Synthesis and characterization of highly conjugated 22-membered octaazamacrocycles and their manganese(II), copper(II), cobalt(II) and zinc(II) complexes

Division of Inorganic Chemistry, Department of Chemistry, Aligarh Muslim University, Aligarh 202 002, India

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A new series of 21-membered macrocyclic complexes \([MLX_2]\) \([M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X=Cl or NO_3]\) has been synthesized by template reaction of phthalaldehyde with hydrazine hydrate and 2,4-pentanedione in methanol. The overall geometry and stereochemistry of these complexes have been elucidated by IR, \(^1\)H NMR, EPR, UV-vis, magnetic susceptibility and conductance values. An octahedral geometry around the metal ion is suggested for all the complexes.

The synthetic, kinetic and structural aspects\(^{1-4}\) of polyazamacrocyclic complexes have received considerable attention. Recently, we have also synthesized a variety of polyazamacroyclic systems\(^ {5-9}\).

Macroyclic complexes are best prepared with the aid of metal ions as templates to direct the steric course of the condensation reaction which ultimately results in ring closure\(^ {10-12}\). We have recently reported several\(^ {13-16}\) macrocyclic complexes incorporating hydrazine moiety in the macrocyclic frame work. Here, we wish to report the synthesis and characterization of octaazamacroyclic complexes \([MLX_2]\) \([M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X=Cl or NO_3]\) synthesized from hydrazine hydrate, 2,4-pentanedione and phthalaldehyde.

**Experimental**

The metal salts MnX_2.4H_2O, CoX_2.6H_2O, NiX_2.6H_2O, CuX_2.2H_2O \((X=Cl\ or NO_3)\), ZnCl_2 and Zn(NO_3)_2.6H_2O (all BDH) were commercially pure samples. The chemicals, phthalaldehyde and hydrazine hydrate were obtained from BDH and were used as received; 2,4-pentanedione was purchased from E. Merck.

Preparation of dichlorodinitrato \((8,9,19,20\text{-dibenzoo}-2,4,13,15\text{-tetramethyl-1,5,6,11,12,16,17,22-octaaazacyclobicose}\ (-1,4,6,10,12,15,17,21\text{-octene})\) \([MLX_2]\) \([M=Mn(II), Co(II), Ni(II), Cu(II) and Zn(II); X=Cl or NO_3]\)

The respective metal salt \((0.01 \text{ mol})\) was dissolved in MeOH in a two-necked round bottomed flask. Hydrazine hydrate \((0.04 \text{ mol})\) and 2,4-pentanedione \((0.02 \text{ mol})\) were both dissolved in MeOH and simultaneously stirring was continued for 30 min and then phthalaldehyde \((0.02 \text{ mol})\) in MeOH was added to the mixture. The mixture was stirred for a further period of 5h at room temperature. The resulting solid product was removed by filtration, washed with MeOH and vacuum dried.

Elemental analyses were obtained from the microanalytical laboratory of CDRI, Lucknow, India. \(^1\)H-NMR spectra in DMSO-\(d_6\) using a Bruker AC 200 E spectrometer with Me_4Si as internal standard were obtained from GNDU, Amritsar, India. Metals\(^ {17}\) and chloride\(^ {18}\) were determined by standard methods. The IR spectra \((4000-200 \text{ cm}^{-1})\) were recorded as KBr discs on a Perkin-Elmer 621 spectrophotometer. The electronic spectra of the compounds in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer at room temperature. EPR spectra were recorded on a JEOL JES RE2X EPR spectrometer. Magnetic susceptibility measurements were carried out using a Faraday balance at 300 K, at BHU, Varanasi, India. The electrical conductivities of \(10^3 \text{ M}\) solutions in DMSO were obtained on a Systronic type 302K conductivity bridge equilibrated at 25°C.
Table 1—Melting point, colour, elemental analysis, $\mu_{\text{eff}}$ (B.M.) and electronic spectral data of the compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>M.P. (°C)</th>
<th>Colour</th>
<th>Found (Calc.) (%)</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>Electronic spectral bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[MnLCl$_2$]</td>
<td>190</td>
<td>Pinkish white</td>
<td>C:54.2, H:5.0, N:19.3, M:9.2</td>
<td>5.80</td>
<td>22500, 19600</td>
</tr>
<tr>
<td>[MnL(NO$_3$)$_2$]</td>
<td>210</td>
<td>White</td>
<td>C:50.0, H:4.2, N:22.0, M:8.9</td>
<td>5.78</td>
<td>23450, 19100</td>
</tr>
<tr>
<td>[CoLCl$_2$]</td>
<td>270</td>
<td>Blue</td>
<td>C:53.7, H:4.9, N:19.3, M:10.5</td>
<td>4.55</td>
<td>21900, 14200</td>
</tr>
<tr>
<td>[CoL(NO$_3$)$_2$]</td>
<td>265</td>
<td>Light blue</td>
<td>C:48.9, H:4.3, N:22.5, M:9.1</td>
<td>4.61</td>
<td>22400, 14000</td>
</tr>
<tr>
<td>[NiLCl$_2$]</td>
<td>&gt;300</td>
<td>Dark green</td>
<td>C:54.0, H:4.3, N:19.5, M:10.2</td>
<td>3.10</td>
<td>17500, 11700</td>
</tr>
<tr>
<td>[NiL(NO$_3$)$_2$]</td>
<td>&gt;300</td>
<td>Greenish yellow</td>
<td>C:48.9, H:4.2, N:22.3, M:9.5</td>
<td>3.15</td>
<td>17900, 11500</td>
</tr>
<tr>
<td>[CuLCl$_2$]</td>
<td>280</td>
<td>Yellowish green</td>
<td>C:53.0, H:4.8, N:19.5, M:10.5</td>
<td>1.75</td>
<td>19000, 16400</td>
</tr>
<tr>
<td>[CuL(NO$_3$)$_2$]</td>
<td>300</td>
<td>Pale fern</td>
<td>C:49.0, H:4.4, N:21.3, M:9.6</td>
<td>1.74</td>
<td>19400, 16200</td>
</tr>
<tr>
<td>[ZnLCl$_2$]</td>
<td>250</td>
<td>Dirty white</td>
<td>C:53.2, H:4.9, N:19.1, M:10.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[ZnL(NO$_3$)$_2$]</td>
<td>260</td>
<td>Cream</td>
<td>C:48.9, H:4.4, N:22.0, M:10.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Results and discussion

