Syntheses of zinc(II) complexes and studies on their spectral characteristics

7.1. Introduction

Zinc is a low-melting metal of Group IIb (zinc group) of the periodic table, essential to life, and one of the most widely used metals. Zinc was known in Roman times only in combination with copper as the alloy brass. The metallurgists of India seem to have isolated the individual metal as early as the 13th century.

Zinc is an essential trace element in the human body, where it is found in high concentration in the red blood cells as an essential part of the enzyme carbonic anhydrase, which promotes many reactions relating to carbon dioxide metabolism. The zinc present in the pancreas may aid in the storage of insulin. Zinc is a component of some enzymes that digest protein in the gastrointestinal tract. The major uses of zinc metal are in galvanizing iron and steel and in making brasses and alloys for die-casting.

Highly pure zinc (99.99 percent) is ductile; the so-called prime western grade (99.8 percent pure) is brittle when cold but above 100 °C (212 °F) can be rolled into sheets that remain flexible. Zinc crystallizes in the hexagonal close-packed structure. When iron and zinc together are exposed to a corrosive medium, they constitute an electrolytic cell, and the zinc is attacked (oxidized to the Zn^{2+} ion) preferentially because of its higher electrode potential. This so-called sacrificial protection, coupled with the much greater corrosion resistance of zinc under atmospheric conditions, is the basis for galvanizing.

Natural zinc is a mixture of five stable isotopes: ^{64}\text{Zn} (48.6 percent), ^{66}\text{Zn} (27.9 percent), ^{67}\text{Zn} (4.1 percent), ^{68}\text{Zn} (18.8 percent), and ^{70}\text{Zn} (0.6 percent) [1].

Zinc is an essential element, necessary for sustaining all life. In the human body, generally, 2-3 g of zinc is present and about 15 mg per day is necessary for
the maintenance of healthy condition. It is estimated that about 3000 proteins in the human body contain zinc. It stimulates the activity of approximately 100 enzymes, which are substances that promote biochemical reactions in the body [2]. In addition, there are over a dozen types of cells in the human body that secrete zinc ions. Brain cells in the mammalian forebrain, cells in the salivary gland, prostate, immune system and intestine are the main types that secrete zinc. Zinc supports a healthy human immune system [3], is needed for wound healing [4], helps maintain the sense of taste and smell [5] and is needed for DNA synthesis. Zinc also supports normal growth and development during pregnancy, childhood and adolescence [6].

Functions of zinc in living systems may be summarized as follows: 1) formation, growth and metabolism of cells; 2) healing of wounds; 3) activation and secretion of hormones; 4) maintenance of neurotransmission system, ability of memory, normal carbohydrate and lipid metabolism, stability of retina and crystalline lens, sensitivity in taste and smell; 5) stabilization of cellular membranes; 6) maintenance and activation of immune system; 7) maintenance of normal alcohol metabolism; 8) reduction of hazardous effect of heavy metals. In these functions, zinc plays an essential role as zinc-containing enzymes in many cases or complexes formed with some components in biological systems.

Advantageous features of zinc in the above-mentioned functions and its applications for medical use are well explained by the following basic physicochemical aspects of zinc ion and its complexes. 1) Zinc ion has a small radius and acts as a Lewis acid and hence it can play an advantageous role as a catalyst in hydrolysis reactions. 2) The stability of zinc complexes with some ligands present in living system is satisfactorily high but not too high, so that zinc is reactive in complexation. This means high probability of ligand-exchange reactions in zinc complexes in living systems. Irving-Williams stability order applicable to various divalent metal complexes with common ligands shows that the stability of zinc complexes is generally lower than that of copper and is comparable to that of nickel and much higher than that of calcium or magnesium. 3) The bivalent state is stable because of the fully occupied 3d orbital, and it is
maintained even in highly oxidizing and reducing environments. 4) Fairly high affinity is shown towards the main coordinating atoms such as sulfur, nitrogen, and oxygen. This means high flexibility in the structure, coordination mode, and coordination number of the complexes produced [7].

