Synthesis and characterization of the complexes of chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) with 5-(2-hydroxybenzylidene)amino-benzopyrazole

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Complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with 5-(2-hydroxybenzylidene)amino-benzopyrazole (HBAB) have been prepared and characterized. The IR spectral studies indicate that the ligand acts as a bidentate donor and coordinates through the nitrogen of the azomethine group and deprotonated OH group. The complexes [M(HBAB)] (M = Cr, Fe) and [M(HBAB)_2·2H_2O] (M = Mn, Co, and Ni) have been assigned an octahedral geometry whereas Cu(HBAB)_2 is proposed to be square-planar. The ligand field parameters, 10Dq and B, have also been calculated.

The chemistry of pyrazole and related ligand has been extensively investigated. Benzopyrazole and its derivatives have been reported to possess corrosion inhibition activities. Considerable interest has centred on the synthesis and structural studies on metal complexes of benzopyrazoles and benzopyrazole-derived ligands in recent years. Some antifungal transition metal chelates of analogous 2-(2'-hydroxybenzylidene)aminobenzimidazole ligand have recently been reported.

In this paper we describe the synthesis and characterization of a new ligand derived from 5-aminobenzopyrazole and salicylaldehyde and its complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II).

Results and discussion

The analytical results and magnetic moments of the complexes are summarized in Table 1. The results of elemental analysis are in good agreement with the proposed formulae of the ligand and its complexes. The IR spectrum of the ligand shows a medium intensity band at 3250-3200 cm⁻¹ attributable to νN-H mode. A broad medium intensity band around 3420 cm⁻¹ is attributed to νOH (phenolic) mode. A strong band at 1640 cm⁻¹ is a characteristic of the azomethine (-HC=N-) group. The present ligand has four potential coordinating positions; the unsaturated nitrogen atom of the heterocyclic ring, the nitrogen of the azomethine group and oxygen and nitrogen atoms of the OH and NH groups. A comparison of the IR spectra of complexes with the ligand shows a shift towards lower wavenumbers by 20-40 cm⁻¹ in νHC=N band which indicates coordination through the nitrogen lone pair.

The νC=O (phenolic) band in the ligand is observed at a relatively higher frequency at 1500 cm⁻¹ presumably due to the partial double bond character of the neighbouring benzene ring. This band is shifted to 1580-1575 cm⁻¹ in its complexes indicating coordination through the oxygen atom of the hydroxyl group. Coordination through oxygen is further substantiated by the disappearance of the O-H deformation band of the ligand (1400 cm⁻¹) in these complexes. The C=N (heterocyclic ring) and N-H stretching frequencies appear at about the same positions. This rules out the possibility of coordination through the carbonyl group.

Experimental

All the reagents were obtained commercially and used as such.

Preparation of 5-(2-hydroxybenzylidene)amino-benzopyrazole and its complexes

The ligand was prepared from 5-aminobenzopyrazole (10g, 75.0 mmol) and salicylaldehyde (9.18g, 75.10 mmol) by usual condensation method. The complexes were prepared by mixing the aqueous solution of 2.10 mmol metal chlorides and HBAB (4.21 mmol) in hot ethanol (50ml). The reaction mixture was magnetically stirred for 2-3 hr and concentrated gradually until the solid product appeared. In some cases, the solid appeared immediately after mixing. The complexes thus obtained were filtered, washed and dried in vacuo.

Analysis for metals was performed by standard methods. Carbon, hydrogen and nitrogen were determined microanalytically. IR spectra (4000-200 cm⁻¹) were recorded with a Perkin-Elmer spectrophotometer model 621. Magnetic moments were determined by a vibrating sample magnetometer model 155. Reflectance spectra were taken on a Carl-Zeiss VSU-2P spectrophotometer.
Table 1—Melting point, magnetic moment and analytical data of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>M.P. (°C)</th>
<th>Feff. (B.M.)</th>
<th>Found (Calc.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_{14}H_{11}N_{3}O</td>
<td>218</td>
<td>-</td>
<td>70.6 4.9 17.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(70.87 4.67 17.7 -)</td>
</tr>
<tr>
<td>Cr(C_{14}H_{10}N_{3}O)_{3}</td>
<td>275</td>
<td>3.68</td>
<td>66.7 4.1 16.8 6.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(66.31 3.97 16.5 6.83)</td>
</tr>
<tr>
<td>Mn(C_{14}H_{10}N_{3}O)<em>{2}H</em>{2}O</td>
<td>230</td>
<td>5.94</td>
<td>59.8 3.7 14.8 9.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(59.68 3.57 14.91 9.75)</td>
</tr>
<tr>
<td>Fe(C_{14}H_{10}N_{3}O)_{3}</td>
<td>250</td>
<td>5.83</td>
<td>65.8 3.8 16.7 7.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(66.01 3.95 16.49 7.25)</td>
</tr>
<tr>
<td>Co(C_{14}H_{10}N_{3}O)<em>{2}H</em>{2}O</td>
<td>240</td>
<td>4.90</td>
<td>59.1 4.0 14.6 10.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(59.26 3.90 14.81 10.38)</td>
</tr>
<tr>
<td>Ni(C_{14}H_{10}N_{3}O)<em>{2}H</em>{2}O</td>
<td>270</td>
<td>3.06</td>
<td>59.0 3.7 14.6 10.6</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(59.29 3.90 14.81 10.35)</td>
</tr>
<tr>
<td>Cu(C_{14}H_{10}N_{3}O)_{2}</td>
<td>260</td>
<td>1.89</td>
<td>62.5 3.9 15.3 11.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(62.73 3.76 15.67 11.85)</td>
</tr>
</tbody>
</table>

nitrogen atoms of these groups.

