Synthesis and physico-chemical studies on transition metal complexes of macrocyclic ligand derived from 2,6-diacetylpyridine dihydrazone

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A novel series of Schiff base decaazamacrocyclic complexes [ML\(^1\)X\(_1\)] [M = Mn(II), Fe(II), Co(II), Ni(II) and Zn(II)]; and [CuL\(^1\)X\(_2\)] (X = Cl, NO\(_3\)) have been synthesized by the reaction between pre-synthesized 2,6-diacetylpyridine dihydrazone (L) and formaldehyde in the presence of metal ions in methanol medium at room temperature. The formation of ligand (L) and the proposed macrocyclic complexes have been confirmed from the results of elemental analyses, the comparative band positions for \(v(C=N)\) and formaldehyde in the presence of metal ions in methanol medium at room temperature. The importance of macrocyclic complexes in coordination chemistry is because of its various applications in biological processes such as photosynthesis and dioxygen transport; catalytic properties; potential applications as metal extractants and as radio-therapeutic and medical imaging agents. In macrocyclic complexes, both the metal ion and the size of the ring play an important role. Lindoy and co-workers have reported a series of studies on the selective complexation of transition metal ions by polydentate ligands. Metal ions act as templates, directing the steric course of the condensation reaction resulting in ring closure. Therefore, the metal template method has been recognized as highly yielding and selective routes to new ligands and their complexes. Several macrocyclic ligands derived from hydrazine precursors have been reported. Recently, divalent metal chelates of macrocycle derived from dihydrazide and aromatic diketone have also been reported. We report herein, a novel series of decaazamacrocyclic complexes derived from the condensation reaction of 2,6-diacyetylpyridine, hydrazine hydrate, formaldehyde and metal ions structure directing agent.

Experimental

The metal salts MX\(_n\)nH\(_2\)O (M = Mn\(^{II}\), Fe\(^{II}\), Co\(^{II}\), Ni\(^{II}\), Cu\(^{II}\) and Zn\(^{II}\); X = Cl, NO\(_3\), and n=1,3,6) (all BDH) were commercially pure samples. The chemicals such as 2, 6-diacyetylpyridine (Aldrich), hydrazine hydrate 85% (Sigma), and formaldehyde solution 37% (E. Merck) were used as received. Solvents were dried before use.

Preparation of 2,6-diacyetylpyridine dihydrazone, \(\text{L}^1\)

To a stirring solution of 2,6-diacyetylpyridine (0.3264 g, 2 mmol) in methanol (~20 ml) was added a solution of hydrazine (0.242 ml, 4 mmol) dissolved in methanol (~20 ml). The stirring continued for 6-8 h, resulting in a colourless solution. The resultant reaction mixture was allowed to stand for 48 h resulting in the isolation of microcrystalline solid.

Synthesis of dichloro/nitrate \(1,3:11,13\)-dipyridyl-4,10,14,20-tetra methyl-2,5,6,9,12,15,16,18,19-decaaza-4,9,14,19-tetraene cyclocicosane metal (II), \([\text{ML}^1\text{X}_{\text{n}}\text{(M = Mn\(^{II}\), Fe\(^{II}\), Co\(^{II}\), Ni\(^{II}\) and Zn\(^{II}\)}) and \([\text{CuL}^1\text{X}_{\text{n}}\text{(X=Cl, NO\(_3\))}\) and \(\text{MX}_{\text{n}}\text{nH\(_2\)O}\) were recorded on a Pye-Unicam 8800 spectrophotometer. EPR spectra were recorded on a JEOL JES RX2X EPR spectrophotometer. Magnetic susceptibility...
measurements were carried out using a Faraday Balance at 25°C. The electrical conductivities of $10^3$ M solutions in DMSO were obtained on a Digital conductivity meter APX 185 equilibrated at 25°C ± 0.05. $^1$H NMR spectra were recorded in DMSO-$d_6$ using a Jeol, Eclipse 400 with Me$_4$Si as an internal standard. The IR spectra (4000-200 cm$^{-1}$) were recorded as KBr discs on a Perkin-Elmer 2400 spectrophotometer.

