Spectral and thermal characterization of new biomimetic polydentate amide ligands

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Complexes of manganese(II) and nickel(II) with N,N’-bis(3-carboxy-1-oxopropanyl)-1, 2-ethylenediamine (C_{11}H_{10}N_{2}O_{6}L_{1}), N,N’-bis(3-carboxy-1-oxopropanyl)-1, 2-phenylenediamine (C_{11}H_{10}N_{2}O_{6}L_{2}), N,N’-bis(2-carboxy-1-oxophenylenyl)-1, 2-phenylenediamine (C_{11}H_{10}N_{2}O_{6}L_{3}) and N,N’-bis(3-carboxy-1-oxoprop-2-etyl)-1, 2-phenylenediamine (C_{11}H_{10}N_{2}O_{6}L_{4}) have been prepared and characterized by elemental analysis, vibrational spectra, magnetic susceptibility measurements, electronic spectra and thermal studies. Vibrational spectra indicates coordination of amide and carboxylate oxygen of the ligands giving a Mo₄ chromophore. Electronic spectra support square planar geometry around nickel(II) and tetrahedral around manganese(II). NiL₄ complex has the maximum activation energy and NiL₂ complex has the minimum activation energy.

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Ligands containing carboxyamide chains having O donor atoms, and their complexes, have been cited as possessing noteworthy pharmacological activity. Weirsem and Windle have reported that salicylamide coordinates through the nitrogen of the amide group. But Panu and co-workers have reported a structure for this complex with oxygen coordinating.

Due to diverse coordinating behaviour of amide ligands, and its biological significance this note describes the synthesis, spectral and thermal study of manganese(II) and nickel(II) complexes derived from N, N’-bis(3-carboxy-1-oxopropanyl)-1, 2-ethylenediamine (L₁), N,N’-bis(3-carboxy-1-oxopropanyl)-1, 2-phenylenediamine (L₂), N, N’-bis(2-carboxy-1-oxophenylenyl)-1, 2-phenylenediamine (L₃), and N,N’-bis(3-carboxy-1-oxoprop-2-etyl)-1, 2-phenylenediamine (L₄).

**Experimental**

Metal salts were purchased from E. Merck and were used as received. Solvents were of analytical grade and were purified by standard methods.

The metal content of each complex was determined by Atomic absorption spectroscopy technique on a AA-640-13, Shimadzu (Japan) instrument. Magnetic moments were measured at room temperature using a vibrating sample magnetometer (VSM) model 155 (Princeton applied research) at 5500 G field strength. Electronic spectra were recorded in DMF on a Beckmann DU-64 spectrophotometer. IR spectra was recorded on a Perkin-Elmer FT-IR spectrophotometer spectrum 2000 in KBr and polycylylene pellets. TG was recorded on a Rigaku 8150 thermoanalyzer at a heating rate of 10° min⁻¹. The number of decomposition steps were identified using TG. The activation energy (Eₐ) of the degradation process were obtained by Coats and Redfern’s method.

All ligands were prepared and purified according to a reported procedure. All ligands were characterized by IR, electronic spectra, H-NMR, mass spectra and elemental analysis; satisfactory results were obtained.

**Synthesis of nickel(II)/manganese(II) L₁, L₂, L₃ and L₄ complexes**

In a typical preparation ligand (0.01 mol) was dissolved or suspended in water (for L₁) and dry ethanol (for L₂, L₃, L₄), to which was added nickel acetate tetrahydrate/manganese acetate tetrahydrate solution (0.01 mol) in the same solvent. The mixture was allowed to stir for 1-2 h at room temperature. The solid product so separated was filtered, washed and air dried.

**Results and discussion**

The complexes were crystalline and stable under normal laboratory conditions, however, were decomposed by dilute mineral acids, and were insoluble in common non-polar solvents. The complexes were appreciably soluble in DMF. The physicochemical and analytical data of complexes are presented in Table 1. The stability constant values for Ni(II) complexes are higher than that of Mn(II) complexes. So complexation is more in case of Ni(II) and hence the yield.
The magnetic susceptibility measurements were carried out in the solid state at 298 K and the results are presented in Table 1. All the nickel complexes in the present case have been found to be diamagnetic in nature. This indicates square planar geometry around nickel(II)\(^{11,12}\).