The non-ligand bands around 430-400 and 360-320 cm\(^{-1}\) may be tentatively assigned to \(\nu M\cdot O\) and \(\nu M\cdot N\) modes, respectively. The bands at 900-800 and 650-610 cm\(^{-1}\) in the Mn(II), Co(II) and Ni(II) complexes may be due to coordinated water.

In case of Cr(III) and Fe(III) complexes the observed magnetic moment values (3.68 and 5.83 BM) are quite close to the calculated value for an octahedral geometry. The reflectance spectrum of Cr(III) complex exhibits three bands at 36200, 24400 and 17300 cm\(^{-1}\) assignable to \(4T_{2g}(P) \rightarrow 4A_{2g},\ 4T_{2g}(F) \rightarrow 4A_{2g}\) and \(4T_{2g}(F) \rightarrow 4A_{2g}\) transitions, respectively. For Fe(III) complex only two bands are observed at 23600 and 19100 cm\(^{-1}\). These bands may be assigned to \(4T_{1g}(G) \rightarrow 6A_{1g}\) and \(4T_{1g}(G) \rightarrow 6A_{1g}\) transitions, respectively in an octahedral field. Using a set of the assigned ligand field transitions on the appropriate Tanabe-Sugano diagram, we calculated 10\(Dq\) and \(B\) values. The 10\(Dq\) and \(B\) values for Cr(III) complex are 10008 and 520 cm\(^{-1}\) respectively. Values of 10\(Dq\) = 10876 and \(B=83\) cm\(^{-1}\) were obtained for Fe(III) complex.

The magnetic moment of the Mn(II) complex suggests that the compound has high-spin octahedral configuration. Three \(d\)-\(d\) transitions at 29000, 24200 and 20000 cm\(^{-1}\) are assigned to \(4A_{1g}(G) \rightarrow 6A_{1g},\ 4T_{2g}(G) \rightarrow 6A_{1g}\) and \(4T_{2g}(G) \rightarrow 6A_{1g}\) respectively suggesting octahedral stereochemistry. The values of 10\(Dq\) and \(B\) are found to be 10008 and 834 cm\(^{-1}\), respectively.

The magnetic moment for the Co(II) complex is 4.9B.M., which cannot be used to distinguish between tetrahedral and octahedral configurations\(^{16}\). Its reflectance spectrum is typical of six-coordinated Co(II) and does not resemble tetrahedral Co(II) spectra which are reported\(^{17}\) not to have ligand-field bands above 18000 cm\(^{-1}\). The lowest energy band at 9900 cm\(^{-1}\) is assigned to \(4T_{2g} \rightarrow 4T_{1g}\) transition (\(v_{1}\)). The main band at 23200 cm\(^{-1}\) may be assigned to \(4T_{1g}(P) \rightarrow 4T_{1g}\) transition (\(v_{2}\)). The position of the \(v_{2}\) band (\(4A_{2g} \rightarrow 4T_{1g}\) transition) which is not observed in the spectrum has been calculated at 20718 cm\(^{-1}\) by the relation \(v_{2} = v_{1} +10Dq\). The ligand-field parameters (10\(Dq\) = 10818 cm\(^{-1}\), \(B=950\) cm\(^{-1}\)) calculated by reported method\(^{18}\) and the \(v_{2}/v_{1}\) ratio (2.09) are consistent with the proposed octahedral structure. Using the relationship \(\lambda = -0.168B/2Dq\), we obtained \(|\lambda|\)-value of 140 cm\(^{-1}\). The lower value of \(|\lambda|\) compared to that of free ion (\(-170\) cm\(^{-1}\)) suggests considerable orbital overlap. The value of the covalency parameters, (\(y=80\%\)) is close to the values reported for some N- and O-donor (84-86\%) ligands\(^{19}\).

The electronic spectrum of the high-spin Ni(II) complex exhibits three ligand-field bands at 10270 (\(v_{1} = 10Dq\)), 17200 (\(v_{2}\)) and 27000 (\(v_{3}\)) cm\(^{-1}\) assigned to the \(3^{3}T_{2g} \rightarrow 3A_{2g},\ 3^{3}T_{1g} \rightarrow 3A_{2g}\) and \(3^{3}T_{1g}(P) \rightarrow 3A_{2g}\) transitions, respectively suggesting octahedral field around Ni(II). The fact that \(v_{2}\) band is stronger than \(v_{1}\) agrees well with their assignment as octahedral structure. The \(v_{2}/v_{1}\) ratio is also well within the characteristic 1.5-1.7 range reported for octahedral Ni(II) complexes. The nephelauxetic parameter, \(B\) has been calculated to
be 846 cm$^{-1}$. Compared to the free-ion value of -315 cm$^{-1}$, there is a reduction in the calculated$^{20}$ $\lambda$-value of -188 cm$^{-1}$ for this complex which indicates significant orbital contribution and covalent character. The low $\beta$ value of 0.80 signifies a fair amount of covalency in Ni–L bond.

Copper(II) complex has a magnetic moment value of 1.89BM frequently attributed to square-planar configuration. The solid reflectance spectrum of the Cu(II) complex displays two $d$-$d$ transitions at 15500 and 20300 cm$^{-1}$ which may be assigned to the transitions $2A_{1g} \rightarrow 2B_{1g}$ and $2E_g \rightarrow 2B_{1g}$ respectively assuming square-planar stereochemistry.

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References