Results and discussion

A new series of decaazamacrocyclic complexes $[ML\ X_2]$ and $[CuL\ X_2]$ (where $M =$ Mn$^{II}$, Fe$^{II}$, Co$^{II}$, Ni$^{II}$ and Zn$^{II}$; $X$=Cl, NO$_3$) have been prepared by the template condensation reaction of 2-6-diacetylpyridine dihydrazone, 'L' and formaldehyde in methanol medium in a 2:2 ratio (Scheme 1). An attempt was made to synthesize metal free macrocyclic ligand which resulted in an oily product. All the complexes are found to be stable to atmosphere at room temperature. These complexes are soluble in distilled water, DMSO and DMF. The results of elemental analyses (Table 1) correspond to the proposed macrocyclic framework. The low conductivity data ascertain the non-electrolytic nature of these complexes.

\[
\text{Scheme 1}
\]

Where, $M =$ Mn$^{II}$, Fe$^{II}$, Co$^{II}$, Ni$^{II}$ and Zn$^{II}$; $X$=Cl or NO$_3$; $Me$ = CH$_3$; $n$ = 1, 3, 6
Table 1—Analytical data and molar conductance values for the compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield</th>
<th>M.pt (°C)</th>
<th>Colour</th>
<th>Calcd (Found) %</th>
<th>( \Lambda_m ) (cm(^2) ohm(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L )</td>
<td>45</td>
<td>150</td>
<td>White</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{MnL'}\text{Cl}_2])</td>
<td>50</td>
<td>290</td>
<td>Dull green</td>
<td>10.16 (10.15)</td>
<td>13.37 (13.35) 45.19 (45.17) 4.89 (4.88) 26.36 (26.34)</td>
</tr>
<tr>
<td>([\text{MnL'}(\text{NO}_3)_2])</td>
<td>52</td>
<td>290</td>
<td>Dull green</td>
<td>9.24 (9.23)</td>
<td>- 41.09 (41.07) 4.45 (4.43) 28.76 (28.75)</td>
</tr>
<tr>
<td>([\text{FeL'}\text{Cl}_2])</td>
<td>60</td>
<td>&gt;300</td>
<td>Wine red</td>
<td>10.33 (10.31)</td>
<td>13.34 (13.33) 45.11 (45.10) 4.88 (4.87) 26.31 (26.30)</td>
</tr>
<tr>
<td>([\text{FeL'}(\text{NO}_3)_2])</td>
<td>55</td>
<td>&gt;300</td>
<td>Wine red</td>
<td>9.40 (9.39)</td>
<td>- 41.02 (41.01) 4.44 (4.43) 28.71 (28.70)</td>
</tr>
<tr>
<td>([\text{CoL'}\text{Cl}_2])</td>
<td>40</td>
<td>&gt;300</td>
<td>Dark brown</td>
<td>10.50 (10.49)</td>
<td>13.32 (13.30) 45.02 (45.01) 4.87 (4.86) 26.26 (26.24)</td>
</tr>
<tr>
<td>([\text{CoL'}(\text{NO}_3)_2])</td>
<td>45</td>
<td>&gt;300</td>
<td>Dark brown</td>
<td>9.55 (9.54)</td>
<td>- 40.95 (40.93) 4.43 (4.41) 28.66 (28.65)</td>
</tr>
<tr>
<td>([\text{NiL'}\text{Cl}_2])</td>
<td>38</td>
<td>185</td>
<td>Rust</td>
<td>10.84 (10.83)</td>
<td>13.27 (13.25) 44.85 (44.83) 4.85 (4.84) 26.16 (26.15)</td>
</tr>
<tr>
<td>([\text{NiL'}(\text{NO}_3)_2])</td>
<td>45</td>
<td>200</td>
<td>Rust</td>
<td>9.86 (9.85)</td>
<td>- 40.81 (40.80) 4.42 (4.41) 28.57 (28.55)</td>
</tr>
<tr>
<td>([\text{CuL'}\text{Cl}_2])</td>
<td>55</td>
<td>220</td>
<td>Yellow</td>
<td>11.66 (11.65)</td>
<td>13.14 (13.13) 44.44 (44.42) 4.81 (4.80) 25.92 (25.91)</td>
</tr>
<tr>
<td>([\text{CuL'}(\text{NO}_3)_2])</td>
<td>60</td>
<td>200</td>
<td>Yellow</td>
<td>10.62 (10.61)</td>
<td>- 40.47 (40.45) 4.38 (4.36) 28.33 (28.32)</td>
</tr>
<tr>
<td>([\text{ZnL'}\text{Cl}_2])</td>
<td>55</td>
<td>&gt;300</td>
<td>Colourless</td>
<td>11.99 (11.97)</td>
<td>13.09 (13.07) 44.28 (44.27) 4.79 (4.78) 25.83 (25.81)</td>
</tr>
<tr>
<td>([\text{ZnL'}(\text{NO}_3)_2])</td>
<td>65</td>
<td>&gt;300</td>
<td>Colourless</td>
<td>10.92 (10.91)</td>
<td>- 40.33 (40.31) 4.36 (4.34) 28.23 (28.22)</td>
</tr>
</tbody>
</table>