The electron configuration \[ \text{[Ar]} \ 3d^{10} \ 4s^2 \] provides a filled \((n-1)d\) state for zinc. In view of the stability of the filled \(d\) sublevel, the element shows few of the characteristics of transition metals despite its position in the \(d\)-block of the periodic table. It resembles other transition metals in the formation of stable complexes with \(O\), \(N\) and \(S\)-donor ligands and with ions like cyanide, halide etc. The \(d^{10}\) configuration affords no crystal field stabilization, which implies that the stereochemistry of a \(\text{Zn}^{2+}\) complex depends on the size and polarizing power of this ion. Because of this versatility towards different kinds of ligands and its flexibility towards coordination number ranging from two to six, the zinc(II) ion provides various types of chelate complexes. Among these complexes, some have attracted special attention as model compounds for the active sites of zinc-containing enzymes [8] and their functions strongly depend upon the coordination environment around the zinc ion. Therefore, for understanding or creating functional zinc complexes, it is important to consider the relationship of the coordination characteristics peculiar to the zinc ion. Heterocyclic carbaldehyde thiosemicarbazones have been extensively investigated for activity against various bacterial and viral infections [9,10]. Biological activity of thiosemicarbazones and semicarbazones are found to increase on complexation with transition metals [11], higher activity being incorporated with substitution at \(N(4)\) position [12]. These observations were the impetus for us to build an \(N(4)\)-substituted semicarbazone moiety on 2-hydroxyacetophenone and on benzaldehyde and synthesize zinc(II) complexes to study the coordinating behavior. In this chapter we describe the spectral studies of eight new \(\text{Zn}^{2+}\) complexes of the ligands \(\text{H}_2\text{L}^1\) and \(\text{H}_2\text{L}^2\).

Tetrahedral as well as octahedral \(\text{Zn}^{2+}\) complexes of thiosemicarbazide and thiosemicarbazone, in which the ligands are known to be bidentate, have been reported [9]. On the other hand, ligands such as ethyl-acetoacetate semicarbazone
and thiosemicarbazone are found to be tridentate in their Zn complexes [13] in which the third coordinating center is provided by the carbonyl group.

The divalent Zn(II) ion has 10 d electrons and the structures of Zn(II) complexes are influenced significantly by the reaction conditions such as the solvent, pH, the stoichiometry and reaction temperature.

7.2. Experimental
7.2.1. Materials

Zinc(II) acetate dihydrate and zinc(II) bromide (Merck) were used as supplied. The solvents were purified by standard procedures before use.

7.2.2. Syntheses of ligands

Syntheses of the ligands H$_2$L$^1$ and H$_2$L$^2$ have been described earlier in Chapter 2.

7.2.3. Syntheses of complexes
7.2.3.1. Synthesis of the complex [Zn$_2$L$^1_2$]·CH$_3$OH (36)

A hot methanolic solution (15 ml) of zinc acetate dihydrate (0.219 g, 1 mmol) and the ligand H$_2$L$^1$ (0.269 g, 1 mmol) were mixed with constant stirring. The mixture was heated under reflux for two hours and cooled. The complex separated was filtered, washed thoroughly with water, methanol and then ether and dried in vacuo over P$_4$O$_{10}$.

7.2.3.2. Synthesis of the complex [ZnL$^1$py]·2H$_2$O (37)

A hot methanolic solution (15 ml) of 0.269 g (1 mmol) the ligand, H$_2$L$^1$ and a methanolic solution of pyridine 0.079 g (1 mmol) were mixed with constant stirring. A hot methanolic solution (10 ml) of 0.219 g (1 mmol) zinc acetate dihydrate was added to it with constant stirring. The mixture was heated under reflux for two hours. On cooling the complex was separated out. It was filtered, washed thoroughly with water, methanol and then ether and dried in vacuo over P$_4$O$_{10}$.

