Syntheses and characterization of fumaryl bis-2-aminobenzothiazole chelate polymers

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ABSTRACT

Chelate polymers of first row transition metal ions viz Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) have been prepared with the ligand derived from fumaryl bis-2-aminobenzothiazole having equimolar stoichiometry of the cations and the ligands. The newly synthesized chelate polymers were characterized by elemental analyses, magnetic, infrared and reflectance spectra. The synthesized chelate polymers are coloured, amorphous, solid and highly insoluble in aqueous and common organic solvents. The structure of the chelate polymers has been assigned on the basis of spectral and magnetic studies.

Key words: Chelate polymers, Infrared spectroscopy, Magnetic measurements, Reflectance spectra.

INTRODUCTION

Polymers are important materials used in commodities such as tyres, textiles, thermosets, composites material, transportation industry, automotive, marine and aerospace. The demand for new materials with practical applications has been promoted research in the design and syntheses of chelate polymers, on account of its various applications. IR spectra have shown potential bidentate behaviour of ligands with different donor groups like nitrogen, oxygen and sulphur etc which could give complexes of varied coordination numbers and properties. The ligands derived from pyridinedicarboxylic acid dichloride with 2-aminobenzothiazole and its complexes were found to be stable 700-800°C, whereas 90% mass loss was recorded upto 552°C.

A new macroacyclic amide ligand N,N'-bis(2-benzothiazolyl)2,6-pyridinedicarboxamide formed by the condensation of 2,6-pyridinedicarboxylic acid dichloride with 2-aminobenzothiazole and its complexes were found to be stable 700-800°C.

We report here the preparation and characterization of fumaryl bis-2-aminobenzothiazole and its Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) chelate polymers.

EXPERIMENTAL

Analytical reagent grade chemicals were used for syntheses purpose. All chemicals and solvents were purified by standard methods.

Preparation of bis-ligand

The bis-ligands were prepared by the condensation of acid dichloride (0.1 mol) with (0.2 mol) of 2-aminobenzothiazole and refluxing it in 100 ml dry benzene for about 5-6 h. The ligand...
was then filtered and washed with hot benzene and then with hot alcohol. The resultant products were then dried and recrystallized.

**Syntheses of Chelate Polymers**

An equimolar quantity of bis ligand (0.1 mol) and metal acetate (0.1 mol) were dissolved separately in minimum quantity of DMF in hot condition. The hot solution are then mixed and refluxed. The temperature of the reaction mixture was kept between 120-160°C, polymers generally appeared after 24h heating in an oil bath. Syntheses of Fumaryl bis-2-aminobenzothiazole ligand (FBABT) is shown in Fig 1. Elemental analyses of the chelate polymers are given in Table 1.

**RESULTS AND DISCUSSION**

On the basis of C, H, N analyses, infrared spectra, magnetic data, reflectance spectra and thermal data, the proposed structure of chelate polymers have shown in fig. 2a & 2b.

**Infra red spectral studies**

Ligand show moderately strong band near 3231 cm⁻¹ which may be assigned due to stretching vibration of a secondary amide -NH- group⁸,⁹,¹⁰. The presence of band around 525-415 cm⁻¹ may be assigned to N→M bond¹¹. The IR spectra of ligand show a peak in the region of 2920-2853 cm⁻¹ that may be attributed to (-CH₃) stretching. The band

![Diagram](image1)

Fig. 1: Syntheses of Fumaryl bis-2-aminobenzothiazole Ligand (FBABT)

![Diagram](image2)

For -(CHₙ)ₙ, n = 2 for Fumaric acid M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II). Fig: 2a X = Coordinated Water, X = 0 in Co(II). (H₂O)ₙ i.e lattice Water in case of Co(II)-FBABT, Ni(II)-FBABT

![Diagram](image3)

Fig 2b: In case of Mn(II)-FBABT, Cu (II)-FBABT, Zn (II)-FBABT
Table 1: Analyses of ligand and its chelate polymers

