Hydrazones derived by the condensation of 4-methoxybenzoyl hydrazide with salicylaldehyde, \(\alpha\)-hydroxyacetophenone and diacetylmonoxime as ligands for cobalt (II & III)

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Reactions of salicylaldehyde 4-methoxybenzoyl hydrazone, \((H_2)SMBHON\), \(\alpha\)-hydroxyacetophenone 4-methoxybenzoyl hydrazone, \((H_2)OHAPMBHON\), and diacetylmonoxime 4-methoxybenzoyl hydrazone \((H_2)DAMMBHON\) with \(Co(OAc)_2\), \(CoCl_2\cdot6H_2O\), \(Co(NO_3)_2\cdot6H_2O\) and \(Co(ac-ac)_2\cdot2H_2O\) under varied reaction conditions have been studied and many new mono-nuclear and di-nuclear complexes of cobalt(II) and cobalt(III) have been isolated. The complexes isolated have been characterised by elemental analyses, molar conductance values, magnetic susceptibilities and spectroscopic (UV-visible and IR) data. It has been concluded that formation of these complexes involves tridentate ONO donor ligands either in the monobasic form or in the dibasic form.

Various hydrazone ligands possess strong bactericidal, herbicidal, insecticidal and fungicidal properties\(^{1-6}\). In addition hydrazones have analytical applications\(^{7-10}\) also, besides other uses\(^{11}\). Hydrazones have interesting ligational properties due to the presence of several potential coordination sites\(^{12}\), and both transition and non-transition metal complexes of these ligands have been synthesised earlier.

Although metal complexes of many aroylhydrazones have been studied in recent years\(^{12}\), no such work on the metal complexes of the hydrazones derived by the condensation of 4-methoxybenzoyl hydrazide with salicylaldehyde (abbreviated to \((H_2)SMBHON\)), \(\alpha\)-hydroxyacetophenone (abbreviated to \((H_2)OHAPMBHON\)) and diacetylmonoxime (abbreviated to \((H_2)DAMMBHON\)) is available. We have therefore, studied the reactions of these three hydrazone ligands (I) with different metal salts and the present paper describes the results obtained in the case of cobalt (II & III).

Although some scanty reports on the Co(II) complexes of \((H_2)SMBHON\) and \((H_2)OHAPMBHON\) have been reported\(^{13}\), detailed and systematic studies are lacking.

Materials and Methods

Physicochemical data were collected as described in our earlier publication\(^{14}\). Satisfactory elemental analyses were obtained for all the complexes. Analysis for carbon, hydrogen and nitrogen were performed at the RSIC, CDRI, Lucknow.

Synthesis of 4-methoxybenzoyl hydrazide, \((H)MBHN\)

4-Methoxybenzoyl hydrazide was prepared via the preparation of 4-methoxymethyl benzoate followed by treatment with hydrazine hydrate (85%) as reported\(^{15,16}\).

Synthesis of hydrazones, \((H_2)SMBHON\), \((H_2)OHAPMBHON\), and \((H_2)DAMMBHON\)

Salicylaldehyde, \(\alpha\)-hydroxyacetophenone or diacetylmonoxime was heated under reflux with the hydrazine \((H)MBHN\) (0.01 molar, 1:1 ratio) in ethanol (40 ml) for 4h, 9h and 11h respectively in the cases of \((H_2)SMBHON\), \((H_2)OHAPMBHON\) and \((H_2)DAMMBHON\). The resulting solution on concentration at reduced pressure yielded the title hydrazones \((H_2)SMBHON\), \((H_2)OHAPMBHON\) and \((H_2)DAMMBHON\) respectively in satisfactory yields.
Synthesis of the complexes

The preparative methods used were almost similar. One representative example is given below. The experimental details for the complexes are shown in three reaction schemes below.

\[ \text{[Co}^2\text{(SMBHON)H}_2\text{O]} \] (1)

The solution of the ligand \((\text{H}_2\text{SMBHON})\) (0.001 mol) in EtOH (20 ml) was added to the suspension of \(\text{Co(OAc)}_2\cdot4\text{H}_2\text{O} \) (0.001 mol) in EtOH (20 ml) under nitrogen atmosphere. Yellowish orange solution \((pH \approx 6)\) along with a small amount of yellow solid was formed immediately, which was heated under reflux for an hour. The yellow compound was filtered off after cooling and washed thoroughly with hot EtOH and dried \textit{in vacuo}; yield 65%.