7.2.3.3. Synthesis of complex [ZnL$^2$py]·H$_2$O (38)

A hot methanolic solution (15 ml) of the ligand H$_2$L$^2$ (0.255 g, 1 mmol) and a methanolic solution of the heterocyclic base, pyridine (0.0791 g, 1 mmol), were
mixed with constant stirring. A hot methanolic solution of 0.219 g (1 mmol) of zinc acetate dihydrate was added to the above mixture with constant stirring. The mixture was heated under reflux for two hours and cooled. The complex separated was filtered, washed thoroughly with water, methanol and then ether and dried in vacuo over P₄O₁₀.

7.2.3.4. Synthesis of the complex [ZnL²phen]·2H₂O (39)

This compound was prepared by refluxing a mixture of hot methanolic solutions of the ligand H₂L² (0.255 g, 1 mmol), 1,10-phenanthroline (0.196 g, 1 mmol) and zinc acetate dihydrate (0.219 g, 1 mmol) for two hours and cooled. The complex separated was filtered, washed thoroughly with water, methanol and then ether and dried in vacuo over P₄O₁₀.

7.2.3.5. Synthesis of the complex [ZnL²bipy]·2H₂O (40)

This compound was prepared by a similar method mentioned above by using bipyridine (0.196 g, 1 mmol) instead of 1,10-phenanthroline.

7.2.3.6. Synthesis of complex [ZnL²(py)]·2H₂O (41)

Hot methanolic solutions of H₂L² (0.255 g, 1 mmol) (30 ml) and 0.158 g pyridine (2 mmol) were mixed with constant stirring. A hot methanolic solution (20 ml) of (0.219 g, 1 mmol) zinc acetate dihydrate was added to it with constant stirring. The mixture was heated under reflux for two hours. On cooling the complex was separated out. It was filtered, washed thoroughly with water, methanol and then ether and dried in vacuo over P₄O₁₀.

7.2.3.7. Synthesis of complex [Zn(HL²)Br] (42)

Hot methanolic solutions (30 ml) of anhydrous zinc bromide (0.450 g, 2 mmol) and the ligand H₂L² (0.510 g, 1 mmol) were mixed with constant stirring. The mixture was heated under reflux for two hours and cooled. The complex separated was filtered, washed thoroughly with water, methanol and then ether and dried in vacuo over P₄O₁₀.
7.2.3.8. Synthesis of complex [Zn(HL$_2$)$_2$] (43)

A hot methanolic solution (30 ml) of zinc acetate dihydrate (0.438 g, 2 mmol) and a hot methanolic solution of the ligand H$_2$L$_2$ (1.020 g, 4 mmol) were mixed with constant stirring. The mixture was heated under reflux for two hours and cooled. The complex separated was filtered, washed thoroughly with water, methanol and then ether and dried \textit{in vacuo} over P$_4$O$_10$.

7.3. Physical measurements

Elemental analyses were carried out using an Elementar Vario EL III CHNS analyzer at SAIF, Kochi, India. Infrared spectra were recorded on a Thermo Nicolet AVATAR 370 DTGS model FT-IR spectrophotometer with KBr pellets at SAIF, Kochi, India. The far IR spectra were recorded using polyethylene pellets in the 500-100 cm$^{-1}$ region on a Nicolet Magna 550 FTIR instrument at Sophisticated Analytical Instruments Facility, Indian Institute of Technology, Bombay. Electronic spectra were recorded on a Cary 5000, version 1.09 UV-Vis-NIR spectrophotometer from a solution in DMF. Molar conductance measurements of the solutions of complexes in DMF. (10$^{-3}$ M) at room temperature were done using a digital conductivity meter at the Department of Applied Chemistry, CUSAT, Kochi.