 complexes, except that of copper complexes, which were found to be 1:2 electrolyte\(^{32}\).

The preliminary information regarding the formation of 'L' has been inferred from bands observed in its IR spectrum. The disappearance of band corresponding to \( \nu(C=O) \) of formaldehyde group and appearance of a new strong intensity band at 1625 cm\(^{-1}\) assigned to \( \nu(C=N) \) of imine group strongly suggest the formation of 'L'. A strong doublet around 3360 cm\(^{-1}\) may be assigned to \( \nu(N-H) \) stretching mode of uncondensed primary amine group of hydrazine moiety. The appearance of bands at 2925 and 985 cm\(^{-1}\) may be assigned to \( \nu(C-H) \), and \( \nu(N-N) \) stretching vibration respectively in 'L'.

The IR spectra of all the complexes exhibit no band corresponding to \( \nu(C=O) \) of formaldehyde group rather a new strong intensity band appears in the region 3210-3260 cm\(^{-1}\) attributable\(^{31}\) to the \( \nu(N-H) \) stretching mode of secondary amines. This suggests that condensation between CO of formaldehyde moiety and NH\(_2\) of hydrazine moiety has occurred in presence of metal ion. The IR spectra of all the macrocyclic complexes
exhibit a medium intensity band in the region 1590-1620 cm\(^{-1}\) which may be assigned\(^{34,37}\) to a coordinated imine \(v(C=N)\) stretching vibration. The band in the region 1140-1220 cm\(^{-1}\) may reasonably be assigned to \(v(C-N)\) stretching vibration. An absorption band appears in the region 2850-2920 cm\(^{-1}\) in all the complexes, may reasonably be assigned to \(v(C-H)\) stretching vibrational modes. A medium intensity band around 940-975 cm\(^{-1}\) may be ascribed to the \(v(N-N)\) stretching mode.\(^{38}\) All the complexes show bands around 403, 601 and 1578 cm\(^{-1}\) consistent\(^{39,40}\) with the pyridine ring vibrations assignable to out-of-plane ring deformation and in-plane ring deformation, respectively. These vibrations do not suffer significant shift towards higher frequencies suggesting that pyridine nitrogen in the macrocyclic complexes is not coordinated to the metal atom.\(^{41}\) The presence of band in the region 330-490 cm\(^{-1}\) may be due to the \(v(M-N)\) bands observed in the regions 207-220 cm\(^{-1}\) and 228-240 cm\(^{-1}\) may be assigned\(^{42}\) to \(v(M-Cl)\) and \(v(M-O)\) stretching vibrations respectively. However, in the copper complex additional bands observed at 1630, 1280, 870 and 705 cm\(^{-1}\) may be reasonably assigned to the free nitrate group.

