Synthesis & Characterization of Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) & Mercury(II) Complexes with 3-Amino-2-acetylbenzofuran

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Preparation and properties of complexes of the type MLCl₂ [M = Co(II), Cu(II), Cd(II) or Hg(II)] and M'L₂Cl₂ [M' = Ni(II) or Zn(II)] with 3-amino-2-acetylbenzofuran (L) are described. The electronic spectra, magnetic moments and infrared spectra of the solid complexes have been used to assign their structures. The ligand field parameters like Dq, B, J and LFSE for Co(II), Ni(II) and Cu(II) complexes have been calculated. These parameters indicate that the complexes have octahedral geometry. The Zn(II) and Hg(II) complexes are sparingly soluble in common organic solvents, whereas Zn(II) and Hg(II) complexes are soluble in acetone, acetonitrile and nitrobenzene. The molar conductance values in DMF (Table 1), indicate that Co(II), Ni(II) and Zn(II) complexes are 1:1 electrolytes and the Cu(II) complex is a 1:2 electrolyte. The Cd(II) and Hg(II) complexes are non-electrolytes. The analytical data (Table 1) suggest 1:2 (metal:ligand) stoichiometry for Ni(II) and Zn(II) complexes, while rest of the complexes have 1:1 stoichiometry.

In continuation of our earlier work1 on the transition and non-transition metal complexes of substituted benzofurans, we report here the preparation and properties of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with 3-amino-2-acetylbenzofuran (L). The benzofuran derivatives are well known as antibacterial and antifungal agents2 but only a limited amount of information is available on metal complexes of such derivatives3,4 and no work has been reported earlier on metal complexes of 3-amino-2-acetylbenzofuran.

The chemicals used were of AR or GR grade. The ligand, 3-amino-2-acetylbenzofuran, was prepared by the known procedure5. The complexes were prepared by adding a hot ethanolic solution of the ligand to a hot solution of metal chloride in ethanol in 1:1 (M:L) [1:2 in the case of Ni(II) and Zn(II)] molar ratio with constant stirring. The Cd(II) complex separated out immediately after refluxing the reaction mixture, but the Zn(II) and Hg(II) complexes were isolated only after refluxing the reaction mixture for about 40-50 min and by adding solid sodium acetate to raise the pH. The solution was further concentrated; the complex separated on cooling; it was filtered and washed with a little alcohol. In the case of Co(II), Ni(II) and Cu(II) the complexes were isolated after refluxing for 1 hr, concentration and treatment with pet-ether (60-80°). The products were filtered, and washed with a little alcohol.

The details of elemental analyses, measurement of magnetic susceptibilities and molar conductances, and recording of infrared spectra are described in an earlier paper1. The electronic spectra were recorded in nujol and in DMF solution (~ 10⁻³ M) in the ranges 1500-300 and 900-340 nm on DMR-21 and Elico model CL-24 spectrophotometers respectively.

The complexes are stable towards light and atmosphere. All the complexes are soluble in DMF and DMSO. The Co(II), Ni(II), Cu(II) and Cd(II) complexes are sparingly soluble in common organic solvents, whereas Zn(II) and Hg(II) complexes are soluble in acetone, acetonitrile and nitrobenzene. The molar conductance values in DMF (Table 1), indicate that Co(II), Ni(II) and Zn(II) complexes are 1:1 electrolytes and the Cu(II) complex is a 1:2 electrolyte. The Cd(II) and Hg(II) complexes are non-electrolytes. The analytical data (Table 1) suggest 1:2 (metal:ligand) stoichiometry for Ni(II) and Zn(II) complexes, while rest of the complexes have 1:1 stoichiometry.

