Original Article

Synthesis and spectral characterization of Ni(II) complexes with $N_2O_2$ and $N_2O_4$ Schiff base Ligands

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Abstract

A series of new heterodentate N, O-donor ligands derived by condensing O-Phthalaldehyde (OPA) with hydroxy benzoic hydrazides (HBHs) and some aromatic amines (AAs) were used to afford new mononuclear Ni(II) coordination compounds. All the complexes were characterized by IR, mass, electronic spectra, conductance, magnetic and thermal studies. Based on the spectral studies their structures have been tentatively proposed. The ligands derived from OPA with HBHs and AAs displayed hexadentate and tetradentate coordination around the metal ion respectively.

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Key words: O-Phthalaldehyde, Schiff base, Metal complex

1. Introduction

Schiff bases have a chelating structure and are in demand because they are straightforward to prepare and are moderate electron donors with easily-tunable electronic and steric effects. The synthesis and application of Schiff bases and their coordination compounds have been highly considered in inorganic and bioinorganic fields, since their structural properties similar to some of the biological systems [1-4]. The synthesis of hetero-dentate N,O donor atoms containing Schiff bases and their metal complexes has being receiving considerable attention in recent years. A variety of tetra and hexadentate Schiff bases composed of N,O donor atoms and their metal complexes have been reported in literature [5,6]. We have long been working on the usage of O-Phthalaldehyde as a versatile aldehyde synthone to condense with different substituted amino acids [7,8] and amines in designing new class of heterodentate Schiff-base ligands including macrocycles [9,10]. We have also been working on the catalytic, analytical and biological applications of these compounds [11-13]. In the present investigation we report the synthesis and spectral characterization of new tetra and hexadentate N, O donor Schiff base Ni(II) complexes derived from the combination of OPA with some hydroxyl benzo/hydrazines and substituted aromatic amines.

2. Experimental

2.1. Physical measurements

The melting points of all the Schiff base metal compounds were obtained on a Buchi-510 melting point apparatus. The percentages of carbon, hydrogen, nitrogen in Schiff base metal compounds were determined using a Perkin–Elmer CHN analyzer at 240°C. Conductance measurements were carried out at room temperature on freshly prepared 10^{-3} M ethanol solutions using a Co-ordination digital conductivity meter. The magnetic studies were carried out at room temperature on a Gouy balance calibrated with Hg [Co(SCN)_2]. The TG-DTG thermo grams of the complexes were recorded on Mettler Toledo star system. The IR spectra were recorded in KBr pellets on a Perkin-Elmer spectrophotometer. ESI and FAB MS were used to obtain mass spectra.

2.2. Synthesis of Schiff base ligands


2.3. Synthesis of Schiff base Ni (II) complexes

Solution of NiCl$_2$.6H$_2$O (0.002mol) in methanol (10 ml) was added drop wise to a methanolic solution (10ml) of Schiff base (0.002mol) and stirred at room temperature with constant stirring. The resulting mixture was allowed to reflux on a water bath for two hours until a solid is separated out (Scheme 1). The precipitates were suction filtered, purified by repeated washing with diethyl ether and dried in vacuum desiccators. All the complexes were
of carbon, hydrogen and nitrogen were determined by using CHN analyzer. The percentage of nickel in Ni(II) complexes was determined by literature method [15]. The physical (Table 1) and analytical data (Table 2) is in good agreement with the proposed molecular formulae.  

3.1. Physical and analytical data

The percentages of carbon, hydrogen and nitrogen were determined by using CHN analyzer. The percentage of nickel in Ni(II) complexes was determined by literature method [15]. The physical (Table 1) and analytical data (Table 2) is in good agreement with the proposed molecular formulae.

3.2. Mass spectral analysis

The mass spectra of Schiff base Ni(II) complexes showed the molecular ion peaks at m/z (M+) 478 (for comp-1), 596 (for comp-2), 510 (for comp-5) and 412 (for comp-6). This data is in good agreement with the respective molecular formulae.

3.3. Conductance measurements

The molar conductance values of Schiff base Ni(II) complexes were determined in dichloromethane and they are found to be low (12.0-20.4 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\)) indicating the non-electrolytic behavior [16] (Table 2).

