6.1 Introduction

Zinc is an essential element for normal functioning of most organisms and is the main constituent in a number of metallo-enzymes like carbonic anhydrase and alcohol dehydrogenase [1,2]. Zinc functions as an antioxidant and is participated in many serious biochemical reactions [3]. It is the second most abundant transition metal ion in human body after iron. It is essential for protein synthesis and which helps to regulate the production of cells in the body's immune system.

Zinc complex of L-carnosine is an anti-ulcer drug in which zinc plays an essential role [4]. More than 1000 enzymes contain zinc in the active centers, and in brief no other metal has as many functions in living organisms as zinc [5]. Yet today the role of zinc in various biological processes is not fully revealed. According to Vahrenkamp [6] may be the ‘non-properties’ of zinc are the basis of this uniqueness, *i.e.* unlike other transition metals zinc has no redox chemistry, no ligand field effects, no typical coordination numbers or geometries, no stability or inertness of its complexes, no typical “hard” or “soft” characteristics.
Reports showed that the salen complexes of zinc can be used as sensing materials for different ions and molecules, emissive materials for organic light emitting diodes and building blocks for various supramolecular architectures [7-9]. Zn(II) ions have a high affinity towards nitrogen, oxygen and sulfur donor ligands [10,11].

Zinc(II) ion provides a number of coordination compounds because of its affinity towards different types of ligands and flexible coordination number ranging from two to eight. The filled d shell does not offer crystal field stabilization on Zn$^{2+}$ hence coordination number and stereochemistry are determined by the size of the Zn(II) cation and the steric requirements of the ligands. In zinc complexes commonly found geometries are tetrahedral and octahedral. Among these tetrahedral geometry predominates. Six coordinate complexes may be octahedral or trigonal prismatic. Among the less common five coordinate complexes trigonal bipyramidal geometry predominates over square pyramidal geometry.

This chapter deals with the syntheses and characterization of Zn(II) complexes derived from different ONO donor hydrazones.

6.2 Experimental

6.2.1 Materials

2-Hydroxy-4-methoxyacetophenone (Aldrich), 2-hydroxy-4-methoxybenzaldehyde (Aldrich), nicotinic acid hydrazide (Aldrich), benzhydrazide (Aldrich), Zn(CH$_3$COO)$_2$·2H$_2$O (S.D.Fine) were used without further purification. Solvent used was methanol.

6.2.2 Syntheses of acylhydrazones

The syntheses of acylhydrazones were done as described in Chapter 2.
6.2.3 Syntheses of Zn(II) complexes

[Zn(hmbn)]\(_2\)·H\(_2\)O (26): To a methanolic solution of H\(_2\)hmbn·H\(_2\)O (0.289 g, 1 mmol), Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O (0.219 g, 1 mmol) in methanol was added and stirred for two hours. The yellow colored product formed was filtered, washed with methanol, followed by ether and dried over P\(_4\)O\(_10\) in vacuo. Elemental Anal. Found (Calcd.) (%): C, 49.05 (48.93); H, 3.01 (3.52); N, 12.50 (12.23).

[Zn(hman)]\(_2\)·H\(_2\)O (27): Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O (0.219 g, 1 mmol) in methanol was added to the H\(_2\)hman solution in methanol (0.285 g, 1 mmol) and stirred for about two hours. The yellow product formed was filtered, washed with methanol, followed by ether and dried over P\(_4\)O\(_10\) in vacuo. Elemental Anal. Found (Calcd.) (%): C, 50.90 (50.37); H, 3.58 (3.94); N, 11.75 (11.75).

[Zn(Hhmbb)OAc] (28): To a methanolic solution of H\(_2\)hmbb (0.270 g, 1 mmol), Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O (0.219 g, 1 mmol) in methanol was added. The yellow colored product formed was filtered washed with methanol, followed by ether and dried over P\(_4\)O\(_10\) in vacuo. Elemental Anal. Found (Calcd.) (%): C, 52.04 (51.86); H, 3.83 (4.10); N, 7.18 (7.11).

[Zn(hmab)]\(_2\) (29): Methanolic solutions of the H\(_2\)hmab (0.284 g, 1 mmol) and Zn(CH\(_3\)COO)\(_2\)·2H\(_2\)O (0.219 g, 1 mmol) were mixed and stirred for about 2 hours. The product separated was yellow colored and it was filtered, washed with methanol, followed by ether and dried over P\(_4\)O\(_10\) in vacuo. Elemental Anal. Found (Calcd.) (%): C, 54.89 (55.27); H, 3.59 (4.06); N, 7.99 (8.06).