<table>
<thead>
<tr>
<th>Composition of Chelate Polymer</th>
<th>Empirical Formula</th>
<th>Formula weight</th>
<th>% yield</th>
<th>% Loses Due to Decomposition</th>
<th>Decomposition Temp. Range °C</th>
<th>Decomposition Temp °C</th>
<th>Elemental Analyses Cal.</th>
<th>Found</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBABT</td>
<td>C₈H₆N₄O₂S₂</td>
<td>380</td>
<td>72</td>
<td></td>
<td>220-700</td>
<td>460</td>
<td></td>
<td></td>
<td>56.84</td>
<td>3.15</td>
<td>14.73</td>
<td>16.84</td>
<td></td>
</tr>
<tr>
<td>[Mn(II)(FBABT)]ₙ</td>
<td>C₈H₆N₄O₂S₂Mn</td>
<td>434.93</td>
<td>66</td>
<td>87</td>
<td></td>
<td>460</td>
<td></td>
<td>49.66</td>
<td>2.78</td>
<td>12.87</td>
<td>14.71</td>
<td>25.26</td>
<td></td>
</tr>
<tr>
<td>[Co(II)(FBABT)]ₙ .(H₂O)₂</td>
<td>C₈H₆N₄O₄S₂Co</td>
<td>466.8</td>
<td>68</td>
<td>88</td>
<td>120-690</td>
<td>375</td>
<td></td>
<td>46.27</td>
<td>2.57</td>
<td>11.9</td>
<td>13.71</td>
<td>25.24</td>
<td></td>
</tr>
<tr>
<td>[Ni(II)(FBABT)(H₂O)₂]ₙ(H₂O)₂</td>
<td>C₈H₆N₄O₄S₂Ni</td>
<td>505.84</td>
<td>74</td>
<td>88</td>
<td>130-640</td>
<td>380</td>
<td></td>
<td>42.7</td>
<td>2.7</td>
<td>11.07</td>
<td>12.6</td>
<td>23.2</td>
<td></td>
</tr>
<tr>
<td>[Cu(II)(FBABT)]ₙ</td>
<td>C₈H₆N₄O₂S₂Cu</td>
<td>443.546</td>
<td>79</td>
<td>89</td>
<td>210-740</td>
<td>475</td>
<td></td>
<td>48.69</td>
<td>2.7</td>
<td>12.62</td>
<td>14.42</td>
<td>28.65</td>
<td></td>
</tr>
</tbody>
</table>

Note: The values in parentheses represent the measured values.
appearing in the region of 1700-1550 cm\(^{-1}\) in the ligand may be assigned to the C = O group\(^{12}\), which gets lowered down in the chelate polymers confirming that the oxygen atom of the C = O group take part in coordination\(^{13}\). The C-N stretching band of primary amides appearing in the range of 1400-1350 cm\(^{-1}\) is found to be lowered in case of chelate polymers which supports the possibility of N→M bond. The C-S stretching vibration is observed in the region of 700-600 cm\(^{-1}\), since there is no considerable change in the band frequencies of ligand and their chelate polymers, it gives an evidence that sulphur has not participated in bonding with the metal\(^{14}\). The new weak band appearing in the region of 670-618 cm\(^{-1}\) in the coordination polymers may be due to the formation of M-O bond\(^{15}\). Medium band appearing in the range of 820-750 cm\(^{-1}\) in case of few chelate polymers may be attributed to the presence of water of coordination\(^{16}\). The important IR spectra of ligands and its chelate polymers are given in Table: 2.

**Electronic spectra and magnetic susceptibility of chelate polymers**

In \([\text{Mn(II)(FBABT)}]\_n\) chelate polymer band appears at 6.18 kk may be assigned due to \(^{6}A_{1g} \rightarrow ^{4}T_{2}(G)\) transition in octahedral field. The magnetic moment value also supported tetrahedral geometry of \([\text{Mn(II)(FBABT)}]\_n\) chelate polymer\(^{16}\). The band appearing in case of \([\text{Co(II)(FBABT)}]_n(H_2O)_2\) at 17.24 kk may be attributed to \(^{4}A_{2} \rightarrow ^{4}T_{1}(P)\) transition in tetrahedral field\(^{17}\). In \([\text{Ni(II)(FBABT)}(H_2O)_2]_n(H_2O)_2\) chelate polymer the bands appear at 16.12 kk may be assigned due to \(^{3}A_{2g} \rightarrow ^{3}T_{1g}\) transition in octahedral field\(^{17}\); respectively which is further supported by magnetic moment value. Zn(II) chelate polymer is diamagnetic in nature and has tetrahedral geometry. The electronic spectra and magnetic susceptibility of chelate polymers are given in Table: 3.

