13.32 ppm and 12.98 ppm were assigned to -OH and -NH of carboxylic and triazole substitutions respectively. In the \([Zn(L12)Cl.\text{H}_2\text{O}]\) complex, disappearance of signal at 13.32 ppm indicates chelation of the ligand accompanied with deprotonation of carboxylic -OH. The retaining of signal corresponding to -NH (\(D_2O\) exchangeable) in the spectrum suggest that the complexation is via thio-keto sulphur. Resonance peak due to methyl group attached to the pyruvic acid, appeared at 2.16 ppm in ligand, remained unaltered in the its zinc complex. Methyl groups attached to the triazole ring appeared as singlet at 3.6 ppm.

The singlets at 13.37 and 13.10 ppm in \(^1\text{H}\) NMR spectrum of \(L_{13}H\) are assigned to -OH and -NH of carboxylic and triazole substitutions. The disappearance of the signal at 13.37 ppm in the corresponding zinc complex, indicates the coordination of the carboxylic -OH via deprotonation. In the \([Zn(L13)\text{Cl.H}_2\text{O}]\) spectrum the singlet at 12.59 ppm is attributed to triazole ring -NH. Presence of this signal indicates the coordination of sulphur in the thioketo form. The methyl group attached to the pyruvic acid moiety resonates at 2.17 ppm, whereas the methylene and methyl protons attached to the triazole ring have appeared as triplet and quartet at 2.55 and 1.26 ppm respectively. It is observed that relative to the free ligands, the zinc complexes show small shift in proton resonance frequencies, which is attributable to variation in electron density and steric constraints brought about in the compounds upon complexation. The representative spectra are provided as Figures 6B.1-4.
6B.3.4. Electronic spectral studies

The electronic spectra of the synthesized ligands in DMF showed two absorption bands, the band at 341 nm represent the \( \pi \rightarrow \pi^* \) transition, while the second one at 360 nm corresponds to the \( n \rightarrow \pi^* \).

All the complexes exhibit electronic transitions around 260-315 nm, assigned to the intra ligand \( n \rightarrow \pi^* \) transitions. A broad band at \( \sim 370 \) nm with a shoulder on low energy side is observed due to \( n \rightarrow \pi^* \) transition associated with azomethine linkage [30]. The peak observed near 400 nm in all the complexes is assigned to \( S \rightarrow M \) (LMCT). Electronic spectra of cobalt complexes show two bands around 450 and 680 nm assignable to \( ^4T_{1g} \rightarrow \rightarrow ^4T_{1g}(P) \) and \( ^4T_{1g} \rightarrow \rightarrow ^4A_{2g} \) transitions as expected for an octahedral Co(II) complex [31]. In Ni(II) complexes the lowest energy band observed around \( \sim 870 \) nm was due to \( ^3A_{2g} \rightarrow \rightarrow ^3T_{2g} \) (\( v_1 \)) and bands at 660-685 and 470-510 nm were assigned to \( ^3A_{2g} \rightarrow \rightarrow ^3T_{1g}(P)(v_3) \) respectively. Appearance of these three spin allowed c-d transitions indicates the octahedral geometry around Ni(II) ion [31, 32]. The Cr(II) complexes exhibit broad absorptions centred at 650-720 nm with low \( \epsilon \) values due to \( ^2A_{1g} \rightarrow ^2E^* \) indicates trigonal bipyramidal geometry around it. Zn(II) complexes did not show any d-d bands. The numerical data are represented in Table 6B.4 and representative electronic spectra are given in spectral/image section as Figures 6B.5-6B.9.

6B.3.5. Magnetochemistry

The experimentally determined room temperature magnetic moments of all the complexes are given in the Table 6B.1. Both the copper complexes exhibit the effective magnetic moments (\( \mu_{\text{eff}} \)) at 1.91 and 1.92 B.M. respectively, at 303 K [33], suggestive of trigonal bipyramidal geometry. The magnetic moment values of Ni(II) complexes in the present investigation fall in the range 2.91 to 3.01 and indicate an octahedral geometry around Ni(II) ion for all the three complexes [33]. The cobalt complexes exhibit paramagnetic susceptibility, with corresponding magnetic moment values lying around 4.29 to 4.33 BM, signifying the octahedral geometry [33].
6B.3.6. EPR spectral studies

The solid state X-band EPR spectra of copper complexes \([\text{Cu}(L12)\text{Cl}.\text{H}_2\text{O}]\) and \([\text{Cu}(L13)\text{Cl}.\text{H}_2\text{O}]\) are shown in Figures 6B.10 and 6B.11 respectively. The EPR spectra of \([\text{Cu}(L12)\text{Cl}.\text{H}_2\text{O}]\) both at 300 and 77K exhibit a broad absorption band. This is isotropic due to the tumbling motion of the molecules. The \(g_{iso}\) values at 300 and 77K 2.01 and 2.02 respectively. Similarly the \([\text{Cu}(L13)\text{Cl}.\text{H}_2\text{O}]\) shows a broad signal with a \(g_{iso}\) value at 2.012 indicating its isotropic nature [34].