7.4. Results and discussion

The colors, molar conductivities and partial elemental analyses data of the complexes are listed in Table 7.1. Zn complexes were found to form readily in methanol medium under reflux. From the elemental analysis, the compounds 37, 38, 39 and 40 were assigned the general formulae [ZnIX] (X=py, bipy, phen) while the compounds 36, 41, 42 and 43 were assigned the formulae [Zn$_2$L$_1$]·CH$_3$OH, [ZnL$_2$(py)$_2$]·2H$_2$O, [Zn(HL)$_2$Br] and [Zn(HL)$_2$] respectively. They are, however soluble in DMF, in which molar conductivity measurements were made, showing all of them are non-electrolytes [14]. The complexes 42 and 43 have ligands in the keto form, whereas in 36, 37, 38, 39, 40 and 41 have ligands coordinated in the enolate form as evidenced by the IR spectra. The complexes are found to be diamagnetic as expected for a $d^{10}$ Zn(II) system.
Table 7.1. Stoichiometries, partial elemental analyses, colors and molar conductivities of the complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Stoichiometries</th>
<th>Anal: Found (Calcd)%</th>
<th>Color</th>
<th>$^\lambda_M$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>N</td>
</tr>
<tr>
<td>[Zn$<em>2$L$</em>{1.5}$]·CH$_3$OH (36)</td>
<td>C$<em>{31}$H$</em>{32}$N$_6$O$_2$Zn$_2$</td>
<td>53.79 (53.23)</td>
<td>4.59 (4.61)</td>
<td>11.46 (12.02)</td>
</tr>
<tr>
<td>[ZnL$_1$py]·2H$_2$O (37)</td>
<td>C$<em>{26}$H$</em>{26}$N$_4$O$_2$Zn</td>
<td>53.84 (53.40)</td>
<td>4.73 (5.38)</td>
<td>12.45 (12.45)</td>
</tr>
<tr>
<td>[ZnL$_2$py]·H$_2$O (38)</td>
<td>C$<em>{16}$H$</em>{18}$N$_4$O$_2$Zn</td>
<td>55.04 (54.62)</td>
<td>4.59 (4.83)</td>
<td>14.02 (13.41)</td>
</tr>
<tr>
<td>[ZnL$_2$phen]·2H$_2$O (39)</td>
<td>C$<em>{26}$H$</em>{23}$N$_3$O$_2$Zn</td>
<td>57.91 (58.16)</td>
<td>4.16 (4.33)</td>
<td>13.91 (13.09)</td>
</tr>
<tr>
<td>[ZnL$_2$bipy]·2H$_2$O (40)</td>
<td>C$<em>{24}$H$</em>{27}$N$_5$O$_2$Zn</td>
<td>56.91 (56.20)</td>
<td>4.03 (4.91)</td>
<td>14.01 (13.65)</td>
</tr>
<tr>
<td>[ZnL$_2$(py)$_2$]·2H$_2$O (41)</td>
<td>C$<em>{24}$H$</em>{27}$N$_5$O$_2$Zn</td>
<td>55.86 (55.98)</td>
<td>4.46 (5.29)</td>
<td>13.94 (13.60)</td>
</tr>
<tr>
<td>[Zn(HL$_2$)$_2$Br] (42)</td>
<td>C$<em>{14}$H$</em>{16}$BrN$_4$O$_2$Zn</td>
<td>42.86 (42.08)</td>
<td>3.25 (3.03)</td>
<td>10.41 (10.52)</td>
</tr>
<tr>
<td>[Zn(HL$_2$)$_2$] (43)</td>
<td>C$<em>{28}$H$</em>{24}$N$_6$O$_4$Zn</td>
<td>58.10 (58.60)</td>
<td>4.63 (4.21)</td>
<td>14.32 (14.64)</td>
</tr>
</tbody>
</table>

$^*$10$^{-3}$ M in DMF and expressed as ohm$^{-1}$ cm$^2$ mol$^{-1}$
7.4.1 Electronic spectra

The electronic spectra of the ligands and complexes were recorded in DMF. The electronic spectral assignments of the two ligands and the complexes are given in Table 7.2. The electronic spectra of the ligand \( \text{H}_2\text{L}^1 \) showed bands at 38100 and at 30120 cm\(^{-1}\).