6.3 Results and discussion

In the case of all the four complexes, experimental and calculated analytical data are in very close agreement. Magnetic susceptibility studies indicate diamagnetic nature of these complexes and it indicates the \(d^{10}\) outer electronic
configuration of zinc. The molar conductivity measured for all the four complexes in 10^3 M DMF solution is found to be below 15 ohm^{-1} cm^2 mol^{-1} which is much less than the value of 65-90 ohm^{-1} cm^2 mol^{-1} obtained for a 1:1 electrolyte in the same solvent [12]. So the conductance measurements in DMF suggest that they are non-electrolytes, the conductivity values are tabulated in Table 6.1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_m )</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(hmbn)]-H_2O (26)</td>
<td>11</td>
</tr>
<tr>
<td>[Zn(hman)]-H_2O (27)</td>
<td>10</td>
</tr>
<tr>
<td>[Zn(Hhmbb)OAc] (28)</td>
<td>12</td>
</tr>
<tr>
<td>[Zn(hmab)] (29)</td>
<td>9</td>
</tr>
</tbody>
</table>

* molar conductivity (in mho cm^2 mol^{-1}) taken in 10^{-3} M DMF.

6.3.1 \(^1\)H NMR spectral studies

Proton Nuclear Magnetic Resonance (\(^1\)H NMR) Spectroscopy is a powerful tool used for the determination of the structure of compounds. Because of their diamagnetic nature, the Zn(II) complexes were studied by NMR spectroscopy. The \(^1\)H NMR spectra of the acylhydrazones and complexes have been recorded with DMSO as solvent. The comparison of the NMR spectra of the complexes with the spectra of ligands gave valuable informations regarding the coordination mode of ligands during complexation. The \(^1\)H NMR spectrum obtained for compound 27 was not good due to the poor solubility of the compound. In the spectra of the free hydrazones there are sharp singlets in the range of 12-14 ppm showing the existence of iminol form in solution. They also gave singlets in the range of 11-12 ppm with an area integral of one which is due to phenolic OH protons. Large \( \delta \) values of these protons may be due to intramolecular hydrogen bonding. Upon D_2O exchange, the intensity of these signals significantly...
decreases, which suggests that these protons are easily exchangeable and confirm the assignment. The singlets with an area integral of three in the range of 3-3.8 ppm indicate the presence of three methoxy hydrogens. Peaks for aromatic protons were found in the region 6-8 ppm. In the spectra of the complexes, there are no peaks are in the region 11-12 ppm, which is an evidence for the coordination of phenolic oxygen to the metal centre. Similarly peaks corresponds to iminol protons found in the spectra of free hydrazones were absent in the spectra of complexes indicating the coordination of iminol oxygen to zinc. In the spectrum of compound 28, a singlet with an area integral of three is found at 2.086 ppm and it is assigned to the methyl group present in acetate which is coordinated to zinc. Also a singlet with area integral one is appeared at 8.524 ppm may indicate the presence of NH proton suggests the coordination of ligand in the amido form. All other peaks observed in the spectra of free hydrazones are slightly shifted. The $^1$H NMR spectra of complexes 26 and 28 are shown in the Figs. 6.1 and 6.2.
6.3.2 Infrared spectra

The IR spectra of the complexes, in comparison with those of the free ligands, display certain changes, which give an idea about the type of coordination and their structure. Significant IR spectral bands of the complexes are listed in Table 6.2. Free hydrazone shows strong absorptions in the 1630-1650 cm\(^{-1}\) region are assigned to carbonyl group, and bands due to azomethine group were observed around 1600 cm\(^{-1}\). In compounds 26 and 27, broad bands were observed at 3409 and 3417 cm\(^{-1}\) due to lattice water. Coordination of hydrazone to the zinc ion through the azomethine nitrogen atom is expected to reduce the electron density in the azomethine link and thus, lower the \(\nu(C=\text{N})\) absorption frequency. Hence this band undergoes a shift to lower wavenumber [13,14]. In complexes 26, 27 and 29, a lower shift is observed in \(\nu(C=\text{N})\) absorption frequency indicates coordination of azomethine nitrogen to zinc. Coordination of azomethine nitrogen is also evident from the increase in N–N
stretching frequency in all the complexes. In complexes 26, 27 and 29, bands correspond to carbonyl groups are absent suggesting the enolization of ligands during complexation. But in compound 28 bands observed around 1645 and 3000 cm\(^{-1}\) are assigned to carbonyl group and NH group respectively, i.e. in this complex, ligand is in the amido form. For the compound 28, bands at 1600 and 1386 cm\(^{-1}\) correspond to symmetric and asymmetric vibrations of the acetate group are consistent with the presence of a unidentate acetate group [15,16]. In compound 28, a very intense band is observed at 1600 cm\(^{-1}\), is a combination band of \(v(C=\text{N})\) and \(v_a(\text{CH}_3\text{COO})\) stretching frequencies. For all the complexes, phenolic C–O stretching occurs at lower wavenumber when compared to that of the ligands indicating the deprotonation and coordination of phenolic OH. Appearance of new bands in the regions of 525-560 and 440-460 cm\(^{-1}\) are assignable to \(v(\text{Zn–O})\) and \(v(\text{Zn–N})\) respectively. The IR spectra of the complexes are shown in the Figs. 6.3-6.6.