6B.3.7. Mass spectral analysis

FAB mass spectra of \([\text{Ni}(L12)\text{Cl}.(\text{H}_2\text{O})_2]\) and \([\text{Co}(L13)\text{Cl}.(\text{H}_2\text{O})_2]\) show molecular ion peaks at 472 and 479 respectively which corresponds to the molecular weight of the respective complexes, representing the monomeric structures for the complexes (with ligand to metal ratio 1:1). Thus FAB mass confirms the proposed composition of the complexes. The FAB mass spectra are given in Figures 6B.12 and 6B.13 respectively.

6B.3.8. Thermal studies

The thermal stability and decomposition pattern of the complexes was analyzed by TG and DTA studies. Thermo gravimetric analysis of the complexes was carried out in nitrogen atmosphere in the range 25 to 1000 °C with heating rate of 10 °C/min.

It is observed that decomposition of \([\text{Ni}(L12)\text{Cl}.(\text{H}_2\text{O})_2]\) (Figure 6B.14) takes place in three stages. The first step of decomposition corresponds to a mass loss of 10.39 % (10.45 %) in the range 90-150 °C and is attributed to the loss of two coordinated water molecules. The corresponding differential peak (DTA) signifies an endothermic process. Second stage of mass loss of 10.30 % (10.16 %) in the range 150-280 °C with respective DTA curve representing the exothermic process corresponds to the liberation of one chloride as HCl. Further reduction of mass in a higher temperature range is ascribed to the ligand decomposition and the final product corresponds to the metal oxide. The cobalt complex \([\text{Co}(L12)\text{Cl}.(\text{H}_2\text{O})_2]\) (Figure
6B.15) also exhibit three step decomposition pattern with 10.29 % (10.44 %) weight loss around 100-140 °C and 10.26 % (10.15 %) weight loss at around 190-280 °C corresponding to the liberation of two water molecules and chloride respectively. A further weight loss 58.00 % (58.02 %) corresponds to the ligand decomposition. The DTA curve indicates the endothermic and exothermic nature of the two processes. The plateau region at higher temperature range indicates the stable metal oxide formation.

Thermograms of the [Zn(L13)Cl(H2O)] and [Co(L13)Cl(H2O)2] (Figure 6B.16) complexes showed weight losses of 4.69 % (4.97 %) and 10.23 % (10.03 %) respectively in the region 140-180 °C indicating the loss of one and two coordinated water molecules respectively. Further weight losses of 68.15 % (68.75 %) and 68.99 % (69.41 %) in the region 190-500 °C are attributed to the combined loss of chlorine and the ligand. The plateau obtained after heating the complexes above 700 °C correspond to the formation of stable metal oxide.

The thermograms of [Cu(L13)Cl.H2O] complex (Figure 6B.17) exhibit several thermal events. The first weight loss of 5.17 % (calcd 4.99 %) in the temperature range of 90-150 °C correspond to the loss of two coordinated water molecules as designated by the endothermic DTA signal at 125 °C and second weight loss of 9.60 % (calcd 9.71%) corresponding to the loss of one coordinated chlorine with an exothermic DTA signal at 230 °C. Decomposition above 250 °C corresponds to the loss of ligand. The plateau obtained after heating the complex above 700 °C corresponds to the formation of stable CuO.

6B.4. CONCLUSION

This section presents the synthesis of L12H and L13H, which were achieved by the condensation 1:1 equivalent of 4 amino-triazoles with pyruvic acid. The preparation of Co(II), Ni(II), Cu(II) and Zn(II) complexes is also considered in the present study. The analitical and physico-chemical studies confirmed the compositions and structures for the complexes. Octahedral geometry was assigned to
Co(II) and Ni(II) complexes of both the ligands while trigonal bipyramidal geometry was assigned to Cu(II) and Zn(II) complexes.

In conclusion the ligand essentially coordinates through thion sulfur of triazole fragment, azomethine nitrogen and carboxylic oxygen of pyruvic acid via deprotonation and act as a monobasic tridentate ligands. The mode of coordination in complexes is presented in Figure 6B.18.

![Figure 6B.18](image)

R= CH₃, C₂H₅, M = Co(II), Ni(II)  
R= CH₃, C₂H₅, M = Cu(II), Zn(II)

Figure 6B.18. Tentatively proposed structures for the complexes.

Note: The newly synthesized ligands L12H and L13H along with their complexes have been screened for the antimicrobial studies. The details of the activity are discussed in Chapter 7C.
Table 6B.1. Analytical, conductance and magnetic moment data for the ligands and their complexes.

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<th>Code</th>
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<th>Het. BM.</th>
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<td>C</td>
<td>H</td>
<td>N</td>
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<td>(4.03)</td>
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<td>(4.10)</td>
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<td>(29.92)</td>
<td>(4.69)</td>
<td>(15.45)</td>
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</table>

° \( \Omega \cdot \text{cm}^2 \text{ mol}^{-1} \), Dia. Diamagnetic. Values in parenthesis are calculated values.
Table 6B.2. IR spectral data of the ligands and their complexes (cm$^{-1}$).

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<td>[Zn(L13)Cl H$_2$O]</td>
<td>---</td>
<td>n.o</td>
<td>1715</td>
<td>1615</td>
<td>1271s</td>
<td>841w</td>
</tr>
</tbody>
</table>

b Broad, s Sharp, w weak, n.o Not observed
### Table 6B.3. NMR spectral data of the ligands and Zn(II) their complexes (ppm).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical shift values in ppm</th>
<th>Triazole ring</th>
<th>Carboxylic</th>
<th>Methyl</th>
<th>Methylene</th>
<th>Methyl CH₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(L12)Cl₂H₂O]</td>
<td>12.99</td>
<td>2.14</td>
<td>2.55</td>
<td>1.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L12H</td>
<td>13.37</td>
<td>13.10</td>
<td>2.16</td>
<td>2.55</td>
<td>1.26</td>
<td></td>
</tr>
<tr>
<td>[Zn(L13)Cl₂H₂O]</td>
<td>13.02</td>
<td>13.22</td>
<td>2.16</td>
<td>2.55</td>
<td>1.29</td>
<td></td>
</tr>
</tbody>
</table>

### Table 6B.4. Electronic spectral data of the ligands and their complexes (nm)

<table>
<thead>
<tr>
<th>Code</th>
<th>Compound</th>
<th>λₘₐₓ</th>
<th>Geometry assigned</th>
</tr>
</thead>
<tbody>
<tr>
<td>L12H &amp; L13H</td>
<td>L:ligands</td>
<td>270, 316 and 383</td>
<td>---</td>
</tr>
<tr>
<td>C49 &amp; C53</td>
<td>Co Complexes</td>
<td>387, 410, 720 and 876</td>
<td>octahedral</td>
</tr>
<tr>
<td>C50 &amp; C54</td>
<td>Ni Complexes</td>
<td>300, 380, 430, 675 and 921</td>
<td>octahedral</td>
</tr>
<tr>
<td>C51 &amp; C55</td>
<td>Cu Complexes</td>
<td>267, 327, 433 and 676</td>
<td>octahedral</td>
</tr>
<tr>
<td>C52 &amp; C56</td>
<td>Zn Complexes</td>
<td>276, 327, 370 and 410</td>
<td>octahedral</td>
</tr>
</tbody>
</table>
Figure 6B.1. $^1$H NMR spectrum of L12H

Figure 6B.2. $^1$H NMR spectrum of [Zn(L12)ClH$_2$O]
Figure 6B.3. $^1$H NMR spectrum of L13H

Figure 6B.4. $^1$H NMR spectrum of [Zn(L13)Cl2H2O]

Figure 6B.5. Electronic spectrum of L12H.
Figure 6B.6. Electronic spectrum of \([\text{Co(L12)Cl(H}_2\text{O)}_2]\).

Figure 6B.7. Electronic spectrum of \([\text{Ni(L13)Cl(H}_2\text{O)}_2]\).

Figure 6B.8. Electronic spectrum of \([\text{Cu(L13)ClH}_2\text{O}]\)
Figure 6B.9. Electronic spectrum of [Cu(L13)Cl2H2O]
Chapter 6 B  
Triazolo-pyruvic acid Schiff bases

Figure 6B.12. FAB mass spectrum of [Ni(L12)Cl(H2O)2]²⁺

Figure 6B.13. FAB mass spectrum of [Co(L13)Cl(H2O)2]²⁺

Figure 6B.14. Thermogram of [Ni(L12)Cl(H2O)2]
Figure 6B.15. Thermogram of [Co(L13)Cl(H2O)]

Figure 6B.16. Thermogram of [Co(L13)Cl(H2O)]

Figure 6B.17. Thermogram of [Cu(L13)ClH2O]
References