All the manganese(II) complexes in the present study have magnetic moment values in the range 5.6-6.02 BM indicating the presence of five unpaired electrons in tetrahedrally coordinated manganese\(^{11,12}\).

In case of nickel complexes, the electronic absorption spectra in DMF show two bands in the 21810-22471 cm\(^{-1}\) and 27260-28210 cm\(^{-1}\) region. The square planar Ni(II) complexes were expected to show three bands\(^{13}\) \(1B_{1g} \leftrightarrow 1A_{1g}, 1A_{2g} \leftrightarrow 1A_{1g}, 1E_g \leftrightarrow 1A_{1g}\) due to d-d transition. But only one or two bands were usually observed. In the present study, higher energy band is assigned for charge transfer and lower energy band is assigned as d-d transition \(1B_{1g} \leftrightarrow 1A_{1g}\). The position of charge transfer band is however doubtful because the band may be due to intraligand transfer also.

Electronic spectra of manganese complexes show weak absorption in the visible region. Two bands were observed at about 20,000 cm\(^{-1}\) and 26,000 cm\(^{-1}\) assignable to \(4A_{1g} \rightarrow 2B_{2g}\) and \(4A_{1g} \rightarrow 4E_{g}, 4A_{1g}\) (G) transitions. This supports tetrahedral environment around the manganese\(^{14}\).

The bands due to the amide \(\nu(N-H)\) mode at 3209-3397 cm\(^{-1}\) for the free ligands L\(_1\), L\(_2\), L\(_3\) and L\(_4\) are shifted towards higher frequencies while the \(\nu(C=O)\) (amide I) frequency undergoes shift towards lower frequency in the all complexes indicating non-involvement of the amide nitrogen and involvement of the carbonyl oxygen atom of amide group in coordination with the metal ion\(^{15}\). This result is explained by the decrease in double bond character of C=O and the subsequent increase of C-N double bond character\(^{16,17}\). In other words, it is the lengthening of the C=O bond and shortening of the C-N bond which cause the decrease and increase of the frequencies respectively, in the IR spectra. Amide II and III bands arising out of \(\nu(C-N)\) as well as \(\delta(N-H)\) modes (coupled to one another), shift towards higher frequencies further confirming the coordination via carbonyl oxygen.

The \(\nu(C=O)\) and \(\nu(C-O)\) stretching frequencies in the 1535-1595 cm\(^{-1}\) and 1400-1420 cm\(^{-1}\) regions have been assigned to \(\nu(COO^-)_{asym}\) and \(\nu(COO^-)_{sym}\) modes respectively in the uncomplexed ligands. A positive and negative shift in complexes indicate a \(\Delta\nu\) enhancement upon complexation and suggest coordination of carboxylate groups in all the complexes of the four ligands in a monodentate fashion\(^{18-20}\). Here \(\Delta\nu\) implies the difference between \(\nu(COO^-)_{asym}\) and \(\nu(COO^-)_{sym}\) (i.e. asymmetric and symmetric stretching modes respectively). The \(\nu(O-H)\) due to the carboxylate groups appearing at 2600 cm\(^{-1}\) in free ligands disappears in the spectra of their complexes. A new band in the 345-375 cm\(^{-1}\) and 220-260 cm\(^{-1}\) region in the spectra of the complexes is assignable to \(\nu(Ni-O)\) and \(\nu(Mn-O)\)\(^{19}\) respectively. This indicates that both the carboxylic groups are involved in complexation.