The observed electronic spectra of Co(II) complex is typical of the high-spin octahedral species.6,9 The bands observed at 8403 and 19610 cm⁻¹ are attributed to ⁴T₁g(F) → ⁴T₂g(F)(v₁) and ⁴T₁g(F) → ⁴T₁g(P)(v₃) transitions respectively. The highest energy band around 30770 cm⁻¹ is assigned to a charge-transfer transition. The v₂ band corresponding to the transition ⁴T₁g(F) → ⁴A₂g(F) could not be observed probably because of low intensity. However, its energy value (17945 cm⁻¹) has been calculated [v₂ = v₁ + 10Dq] which lies close to the value for v₃ band. The solid, brown-coloured Co(II) complex dissolves in DMF forming a blue-coloured solution, which may probably be due to change of configuration from the polymeric octahedral species to a tetrahedral monomeric form. The calculated values of Dq, Racah parameter (B'),

<p>| Table 1 — Analytical, Molar Conductance and Magnetic Susceptibility Data of the Complexes |</p>
<table>
<thead>
<tr>
<th>Complex</th>
<th>µₑff (B.M.)</th>
<th>Found</th>
<th>Calcd.</th>
<th>λₑff (ohm⁻¹ cm² mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoLCl₂</td>
<td>4.8</td>
<td>19.60</td>
<td>4.32</td>
<td>23.60</td>
</tr>
<tr>
<td>NiL₂Cl₂</td>
<td>3.22</td>
<td>12.11</td>
<td>5.62</td>
<td>14.61</td>
</tr>
<tr>
<td>CuLCl₂</td>
<td>1.92</td>
<td>20.84</td>
<td>4.30</td>
<td>22.55</td>
</tr>
<tr>
<td>ZnL₂Cl₂</td>
<td>—</td>
<td>13.55</td>
<td>5.59</td>
<td>14.54</td>
</tr>
<tr>
<td>CdLCl₂</td>
<td>—</td>
<td>31.52</td>
<td>3.85</td>
<td>19.62</td>
</tr>
<tr>
<td>HgLCl₂</td>
<td>—</td>
<td>44.50</td>
<td>3.34</td>
<td>15.72</td>
</tr>
</tbody>
</table>
nephelauxetic parameter $\beta$, the ratio $v_2/v_1$ and ligand field stabilisation energy are 954 cm$^{-1}$, 823 cm$^{-1}$, 0.85, 2.13 and 16.35 kcal/mol respectively\textsuperscript{10}. These values suggest an octahedral geometry around Co(II) ion\textsuperscript{11}. The octahedral geometry is further supported by the magnetic moment data (Table I).

The electronic spectrum of Ni(II) complex exhibits three bands around 8333, 13,700 and 25,640 cm$^{-1}$ which are assigned to $(v_1)A_2g\rightarrow T_2g(F)$; $(v_2)^3A_2g\rightarrow T_2g(F)$ and $(v_3)^3A_2g\rightarrow T_1g(P)$ transitions respectively in an octahedral environment. The value of Racah parameter, $B'$ (973), is less than the free ion value (1040) indicating a considerable covalent character of the metal-ligand bond. The $v_2/v_1$ ratio (1.64) is in the usual range (1.6-1.82) expected for octahedral symmetry\textsuperscript{12}. The $\mu_{\text{eff}}$ value calculated from the spectral data by using the equation\textsuperscript{13}: $\mu_{\text{eff}} = 2.83 \times (1-4 \lambda/10 Dq)$, where $\lambda = -315$ and $10 Dq = 8333$; is 3.25 B.M., which is very close to the observed value of 3.20 B.M. The light-green coloured Ni(II) complex retains its colour in DMF solution, and the electronic spectrum of this solution shows two bands at 14,814 and 25,000 cm$^{-1}$ assignable to $v_2$ and $v_3$ transitions in an octahedral geometry. Hence Ni(II) complex retains its geometry in solution. The band around 28,000 cm$^{-1}$ is assigned to a charge-transfer transition.