Results and Discussion

The reactions of \((\text{H}_2\text{SMBHON})\), \((\text{H}_2\text{OHAPMBBHON})\) and \((\text{H}_2\text{DAMMBHON})\) with \(\text{CoCl}_2\cdot6\text{H}_2\text{O}\), \(\text{Co(OAc)}_2\cdot4\text{H}_2\text{O}\) and \(\text{Co(acac)}_2\cdot2\text{H}_2\text{O}\) under varied reaction conditions yielded coloured cobalt (II & III) complexes of the types \([\text{Co}^2\text{I(SMBHON)H}_2\text{O]}\), (1), \([\text{Co}^\text{II} \{(\text{H})\text{OHAPMBBHON}\}_{\text{II}}\text{H}_2\text{O}\] (2), \([\text{Co}^\text{II} \{(\text{H})\text{DAMMBHON}\}_{\text{II}}\text{H}_2\text{O}\] (3), \([\text{Co}^\text{III} \{(\text{H})\text{SMBHON}\}_{\text{III}}\text{H}_2\text{O}\] (X = \text{NO}_3, (4), X = Cl, (5)), \([\text{Co}^\text{III} \{(\text{H})\text{OHAPMBBHON}\}_{\text{III}}\text{H}_2\text{O}\] (6), \([\text{Co}^\text{III} \{(\text{H})\text{OHAPMBBHON}\}_{\text{III}}\text{H}_2\text{O}\] (7), \([\text{Co}^\text{III} \{(\text{H})\text{SMBHON}\}_{\text{III}}\text{H}_2\text{O}\] (8), \([\text{Co}^\text{III} \{(\text{H})\text{OHAPMBBHON}\}_{\text{III}}\text{H}_2\text{O}\] (9), \([\text{Co}^\text{III} \{(\text{H})\text{OHAPMBBHON}\}_{\text{III}}\text{H}_2\text{O}\] (10), \([\text{Co}^\text{III} \{(\text{H})\text{OHAPMBBHON}\}_{\text{III}}\text{H}_2\text{O}\] (11), \([\text{NH}_4]\) \([\text{Co}^\text{III} \{(\text{H})\text{SMBHON}\}_{\text{III}}\text{H}_2\text{O}\] (12), \([\text{NH}_4]\) \([\text{Co}^\text{III} \{(\text{H})\text{OHAPMBBHON}\}_{\text{III}}\text{H}_2\text{O}\] (13), \([\text{Co}^\text{III} \{(\text{H})\text{DAMMBHON}\}_{\text{III}}\text{H}_2\text{O}\] (14), \([\text{Co}^\text{III} \{(\text{H})\text{DAMMBHON}\}_{\text{III}}\text{H}_2\text{O}\] (15), and \([\text{Co}^\text{III} \{(\text{H})\text{DAMMBHON}\}_{\text{III}}\text{H}_2\text{O}\] (16), shown in the Schemes 1 to 3. The yields of the compounds varied between 50 and 75%.

All the isolated compounds were found to be stable and were characterised on the basis of elemental analyses, molar conductance values, magnetic moments (Table 1) and spectroscopic data. The stoichiometry of the complexes fits well the proposed formulations. Most of the compounds are insoluble in common organic solvents but are soluble in coordinating solvents like DMSO, DMF and py. However, the compounds (7)-(11) and (13) are also soluble in EtOH, \(\text{CH}_3\text{OH}\) and other common organic solvents. The results of present synthesis show that the enolisation and the final basicity of the ligands are dependent on the \(pH\) of the solution and also on the nature of the cobalt salts/compounds used as reactants.
suggest octahedral geometry for the complexes. The room temperature magnetic moment value of 3.79 B.M. obtained for the complex (6) is slightly lower than the usually observed value for a tetrahedral cobalt(II) compound, which is slightly higher than values for square-planar or spin-paired octahedral cobalt(II) species. However, this lower value may be explained on the basis of a tetrahedral dimeric structure\(^{13,19-21}\)(II). This is also substantiated by molecular weight determination of the complex (Rast's method).

The complex (2) shows magnetic moment value
of 3.15 B.M. at room temperature which is much below the expected range of tetrahedral or high spin octahedral complexes. The stoichiometry of the complex suggest an octahedral geometry around cobalt(II) ion in this complex, which is also substantiated by electronic spectral data (see later discussion). It may attain a dinuclear structure (III) in the solid state, which is also supported by the molecular weight determination of the complex (Rast’s method).

Similar observations were earlier made by other workers.