The template reaction of hydrazine hydrate, 2,4-pentanedione, phthalaldehyde and with metal ion in a 4:2:2:1 molar ratio resulted in the isolation of a new class of octaazaimine macrocyclic complexes. The elemental analysis results (Table 1) are consistent with the proposed 1:1 (metal-to-ligand) stoichiometry as shown in Scheme 1. The molar conductance values of all these complexes are indicative of their non-electrolytic nature. They are stable in air and insoluble in most of the organic solvents except DMSO and DMF.

The IR spectra of all the complexes exhibit a single sharp absorption band in the 1590-1620 cm$^{-1}$ region, attributed to the coordinated v(C=N). The bands characteristic of amino or keto groups were not observed. However, a medium intensity band observed in the 410-440 cm$^{-1}$ region may reasonably be assigned to the (M-N) stretching vibration. Bands appearing in the regions 2890-2930 and 1410-1450 cm$^{-1}$ in all the complexes may be due to v(C-H) and $\delta$(C-H), respectively. The spectra of nitrat complexes gave additional bands around 1230, 1050 and 870 cm$^{-1}$, which are consistent with the monodentate nature of this group. Bands observed at 230-240 and 275-300 cm$^{-1}$ in the nitrate and chloro complexes are assignable to v(M-O) and v(M-Cl), respectively.

The EPR spectra of the polycrystalline copper(II) macrocyclic complexes were recorded at room temperature. Their $g_{\parallel}$ and $g_{\perp}$ values have been calculated. The spectra exhibit no hyperfine splitting which may be due to the fact that the paramagnetic centers are not diluted. In a $d_{x^2-y^2}$ ground state, the EPR spectrum should give $g_{\perp}>g_{\parallel}>2.02$ whilst a $d_{z^2}$ ground state usually gives a spectrum with $g_{\perp}>g_{\parallel}$ $\sim$ 2.02. The copper complexes, [CuLCl$_2$] show $g_{\parallel}$ and
$d_{x^2-y^2}$ and $d_{z^2}$ orbitals, respectively, which suggest that there may be a ligand to metal charge transfer excitation and a broad absorption around the Ni($\text{II}$) ion. The electronic spectra of the complexes show two bands in the 19,000-19,400 cm$^{-1}$ region which may be assigned to an octahedral geometry for the manganese ion. The complexes show a multiplet in the region 7.16-7.32 ppm which may be assigned to aromatic ring protons. The spectra show singlet at 8.30-8.38 ppm which may be assigned to the four equivalent carboximine protons (CH=N; 4H).

The electronic spectra of manganese complexes exhibit two bands in the 22,500-23,450 and 19,100-19,600 cm$^{-1}$ regions assignable to $A_{1g} \rightarrow T_{2g}$ and $A_{1g} \rightarrow T_{1g}$ transitions, respectively, corresponding to an octahedral geometry for the manganese ion. The cobalt complexes show two bands appearing at 21,900-22,400 and 14,000-14,200 cm$^{-1}$ assignable to the transition $T_{1g}(F) \rightarrow T_{1g}(P)$ and $T_{1g}(F) \rightarrow A_{2g}(F)$. However, the electronic spectra of nickel(II) complexes show two bands in the 17,500-17,900 and 11,500-11,700 cm$^{-1}$ region which may be assigned to $A_{2g} \rightarrow T_{1g}(P)$ and $A_{2g} \rightarrow T_{1g}(F)$ transitions, respectively, suggesting an octahedral geometry around the Ni(II) ion. The electronic spectra of the macrocyclic copper(II) complexes show a broad band in the region 19,000-19,400 cm$^{-1}$ which may be ascribed to $B_{1g} \rightarrow 2E_g$ and $B_{1g} \rightarrow 2B_{2g}$ transitions, respectively, corresponding to a distorted octahedral geometry around the copper(II) ion. The high intensity band observed at ca 37,000 cm$^{-1}$ for all the complexes in the U.V. region may be assigned to a ligand to metal charge transfer excitation and a broad absorption maximum at ca 29,500 cm$^{-1}$ may be due to the n-$\pi^*$ ligand transition.

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**References**