**Thermogravimetric analyses of chelate polymers**

Thermogram of Mn(II)(FBABT) Chelate polymer shows the absence of lattice and

### Table: 2: IR spectra of Ligand (FBABT) and its chelate polymers

<table>
<thead>
<tr>
<th>Ligand &amp; Chelate Polymers</th>
<th>C=O</th>
<th>CHN</th>
<th>NHH</th>
<th>HCH(_2)</th>
<th>H-O-H</th>
<th>MHO</th>
<th>CHS</th>
<th>N→M</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBABT</td>
<td>1651</td>
<td>1469</td>
<td>3231</td>
<td>2921</td>
<td>-</td>
<td>-</td>
<td>625</td>
<td>-</td>
</tr>
<tr>
<td>([\text{Mn(II)(FBABT)}]_n)</td>
<td>1586</td>
<td>1447</td>
<td>3161</td>
<td>2920</td>
<td>-</td>
<td>652</td>
<td>625</td>
<td>485</td>
</tr>
<tr>
<td>([\text{Co(II)(FBABT)}]_n(H_2O)_2)</td>
<td>1585</td>
<td>1450</td>
<td>3112</td>
<td>2920</td>
<td>-</td>
<td>653</td>
<td>624</td>
<td>482</td>
</tr>
<tr>
<td>([\text{Ni(II)(FBABT)}(H_2O)_2]_n(H_2O)_2)</td>
<td>1589</td>
<td>1459</td>
<td>3151</td>
<td>2920</td>
<td>802</td>
<td>654</td>
<td>627</td>
<td>475</td>
</tr>
<tr>
<td>([\text{Cu(II)(FBABT)}]_n)</td>
<td>1620</td>
<td>1462</td>
<td>3110</td>
<td>2924</td>
<td>-</td>
<td>650</td>
<td>627</td>
<td>489</td>
</tr>
</tbody>
</table>

### Table: 3: The Electronic Spectra and Magnetic Susceptibility of Chelate Polymers

<table>
<thead>
<tr>
<th>Chelate Polymer</th>
<th>Colour</th>
<th>(\mu_{\text{eff}}(B.M))</th>
<th>Electronic Spectra</th>
<th>Electronic Assignments</th>
<th>Stereochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mn(II)(FBABT)}]_n)</td>
<td>Cream</td>
<td>6.18</td>
<td>27.7</td>
<td>(^{6}A_{1g} \rightarrow ^{4}T_{2}(G))</td>
<td>Octahedral</td>
</tr>
<tr>
<td>([\text{Co(II)(FBABT)}]_n(H_2O)_2)</td>
<td>Purple</td>
<td>4.14</td>
<td>17.24</td>
<td>(^{4}A_{2} \rightarrow ^{4}T_{1}(P))</td>
<td>Tetrahedral</td>
</tr>
<tr>
<td>([\text{Ni(II)(FBABT)}(H_2O)_2]_n(H_2O)_2)</td>
<td>Green</td>
<td>3.39</td>
<td>16.12</td>
<td>(^{3}A_{2g} \rightarrow ^{3}T_{1g})</td>
<td>Octahedral</td>
</tr>
<tr>
<td>([\text{Cu(II)(FBABT)}]_n)</td>
<td>Light Green</td>
<td>2.37</td>
<td>14.7</td>
<td>(d_{xy}, d_{yz} \rightarrow d_{x^2-y^2})</td>
<td>Sq .Planar</td>
</tr>
<tr>
<td>([\text{Zn(II)(FBABT)}]_n)</td>
<td>Light Brown</td>
<td>2.37</td>
<td>14.7</td>
<td>-</td>
<td>Tetrahedral</td>
</tr>
</tbody>
</table>
coordinated water as no mass loss was observed upto 200°C. A gradual mass loss was seen from 220°C-700°C which may be due to the ligand attached to the metal ion and then no weight loss was observed after 700°C due to formation of stable metal oxide. In Co(II)(FBABT) Chelate polymer shows weight loss between 60°C to 100°C indicating presence of two lattice water molecules. Then a gradual weight loss was observed up to 690°C because of decomposition of ligand attached to the metal ion. In Ni(II)(FBABT) Chelate polymer shows weight loss between 80°C to 100°C & 110°C to 130°C indicating presence of two lattice water molecules two coordinated water molecules respectively. It then shows a gradual weight loss was observed up to 640°C because of decomposition of ligand attached to the metal ion. TG Curve of Cu(II)(FBABT) and Zn(II)(FBABT) shows no mass loss till 200°C. It later shows a gradual decrease in mass between 210°C-740°C and 200°C to 680°C which may be due to the decomposition of ligand attached to the metal ion species; hereafter no further mass loss was observed indicating the formation of metal oxide. The decomposition temperatures of chelate polymers are given in Table 1. To economize the space only the TG curve of Zn(II) FBABT has been shown in Fig 3.

**REFERENCES**