Table 7.2. Electronic spectral assignments (cm\(^{-1}\)) of the semicarbazones and their complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\pi\rightarrow\pi^*)</th>
<th>(n\rightarrow\pi^*)</th>
<th>LMCT</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{L}^1)</td>
<td>38100</td>
<td>30120</td>
<td>-</td>
</tr>
<tr>
<td>([\text{ZnL}^1\text{py}]\cdot\text{H}_2\text{O} (36))</td>
<td>37560, 35240</td>
<td>30520</td>
<td>26630</td>
</tr>
<tr>
<td>([\text{ZnL}^1\text{phen}]\cdot\text{H}_2\text{O} (37))</td>
<td>37590, 35840, 34600</td>
<td>31740</td>
<td>27620</td>
</tr>
<tr>
<td>(\text{H}_2\text{L}^2)</td>
<td>36750</td>
<td>29070</td>
<td>-</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{py}]\cdot\text{H}_2\text{O} (38))</td>
<td>36780, 34430</td>
<td>-</td>
<td>26320</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{phen}]\cdot\text{H}_2\text{O} (39))</td>
<td>37590, 35210, 33560</td>
<td>30760</td>
<td>26810</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{bipy}]\cdot\text{H}_2\text{O} (40))</td>
<td>37230, 35320</td>
<td>30520</td>
<td>25210</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{py}^2]\cdot\text{H}_2\text{O} (41))</td>
<td>37450, 34840, 33900</td>
<td>30770</td>
<td>26880</td>
</tr>
<tr>
<td>([\text{Zn(HL}^2\text{)}\text{Br}] (42))</td>
<td>37190, 35210</td>
<td>29820</td>
<td>25450</td>
</tr>
<tr>
<td>([\text{Zn(HL}^2\text{)}_2]^) (43)</td>
<td>37230, 34560</td>
<td>29320</td>
<td>26660</td>
</tr>
</tbody>
</table>

The ligand \(\text{H}_2\text{L}^2\) showed bands at 36750 and 29070 cm\(^{-1}\) attributable to the \(\pi\rightarrow\pi^*\) and \(n\rightarrow\pi^*\) transitions of the azomethine group [15,16]. The energy of these bands are slightly shifted on complexation (Figs 7.1-7.3). The shift showing donation of a lone pair of electrons to the metal by the coordination of azomethine nitrogen [17,18].

In addition to this intra-ligand bands, a new band at ca. 27000 cm\(^{-1}\) is observed in the spectra of the complexes. This band can safely be assigned to O\(\rightarrow\)metal charge-transfer band. The appearance of O\(\rightarrow\)metal charge-transfer band in the electronic spectra of Zn(II) complex is a strong evidence that the keto oxygen atoms of the ligands are coordinated to the Zn(II) ion. The LMCT maxima of the complexes show line broadening into the visible part of the spectra. No appreciable absorption are observed below 18000 cm\(^{-1}\) in DMF solution which is in accordance with the d\(^{10}\) electronic configuration of Zn(II) ion.
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7.4.2. Infrared spectra