**Table 6.2 Selected IR bands (cm\(^{-1}\)) with tentative assignments of Zn(II) complexes**

<table>
<thead>
<tr>
<th>Compound</th>
<th>(v(C=\text{N}))</th>
<th>(v(C=\text{N})^a)</th>
<th>(v(N=\text{N}))</th>
<th>(v(C–\text{O}))</th>
<th>(v(\text{Zn–O}))</th>
<th>(v(\text{Zn–N}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(hmbn)](\cdot)H(_2)O (26)</td>
<td>1597</td>
<td>1527</td>
<td>1167</td>
<td>1210</td>
<td>527</td>
<td>454</td>
</tr>
<tr>
<td>[Zn(hman)](\cdot)H(_2)O (27)</td>
<td>1598</td>
<td>1524</td>
<td>1161</td>
<td>1244</td>
<td>547</td>
<td>445</td>
</tr>
<tr>
<td>[Zn(Hhmbb)OAc] (28)</td>
<td>1600</td>
<td>-</td>
<td>1124</td>
<td>1247</td>
<td>560</td>
<td>460</td>
</tr>
<tr>
<td>[Zn(hmab)](\cdot) (29)</td>
<td>1593</td>
<td>1540</td>
<td>1150</td>
<td>1223</td>
<td>540</td>
<td>459</td>
</tr>
</tbody>
</table>

\(^a\)newly formed
Fig. 6.3. IR spectrum of [Zn(hmbn)]$_2$·H$_2$O (26).

Fig. 6.4. IR spectrum of [Zn(hman)]$_2$·H$_2$O (27).
Syntheses and characterization of Zn(II) complexes derived from ONO donor acylhydrazones

Fig. 6.5. IR spectrum of [Zn(Hhmbb)OAc] (28).

Fig. 6.6. IR spectrum of [Zn(hmab)]_2 (29).
6.3.3 Electronic spectra

The electronic spectra of the ligands and complexes were recorded in acetonitrile solutions on a UVD-3500, UV-vis Double Beam Spectrophotometer. Due to filled $d$ orbitals, $d - d$ transitions are not expected in the case of Zn(II) complexes. But these complexes are yellow colored and the colors of the complexes are attributed to metal to ligand charge transfer transitions. Here MLCT bands were observed in the range of 24000-28000 cm$^{-1}$ [17]. The electronic spectra of all the four acylhydrazones showed bands in the region 30400-46000 cm$^{-1}$ due to $\pi-\pi^*$ transitions and $n-\pi^*$ transitions. These intraligand transitions were found to be slightly shifted during complexation. Table 6.3 summarized the electronic absorptions of the complexes and the spectra of the complexes are shown in Figs 6.7-6.10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Intraligand transitions</th>
<th>Charge transfer transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn(hmbn)]$_2$·H$_2$O (26)</td>
<td>30880, 36520, 42970</td>
<td>25530</td>
</tr>
<tr>
<td>[Zn(hman)]$_2$·H$_2$O (27)</td>
<td>30130, 35960, 42150</td>
<td>24630</td>
</tr>
<tr>
<td>[Zn(Hhmbb)OAc] (28)</td>
<td>30950, 37270, 43740</td>
<td>24280</td>
</tr>
<tr>
<td>[Zn(hmab)]$_2$ (29)</td>
<td>31570, 39430, 43210</td>
<td>27800</td>
</tr>
</tbody>
</table>

Table 6.3 Electronic spectral assignments (cm$^{-1}$) of Zn(II) complexes

![Fig. 6.7. Electronic spectrum of [Zn(hmbn)]$_2$ (26).](image1)

![Fig. 6.8. Electronic spectrum of [Zn(hman)]$_2$ (27).](image2)
6.3.4 Thermal analyses

Thermogravimetric analyses of the complexes will give information concerning the thermal stability of the complex and to decide whether the water molecules are in the inner or outer coordination sphere of the central metal ion [18]. Here Thermogravimetric analyses were carried out from 50 to 1000 °C under nitrogen atmosphere. In complexes 26 and 27, there is a weight loss below 120 °C indicating the presence of lattice water. In complexes 28 and 29, no weight loss is observed in between 50-250 °C indicating absence of water molecules in these complexes. Above 400 °C the complexes begin to decompose and the decomposition was not seen to be completed even at 1000 °C. TG – DTG plots of complexes 26 and 28 are shown in Figs. 6.11 and 6.12.
Fig. 6.11. TG-DTG plots of [Zn(hmbn)]₂·H₂O (26).

Fig. 6.12. TG-DTG plots of [Zn(Hhmbb)OAc] (28).

References


*****cahp*****