Electronic spectra

The electronic spectra of cobalt(II & III) complexes (1)-(16) were recorded in solution. The visible spectra of cobalt(II) complexes with ligands having N₂O₄ donor sets are known to show two bands in the region 20,000-17,390 cm⁻¹ and 10,000-8,330 cm⁻¹ corresponding to the transi-

<table>
<thead>
<tr>
<th>Complexes</th>
<th>m.p. (°C)</th>
<th>Found (Calc.), %</th>
<th>µₑₑₑ (B.M.)</th>
<th>Λₐₐₐ (10⁻³ M)</th>
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</thead>
<tbody>
<tr>
<td>[Co⁶{(H)SMBHON}H₂O]⁺ (Yellow)</td>
<td>290-293(d)</td>
<td>52.05 4.15 7.92 17.5</td>
<td>4.48</td>
<td>8.1</td>
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<tr>
<td>[Co⁶{(OH)APMBHON}]²⁻ (Brown)</td>
<td>&gt; 310</td>
<td>59.00 4.78 8.08 12.09</td>
<td>3.45</td>
<td>12.5</td>
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<td>150-152</td>
<td>50.40 5.08 14.48 10.02</td>
<td>Dia</td>
<td>11.7</td>
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<tr>
<td>[Co⁶{(H)SMBHON}H₂O₃N⁺ (Red-violet)</td>
<td>200-208(d)</td>
<td>40.35 4.58 9.59 13.34</td>
<td>5.19</td>
<td>43.8</td>
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<tr>
<td>[Co⁶{(H)SMBHON}H₂O₃Cl⁻ (Orange-red)</td>
<td>216-218</td>
<td>43.74 4.23 7.08 14.50</td>
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<td>39.6</td>
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<tr>
<td>[Co⁶{(OH)APMBHON}]H₂O₆⁻ (Reddish brown)</td>
<td>&gt; 250</td>
<td>55.50 4.19 8.21 16.99</td>
<td>3.79</td>
<td>10.5</td>
</tr>
<tr>
<td>[Co⁶{(OH)APMBHON}]H₂O₆⁻ (Brown)</td>
<td>&gt; 250</td>
<td>45.20 5.30 13.10 13.29</td>
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<td>198-200</td>
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<td>[Co⁶{(H)SMBHON}NH₃₂NO₃⁻ (Brown)</td>
<td>210-215</td>
<td>40.81 4.88 19.08 13.38</td>
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<td>60.92 4.40 8.76 9.60</td>
<td>Dia</td>
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<tr>
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<td>280(d)</td>
<td>51.30 5.14 14.98 10.23</td>
<td>4.92</td>
<td>11.3</td>
</tr>
</tbody>
</table>

a 10⁻³ M solution in DMSO at room temperature; b 10⁻³ M solution in EtOH at room temperature.
Infrared spectra

The infrared spectra of the ligands $(\text{H}_2)\text{SMBHON}$, $(\text{H}_2)\text{OHAPMBHON}$ and $(\text{H}_2)\text{DAMMBHON}$ and their cobalt(II) complexes have been measured in KBr phase.

The spectra of the ligands show medium to strong bands in the range 3200-3280 cm$^{-1}$ assignable to $\nu_{\text{OH}}$ in the case of $(\text{H}_2)\text{SMBHON}$ and $(\text{H}_2)\text{OHAPMBHON}$ and a band at 3000-3400 cm$^{-1}$ assignable to $\nu_{\text{OH(oxime)}}$ in the case of ligand $(\text{H}_2)\text{DAMMBHON}$. The broad nature of the bands suggests hydrogen bonding$^{24,26}$. The free ligands also show bands at 3020-3080 and 1640-1650 cm$^{-1}$ assignable to $\nu_{\text{NH}}$ and $\nu_{\text{C=O}}$ modes. The $\nu_{\text{C=N(oxime linkage)}}$ in the ligands appeared at 1610-1615 cm$^{-1}$. The $\nu_{\text{C=N(oxime linkage)}}$ mode in the free ligand $(\text{H}_2)\text{DAMMBHON}$ is possibly submerged by the strong band at 1610 cm$^{-1}$.