The light-green coloured Cu(II) complex exhibits a broad asymmetric band around 14,080 cm$^{-1}$ attributable to $d$-$d$ transition in a distorted octahedral geometry. The broadness of the band may be due to Jahn-Teller distortion. Duff et al.\textsuperscript{14} have reported that the absorption band in this region is due to the tetragonally distorted octahedral environment around the metal ion. The $\mu_{\text{eff}}$ value has been calculated by using the formula. $\mu_{\text{eff}} = 1.73 \times (1-2 \lambda/10 Dq)$, where $\lambda = -830$; the value is very close to the observed value (1.92 B.M.). The solution spectrum of Cu(II) in DMF shows a broad band around 14,710 cm$^{-1}$. This indicates that the geometry around Cu(II) ion in solution is unchanged. The band around 26,320 cm$^{-1}$ has been assigned to a charge-transfer transition.

The ligand exhibits strong IR bands in the region 3430-3210 cm$^{-1}$ in nujol mull, while in chloroform these bands shift to the region 3490-3370 cm$^{-1}$; thus these may be attributed to hydrogen bonded NH$_2$ stretch\textsuperscript{15}. The strong bands observed at 1645 and 1605 cm$^{-1}$ in nujol also show a large positive shift and are observed around 1760 cm$^{-1}$ in the solution (chloroform) spectrum; these bands are attributable to H-bonded carbonyl stretching frequencies\textsuperscript{15}. The H-bonding in the free ligand can be through oxygen of C = O group and hydrogen of NH$_2$ group, thus forming the quasi-aromatic six membered ring. On complex formation the H-bonding breaks up and coordination occurs with NH$_2$ and/or CO groups. The coordination of these groups and breaking up of H-bonding have opposite effects on the NH/CO stretching frequencies, thereby showing no appreciable shift in NH/CO stretching frequencies in spectra of complexes\textsuperscript{16}. Thus, the bands due to NH$_2$ stretch remain unperturbed or show slight red shifts in all the complexes except in the cases of Cu(II) and Cd(II) complexes. For the latter two complexes, a blue shift of about 75-20 cm$^{-1}$ occurs showing non-involvement of NH$_2$ group in bonding. In all the complexes the bands due to C = O stretch shift only slightly to lower frequency side (~5-10 cm$^{-1}$).

The ligand bands (nujol) observed in the region 1200-1100 cm$^{-1}$ are attributed to C - O - C (furan ring) stretch\textsuperscript{17,18}. These bands remain unaltered or shift towards higher frequency side in all the complexes except in the cases of Cu(II) and Cd(II) complexes, suggesting non-involvement of furan oxygen in coordination. In Cu(II) and Cd(II) complexes, these bands show negative shift of about 10-15 cm$^{-1}$ indicating coordination. The involvement of furan oxygen in coordination in the latter two complexes is further supported by the appearance of non-ligand bands at 510 and 555 cm$^{-1}$ which may be attributed to M - O stretching vibrations\textsuperscript{19}. The low frequency bands in the regions 460-405 and 350-310 cm$^{-1}$ are assigned to M - N and M - O (carbonyl) stretching vibrations respectively\textsuperscript{20,21}. The bands observed in the region 290-250 cm$^{-1}$ are ascribed to $v$M - Cl (terminal) vibrations\textsuperscript{22}. The low intensity bands at 265 and 250 cm$^{-1}$ are attributed to $v$M - Cl (bridging) vibrations\textsuperscript{23} in the case of Co(II) and Cu(II) complexes respectively in view of their polymeric nature.

Based upon the above spectral features, magnetic moments and insolubility in common organic solvents, the halogen-bridged polymeric octahedral structure may be assigned to Co(II) and Cu(II) complexes, while a ligand-bridged polymeric octahedral structure may be assigned to Ni(II) complex. The high conductivity of this complex suggests the presence of ionic chloride in DMF. But the electronic and IR spectra indicate that the chloride ions are weakly coordinated in solid state\textsuperscript{14}. The Zn(II) and Hg(II) complexes may have monomeric octahedral and tetrahedral structures respectively and the Cd(II) complex may be of ligand-bridged polymeric tetrahedral type.

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References

7 Geary W J, Coord chem Rev, 7 (1971) 81.