3.4. Thermal analysis

Thermograms of TGA and DTA of Schiff base Ni(II) complexes were critically examined to ascertain the presence of lattice held, coordinated water molecules and decomposition patterns etc. In the TGA dehydration curve of Schiff base Ni(II) complexes with ligands HBHBC, HNIHNC, HNMAN and HPMAP two clear-cut stages were observed one is corresponding to loss of water molecule and second is due to the loss of organic moiety. The thermograms of Ni(II) complexes of HBHBC, HNIHNC show initial weight loss in the temperature range of 102-110 °C. Also, the DSC curve of these complexes shows an endothermic peak in the above range further giving evidence for the presence of water molecules. The loss of water molecules in this temperature range indicates that they are present as lattice-held water [17]. Whereas the thermograms of Ni(II) complexes of HNMAN and HPMAP exhibit weight loss at the temperatures 182 and 218 °C respectively. Also, the DSC curve of the complexes show an endothermic peak in the above temperature range further giving evidence for the presence of coordinated water molecules [18]. The percentage weight loss in this temperature range indicates that there are two water molecules each in these two complexes as coordinated water. All these complexes showed second decomposition curve around 300 °C corresponding to loss of organic moiety. This is further evidenced by the DSC curve, which show exothermic peak around this temperature range. The analysis of thermograms gives further support to the composition of the complexes proposed on the basis of elemental and thermal analysis. The thermal data of complexes obtained from their thermo grams are presented (Table 3).

3.5. Infrared spectral analysis

The infrared spectra of free ligands were compared with the spectra of new Schiff base Ni(II) complexes and observed probable binding modes of the ligands (Table 4). A medium intensity \(\nu_{C=\alpha}\) band was observed in the range of

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**Table 1.** Physical data of Schiff base Ni(II) complexes.

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Ni(II) complex Formed</th>
<th>Reaction time (min)</th>
<th>Decomp Temp (°C)</th>
<th>Color</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ni(HBBHBC)].H(_2)O</td>
<td>85</td>
<td>242</td>
<td>Green</td>
<td>72</td>
</tr>
<tr>
<td>2</td>
<td>[Ni(HNHHNC)].2.H(_2)O</td>
<td>75</td>
<td>230</td>
<td>Light Green</td>
<td>69</td>
</tr>
<tr>
<td>3</td>
<td>[Ni(HNMAN)].(H(_2)O)(_2)</td>
<td>105</td>
<td>219</td>
<td>Light Green</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(HPMAP)].(H(_2)O)(_2)</td>
<td>85</td>
<td>265</td>
<td>Dark Green</td>
<td>63</td>
</tr>
</tbody>
</table>

**Table 2.** Molar conductance, magnetic moment and electronic spectral data and analytical data of Schiff base Ni(II) complexes.

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Ni(II) complex/ Molecular formula</th>
<th>(\Lambda_M) (Ω(^{-1}) cm(^2) mol(^{-1}))</th>
<th>(\mu_{\text{eff}}) (B. M.)</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>Analyses (%) Found (Calculated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[Ni(HBBHBC)].H(_2)O C(_2)H(_4)N(_2)O(_2)Ni</td>
<td>12.0</td>
<td>3.09</td>
<td>1029, 681, 389</td>
<td>C (5.38) H (3.80)  Ni (12.01)</td>
</tr>
<tr>
<td>2</td>
<td>[Ni(HNHHNC)].2.H(_2)O C(_2)H(_4)N(_2)O(_2)Ni</td>
<td>15.6</td>
<td>3.02</td>
<td>1074, 686, 364</td>
<td>C (60.53) H (3.86) Ni (9.41)</td>
</tr>
<tr>
<td>3</td>
<td>[Ni(HNMAN)].(H(_2)O)(_2) C(_2)H(_4)N(_2)O(_2)Ni</td>
<td>13.6</td>
<td>3.45</td>
<td>1067, 642, 373</td>
<td>C (66.05) H (4.52) Ni (10.07)</td>
</tr>
<tr>
<td>4</td>
<td>[Ni(HPMAP)].(H(_2)O)(_2) C(_2)H(_4)N(_2)O(_2)Ni</td>
<td>20.4</td>
<td>3.34</td>
<td>1012, 669, 384</td>
<td>C (52.32) H (4.09) Ni (13.78)</td>
</tr>
</tbody>
</table>

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Scheme 1: Synthesis of ligands and their metal complexes

![Scheme 1](image-url)

4. Conclusions
Four new air stable Ni(II) complexes have been synthesized by the treatment of NiCl₂.6H₂O with Schiff base ligands. The complexes 1 and 2 possess chelation with two nitrogen atoms of imine group, two oxygen atoms of keto group and two oxygen atoms of phenolic group. Whereas, in the complexes 3 and 4 the coordination occurs through two nitrogen atoms of imine group and two oxygen atoms of two phenolic groups. Based on the elemental and spectral data octahedral geometry has been tentatively assigned for all the complexes.

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References

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