The \(^1^H\) NMR spectrum of \('L'\) shows peaks at 2.63 ppm which may be assigned to the methyl protons (CH\(_3\); 6H) of the 2,6-diacetylpyridine moiety. Multiplets in the region 7.75 and 7.38 ppm may be assigned\(^{45}\) to aryl protons \((H_u)\) and to \((2H_d)\) of \('L'\). Multiplets in the region 4.99 ppm may be attributed\(^{46}\) to \((N-NH,; 4H)\) protons of \('L'\).

The \(^1^H\) NMR spectra of the Zn(II) complexes show a major peak at 7.74-7.77 ppm and 7.35-7.39 ppm which may be assigned to the aryl \((2H_u)\) and \((4H_d)\) respectively. A singlet at 2.68-2.70 ppm may be reasonably assigned to the methyl \((CH_3; 12H)\) protons of the 2,6-diacetylpyridine moiety. The multiplets observed at 3.11-3.13 ppm may be attributed to the methylene.

### Table 2 - Magnetic moment values, electronic spectral data assignments and EPR data of the compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\mu_{\text{eff}}) (B.M.)</th>
<th>Band position (cm(^{-1}))</th>
<th>Assignments</th>
<th>EPR</th>
</tr>
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<tbody>
<tr>
<td>([\text{MnL}'\text{Cl}_2])</td>
<td>5.80</td>
<td>22,300</td>
<td>(^{g}A_g \rightarrow {^{g}T_g})</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18,750</td>
<td>(^{g}A_g \rightarrow {^{g}T_g})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{MnL}'(\text{NO}_3)_2])</td>
<td>5.78</td>
<td>22,350</td>
<td>(^{g}A_g \rightarrow {^{g}T_g})</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>18,800</td>
<td>(^{g}A_g \rightarrow {^{g}T_g})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{FeL}'\text{Cl}_2])</td>
<td>5.44</td>
<td>11,450</td>
<td>(^{g}T_g \rightarrow {^{g}E_g})</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11,850</td>
<td>(^{g}T_g \rightarrow {^{g}E_g})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{FeL}'(\text{NO}_3)_2])</td>
<td>5.40</td>
<td>11,850</td>
<td>(^{g}T_g \rightarrow {^{g}E_g})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{CoL}'\text{Cl}_2])</td>
<td>4.55</td>
<td>16,800</td>
<td>(^{g}T_g(F) \rightarrow {^{g}A_g(F)})</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22,200</td>
<td>(^{g}T_g(F) \rightarrow {^{g}T_g(P)})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{CoL}'(\text{NO}_3)_2])</td>
<td>4.54</td>
<td>16,500</td>
<td>(^{g}T_g(F) \rightarrow {^{g}A_g(F)})</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22,400</td>
<td>(^{g}T_g(F) \rightarrow {^{g}T_g(P)})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{NiL}'\text{Cl}_2])</td>
<td>3.05</td>
<td>11,500</td>
<td>(^{g}A_g(F) \rightarrow {^{g}T_g(F)})</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17,850</td>
<td>(^{g}A_g(F) \rightarrow {^{g}T_g(P)})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{NiL}'(\text{NO}_3)_2])</td>
<td>3.06</td>
<td>12,000</td>
<td>(^{g}A_g(F) \rightarrow {^{g}T_g(F)})</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>17,400</td>
<td>(^{g}A_g(F) \rightarrow {^{g}T_g(P)})</td>
<td>-</td>
</tr>
<tr>
<td>([\text{CuL}'\text{Cl}_2])</td>
<td>1.76</td>
<td>13,000</td>
<td>(^{3}B_g \rightarrow {^{3}B_g})</td>
<td>2.22</td>
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<tr>
<td></td>
<td></td>
<td>16,100</td>
<td>(^{3}B_g \rightarrow {^{3}A_g})</td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21,950</td>
<td>(^{3}B_g \rightarrow {^{3}E_g})</td>
<td>3.66</td>
</tr>
<tr>
<td>([\text{CuL}'(\text{NO}_3)_2])</td>
<td>1.77</td>
<td>12,100</td>
<td>(^{3}B_g \rightarrow {^{3}B_g})</td>
<td>2.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16,200</td>
<td>(^{3}B_g \rightarrow {^{3}A_g})</td>
<td>2.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21,600</td>
<td>(^{3}B_g \rightarrow {^{3}E_g})</td>
<td>3.42</td>
</tr>
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</table>
protons (N-CH$_2$-N; 4H) of the aldehyde moiety. The multiplets observed at 6.83-6.84 ppm may be assigned to the secondary amino group of the hydrazine moiety. But, no NMR signal has been observed in the complexes [Zn L*Cl] and [Zn L*(NO$_3$)$_2$] which correspond to the NH$_2$ protons of 'L' suggesting that condensation has taken place (Scheme 1.)