The $\nu_{\text{N=O}}$ mode for the ligand $(\text{H}_2)\text{DAMMBHON}$ is observed as a strong band$^{27}$ at 940 cm$^{-1}$. The bands observed at 1515-1545 cm$^{-1}$ and at 1260 cm$^{-1}$ are assignable to amide-II and amide-III. The C–O stretch (phenolic) of the ligands $(\text{H}_2)\text{SMBHON}$ and $(\text{H}_2)\text{OHAPMBHON}$ is observed around 1520 cm$^{-1}$, while the amide-III bands of all the ligands are observed around 1575 cm$^{-1}$. These data suggest that the free ligands exist in the keto form$^{24-26}$.

The infrared spectra of the compounds (4), (5) and (12) exhibit $\nu_{\text{NH}}$ at 3000-3040 cm$^{-1}$ along with the following changes in amide group vibrations: amide-II increases in frequency (1530-1545 cm$^{-1}$) and amide-III splits into two components at 1205-1215 cm$^{-1}$ and 1375-1385 cm$^{-1}$. These changes in amide group vibrations suggest amide oxygen coordination to metal ion as well as coordination of ligands in keto form$^{26,28}$. The coordination of amide oxygen is supported by the appearance of a band at 415-420 cm$^{-1}$ which may be assigned$^{26}$ to $\nu_{\text{Co–O}}$. The disappearance of the band due to $\nu_{\text{OH}}$ at 3200-3280 cm$^{-1}$ in the compounds (4), (5) and (12) indicates the involvement of phenolic oxygen in coordination after deprotonation. The appearance of a new band at 480-910 cm$^{-1}$ suggests metal-oxygen (phenolic) coordination$^{26,29}$. The band observed at 450-470 cm$^{-1}$ is assigned to $\nu_{\text{Co–N}}$ vibration$^{29}$. In the complexes (4), (5) and (12) $\nu_{\text{C=N}}$ is lowered by $\sim 20$ cm$^{-1}$ suggesting coordination of nitrogen of the azomethine group to the metal atom. It is, therefore, inferred that the ligands in the complexes (4), (5) and (12) coordinate as monobasic tridentate ligand. The bands at 3300-3600 and 840-860 cm$^{-1}$ in the chelates (2), (4) and (5) indicate the presence of coordinated water molecule$^{24}$.

The bands at 800, 1025 and 1045 cm$^{-1}$ indicate the presence of $\text{NO}_3^-$ in the compound (4)$^{24,30}$. The infrared spectra of the compound (2), (3), (14) and (15) are complicated. On complexation, the $\nu_{\text{NH}}$ bands of the above ligands lose both sharpness and intensity. Sharp, strong bands in the infrared spectra of the complexes at 1600-1610 cm$^{-1}$ have been assigned$^{31}$ to the (C=N=N=C) skeleton and the $\nu_{\text{C=O}}$ (amide-I) band. The phenolic $\nu_{\text{C–O}}$ shows an upward shift ($\Delta \nu = 30$ cm$^{-1}$). All these indicate that the two ligands are attached to the metal ion in two forms$^{32}$. One of the ligands is attached as a dibasic tridentate ONO donor and the other as a monobasic ONO donor in the keto form.

Dramatic changes are observed in the spectra of the complexes (1), (6)-(11) and (13) which do not show any characteristic band of amide and amino groups suggesting that the ligand is coordinated in ‘enol’ form assigned to the skeleton$^{31}$ C=N–N=C. The disappearance of a band due to $\nu_{\text{OH}}$ at 3200-3280 cm$^{-1}$ in all the said complexes indicates the involvement of phenolic oxygen in coordination through deprotonation. It is, therefore, suggested that the ligands in the complexes (1), (6)-(11) and (13) coordinate in dibasic tridentate fashion. The bands observed at 1540-1545 and 1300-1305 cm$^{-1}$ indicate the presence of phenolic oxygen bridging$^{26}$ in the compound (6) and (11). The bands observed at 3200-3500 and 850 cm$^{-1}$ indicate the presence of coordinat-
ed NH$_3$ molecule$^{24,34}$ in the chelates (7)-(11). The bands observed at 3060-3580 and 1410 cm$^{-1}$ indicate the presence of NH$_2$ ion in the compound (13)$^{24,35}$. The bands at 1640 and 1330 cm$^{-1}$ in the compound (8) indicate the presence of coordinated acetato group$^{24}$.

The presence of water molecule in the complexes (1) to (9) and (13) complicates the band assignment (see above). Heating of these complexes at 151±2°C indicated the presence of non-coordinate water in the complexes (3), (6) and (13), and coordinated water in rest of the complexes.

The above discussion corroborates the structural feature of the Co(II & III) complexes depicted in the Schemes 1 to 3.

Acknowledgement

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