### Table 1—Analytical, physical, magnetic moment and electronic spectral data of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Yield (%)</th>
<th>Found (Calcd.)</th>
<th>M</th>
<th>(\mu_{\text{eff}}) (BM)</th>
<th>Electronic spectral assignments (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiL(_1)</td>
<td>Green</td>
<td>90</td>
<td>36.9 (37.66)</td>
<td>5.04 (5.02)</td>
<td>7.97 (8.79)</td>
<td>18.19 (18.39)</td>
</tr>
<tr>
<td>NiL(_2)</td>
<td>Pale green</td>
<td>90</td>
<td>45.6 (45.82)</td>
<td>4.29 (4.36)</td>
<td>7.50 (7.63)</td>
<td>15.95 (15.98)</td>
</tr>
<tr>
<td>NiL(_3)</td>
<td>Green</td>
<td>80</td>
<td>56.88 (57.07)</td>
<td>3.73 (3.46)</td>
<td>6.81 (6.05)</td>
<td>12.53 (12.66)</td>
</tr>
<tr>
<td>NiL(_4)</td>
<td>Blue green</td>
<td>60</td>
<td>45.56 (46.33)</td>
<td>3.34 (3.31)</td>
<td>7.60 (7.72)</td>
<td>16.11 (16.16)</td>
</tr>
<tr>
<td>MnL(_1)</td>
<td>Off white</td>
<td>40</td>
<td>38.23 (38.10)</td>
<td>5.13 (5.08)</td>
<td>4.95 (5.08)</td>
<td>17.10 (17.43)</td>
</tr>
<tr>
<td>MnL(_2)</td>
<td>Brown</td>
<td>30</td>
<td>46.37 (46.29)</td>
<td>4.38 (4.41)</td>
<td>4.38 (4.41)</td>
<td>15.00 (15.12)</td>
</tr>
<tr>
<td>MnL(_3)</td>
<td>Brown</td>
<td>20</td>
<td>56.42 (57.33)</td>
<td>3.41 (3.48)</td>
<td>3.41 (3.48)</td>
<td>10.94 (11.96)</td>
</tr>
<tr>
<td>MnL(_4)</td>
<td>Brown</td>
<td>30</td>
<td>44.79 (46.81)</td>
<td>3.28 (3.34)</td>
<td>3.28 (3.34)</td>
<td>15.10 (15.29)</td>
</tr>
</tbody>
</table>

\(^a\)Diamagnetic

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Kinetic parameters of only nickel complexes were evaluated from TG curve and are given in Table 2. All nickel complexes were decomposed in one step and via first order kinetics. Activation energy (E_a) of all complexes lies between 23-79 kcal mol^{-1} and the order of activation energy is: L_4 > L_3 > L_2 > L_1 for nickel(II) complexes. NiL_4 complex has the maximum activation energy and NiL_2 complex has the minimum activation energy. Ligand L_2 is more bulky than ligand L_1. The complex formed by L_1 with Ni(II) is stronger (logβ_2 = 11.52) than L_2-Ni(II) complex (logβ_1 = 7.85). Hence there is large difference between activation energy of these complexes. The literature contain various explanations of the relative order of thermal stability of complexes.

All complexes are found to be monomers and involved coordination through carbonyl oxygens of amide groups, carboxylate oxygens giving a MO₄ environment. Magnetic susceptibility measurements and electronic spectra support square planar geometry for nickel(II) complexes and tetrahedral for manganese(II) complexes. Ligand L_1 found to form most stable nickel(II) complex.

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References

Table 2—Thermal data and kinetic parameters of nickel(II) complexes from TG curves

<table>
<thead>
<tr>
<th>Complex</th>
<th>Decomposition range (K)</th>
<th>Order of reaction (n)</th>
<th>Activation energy (E_a) (kcal mol⁻¹)</th>
<th>Weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiL₁</td>
<td>513-763</td>
<td>1</td>
<td>78.8</td>
<td>80.2 (81.6)</td>
</tr>
<tr>
<td>NiL₂</td>
<td>500-742</td>
<td>1</td>
<td>23.5</td>
<td>79.5 (84.6)</td>
</tr>
<tr>
<td>NiL₃</td>
<td>500-712</td>
<td>1</td>
<td>32.4</td>
<td>84.6 (87.5)</td>
</tr>
<tr>
<td>NiL₄</td>
<td>521-732</td>
<td>1</td>
<td>33.7</td>
<td>78.5 (83.8)</td>
</tr>
</tbody>
</table>