The EPR spectra of both the polycrystalline Cu(II) macrocyclic complexes were recorded at room temperature, and their $g_H$ and $g_A$ values were calculated. Neither of the decaazaamacroyclic Cu(II) complexes studied showed any hyperfine splitting, but gave only a derivative curve giving $g_H$ and $g_A$ values, (Table 2), as characteristic$^{49}$ of square planar copper (II) complexes. This suggests that the unpaired electron is present in the $d_{xy}$ orbital as $g_H > g_A > 2.02$. In an axial symmetry, the $g$ values are related by the expression $G = (g_H^2 - 2)/(g_A^2 - 2)$, which measures the interaction between copper centres in the unit cell. The calculated 'G' values for the present complexes appeared in the range 3.42 and 3.66, suggesting the existence of a considerable exchange interaction between copper, as G<4. All the complexes show $g_H < 2.3$. It should be noted$^{44}$ that for an ionic environment while for a covalent environment $g_H < 2.3$, indicating that the present complexes exhibit considerable covalent character.

The appearance of two bands in the electronic spectra (Table 2) of the manganese complex in the regions 18,750-18,800 cm$^{-1}$ and 22,300-22,350 cm$^{-1}$ may reasonably correspond$^{52}$ to the $^6A_1g \rightarrow ^4T_{2g}g$ and $^6A_1g \rightarrow ^4T_{2g}$ transitions, respectively consistent with an octahedral geometry around the manganese (II) ion. The electronic spectra of the iron complexes exhibit a weak intensity (d-d) transition in the region 11,450-11,850 cm$^{-1}$, which may be reasonably assigned to the $^5T_{2g} \rightarrow ^5E_g$ transition, consistent with a high-spin octahedral environment around iron (II) ion. However, the electronic spectra of the cobalt complexes exhibit two bands in the regions 16,500-16,800 cm$^{-1}$ and 22,200-22,400 cm$^{-1}$ which may reasonably correspond to the $^4T_{1g}(F) \rightarrow ^4A_{2g}(F)$ and $^4T_{1g}(P) \rightarrow ^4T_{1g}(P)$ transitions, respectively, suggesting$^{53}$ an octahedral geometry for the complexes. The ligand field spectra for nickel(II) macrocyclic complexes show two bands in the regions 11,500-12,000 cm$^{-1}$ and 17,400-17,850 cm$^{-1}$ which may be ascribed$^{54}$ to the $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ and $^3A_{2g}(P) \rightarrow ^3T_{1g}(P)$ transitions, respectively, indicating an octahedral environment around the nickel(II) ion. The copper complexes gave three bands in their electronic spectra in the regions 12,100-13,000 cm$^{-1}$; 16,100-16,200 cm$^{-1}$ and 21,600-21,950 cm$^{-1}$ and these bands may reasonably assigned to the $^3B_{1u} \rightarrow ^3B_{2g}$, $^3B_{1u} \rightarrow ^3A_{1g}$ and $^3B_{1u} \rightarrow ^3E_g$ transitions respectively. The above results are consistent with the square planar geometry of copper (II) complexes.

The observed magnetic moment values (Table 2) for all these metal complexes are in close agreement with electronic spectral data which further support their proposed geometry.

Acknowledgements

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References

NOTES

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