The IR spectra of the free ligands when compared with those of complexes confirm the coordination of the semicarbazone to the metal. The significant bands observed in the IR spectra of ligands and its complexes with the tentative assignments are presented in the Table 7.3.
Table 7.3. Infrared spectral assignments (cm\(^{-1}\)) of semicarbazones and their Zn(II) complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu(C=N))</th>
<th>(\nu(\text{^{2}N-C}))</th>
<th>(\nu(\text{N-N}))</th>
<th>(\nu(\text{Zn-N}_\text{azo}))</th>
<th>(\nu(\text{Zn-O}))</th>
<th>(\nu(\text{C=O}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{L}^1)</td>
<td>1621</td>
<td>-</td>
<td>1030</td>
<td>-</td>
<td>-</td>
<td>1696</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{py}]\cdot\text{CH}_3\text{OH}) (36)</td>
<td>1598</td>
<td>1572</td>
<td>1035</td>
<td>424</td>
<td>554</td>
<td>-</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{py}]\cdot2\text{H}_2\text{O}) (37)</td>
<td>1596</td>
<td>1570</td>
<td>1039</td>
<td>429</td>
<td>551</td>
<td>-</td>
</tr>
<tr>
<td>(\text{H}_2\text{L}^2)</td>
<td>1607</td>
<td>-</td>
<td>1035</td>
<td>-</td>
<td>-</td>
<td>1648</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{py}]\cdot\text{H}_2\text{O}) (38)</td>
<td>1599</td>
<td>1568</td>
<td>1052</td>
<td>430</td>
<td>553</td>
<td>-</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{phen}]\cdot2\text{H}_2\text{O}) (39)</td>
<td>1595</td>
<td>1565</td>
<td>1040</td>
<td>435</td>
<td>550</td>
<td>-</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{bipy}]\cdot2\text{H}_2\text{O}) (40)</td>
<td>1593</td>
<td>1569</td>
<td>1038</td>
<td>428</td>
<td>555</td>
<td>-</td>
</tr>
<tr>
<td>([\text{ZnL}^2\text{(py)}_2]\cdot2\text{H}_2\text{O}) (41)</td>
<td>1599</td>
<td>1570</td>
<td>1045</td>
<td>425</td>
<td>554</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Zn(HL}^2\text{)}\text{Br}]) (42)</td>
<td>1594</td>
<td>-</td>
<td>1043</td>
<td>429</td>
<td>552</td>
<td>1638</td>
</tr>
<tr>
<td>([\text{Zn(HL}^2\text{)}^2]) (43)</td>
<td>1595</td>
<td>-</td>
<td>1051</td>
<td>427</td>
<td>547</td>
<td>1645</td>
</tr>
</tbody>
</table>

The IR spectra of the complexes do not exhibit a broad absorption band at 3420 cm\(^{-1}\), which is due to the \(-\text{OH}\) stretching mode of phenolic oxygen, indicating deprotonation during coordination. Weak bands in the region 547-555 cm\(^{-1}\) indicate the presence of Zn-O bond, resulting from the coordination of the phenolic oxygen [19]. Besides, the shifting of the band due to the Ar-O group to lower frequencies indicates the weakening of the Ar-O group due to coordination. In the IR spectra of the ligands \(\text{H}_2\text{L}^1\) and \(\text{H}_2\text{L}^2\), the bands at 3134 and 3187 cm\(^{-1}\) respectively corresponding to the \(\nu(\text{\^{2}N-H})\) indicate that the ligands remain as keto tautomers in the solid state [20]. These bands are absent in all the complexes except in 42 and 43. A band in the 1645-1700 cm\(^{-1}\) range attributable to \(\nu(\text{C=O})\) stretching in the ligand spectrum is absent in all the complexes except in compounds 42 and 43 indicate the coordination in the enolate form. In compounds 42 and 43 the ligand is coordinated in the keto form. In the spectra of complexes 36-41 (Figs. 7.5-7.7), the bands corresponding to the newly formed N=C bond \([\nu(\text{\^{2}N=C})]\) due to the enolization of the ligands are observed at ca. 1570 cm\(^{-1}\). In these complexes, the \(\nu(\text{N-N})\) frequency shifts from 1030 to 1045 cm\(^{-1}\). These bands confirm the enolization and the subsequent deprotonation of the ligands during complexation. But these bands are absent in compounds 42 and 43 indicating that the ligand is in the keto form in these two complexes. This is
further confirmed by the appearance of bands at 1638 and 1645 cm\(^{-1}\) (Figs. 7.8 and 7.9), due to >C=O in these complexes. The \(\nu(C=N)\) bands of semicarbazones are found to be shifted to lower frequencies by 10-25 cm\(^{-1}\) in all complexes indicating the coordination via the azomethine nitrogen. The coordination of this nitrogen is also supported by a shift in \(\nu(N-N)\) frequencies [21]. A shift to lower frequency is due to the conjugation of p-orbital on the double bond with the d-orbital on the metal atom with the reduction of the force constant. The bands corresponding to \(\nu(N-H)\) appear at 3310 and 3374 cm\(^{-1}\) in the ligands spectra. In the far IR spectra of the complexes, the bands at 424-435 cm\(^{-1}\) assignable to \(\nu(Zn-N_{azo})\) further confirms the coordination of the metal through azomethine nitrogen [22].

![Fig. 7.4. IR spectrum of [ZnL\(^1\)py]2H\(_2\)O (37)](image)

The coordination of the bases 2,2'-bipyridine and 1,10-phenanthroline are indicated by the presence of weak bands in the region 410-485 cm\(^{-1}\) and bands in the range 198-228 cm\(^{-1}\) in pyridine complexes 37, 38 and 41 correspond to \(\nu(Zn-py)\). In the complex 39, medium bands around 1500 cm\(^{-1}\) shows the presence of 1,10-phenanthroline. The spectrum of the complex 40 shows medium bands at 1502, 1445, 1384 cm\(^{-1}\) due to \(\nu(bipy)\). In the far IR spectrum of the compound 42, the band at 236 cm\(^{-1}\) can be assigned to \(\nu(Zn-Br)\). It shows the presence of terminally coordinated bromine [23].
According to Stefov et al., coordinated water should exhibit bands at 825, 575 and 500 cm\(^{-1}\). The absence of bands in these regions in the spectrum of complexes shows that the water molecules are not coordinated but are present as lattice water [24].

![Fig. 7.5. IR spectrum of [ZnL\(^2\)py\(\cdot\)H\(_2\)O (38)](image)

![Fig. 7.6. IR spectrum of [ZnL\(^2\)(py)\(_2\)]\(\cdot\)2H\(_2\)O (41)](image)
Syntheses of zinc(II) complexes and studies on their spectral characteristics

Fig. 7.7. IR spectrum of [Zn(HL²)Br] (42)

Fig. 7.8. IR spectrum of [Zn(HL²)₂] (43)
The tentative structures of the compounds are given below. Methanol and water molecules are omitted.

\[
[Zn_2L_2^1] \cdot CH_3OH (36)
\]

\[
[ZnL^1py] \cdot 2H_2O (37)
\]

\[
[ZnL^2py] \cdot H_2O (38)
\]
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[\text{ZnL}^2\text{phen}] \cdot 2\text{H}_2\text{O} (39)

[\text{ZnL}^2\text{bipy}] \cdot 2\text{H}_2\text{O} (40)

[\text{ZnL}^2(\text{py})_2] \cdot 2\text{H}_2\text{O} (41)
Conclusion

This chapter describes the syntheses and physico-chemical characterizations of eight zinc(II) complexes of the semicarbazones $\text{H}_2\text{L}^1$ and $\text{H}_2\text{L}^2$. The semicarbazones are obtained by the direct condensation of 2-hydroxyacetophenone and salicylaldehyde with N(4)-phenylsemicarbazide, a tridentate chelating agent having ONO donor sites. They readily form four, five and six coordinate Zn(II) complexes. These are characterized by means of partial elemental analyses, molar conductivity measurements, electronic, and infrared spectral studies. In the complexes 36-41, the semicarbazone is coordinated in the enolate form and in 42 and 43 it is in the keto form according to IR spectral data.
References:

