Synthesis and physicochemical characterization of some Schiff base complexes of chromium(III)

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Received 20 December 2007; revised 22 July 2008

Some chromium(III) complexes of the type, [Cr(L) 2(H 2O) 2]Cl (1-10) [where L = Schiff bases (sbH, derived from the condensation of 2-amino pyridine, 2-aminophenol, o-toluidine, p-toluidine, 3-nitroaniline and anthranilic acid with salicylaldehyde/vanillin) and substituted benzimidazole/ benzoxazole or mercaptobenzimidazole] have been prepared by the reaction of chromium(III) chloride with corresponding ligands followed by immediate addition of ethanolic solution of anhydrous sodium acetate in 1:2 molar ratio. The resulting products have been characterized by elemental analysis, spectral (IR, UV-visible and FAB-mass) as well as magnetic susceptibility measurements. Octahedral structure is proposed for the complexes.

Chromium (III) complexes containing Schiff bases and substituted benzimidazole/benzoxazole have attracted many workers 1-3 due to their biological, pharmacological, clinical and analytical importance. The biologically important form of chromium is the trivalent ion, Cr 3+, which is required for proper carbohydrate and lipid metabolism in mammals. Although chromium deficiency is difficult to achieve, it is excreted after insulin challenge in the form of oligopeptide. Chromodulin may be the key to understanding the role of chromium at molecular level as the molecule has been found to bind the activated insulin receptor, stimulating its kinase activity. Chromium picolinate, Cr(pic) 3, has been proposed to be the biological form of chromium. It has been used as the supplement in numerous forms including pills, chewing gums, drinks and nutrition bars 4-8.

We report herein the synthesis of some mixed ligand complexes (containing different donor atoms) and their characterization by means of spectral and magnetic studies. Structural correlation of these complexes have also been made and an octahedral geometry around chromium (III) is proposed on the basis of electronic and mass spectrometric studies.

Experimental
Reagent grade (BDH) precursors to ligands and solvents were purified by the standard procedures. Chromium chloride was purchased from Loba and used as received. All other chemicals were purchased from commercial sources and used as such. Chromium was determined by atomic absorption spectroscopy GBC-932 AA and chloride present in the complexes was estimated by Volhard's method. Elemental analysis (CHN) were carried out on Herbaceous Carlo Erba 1108 analyser. IR and electronic spectra were recorded on Perkin Elmer grating spectrophotometer. FAB-mass spectra were recorded on JEOLSX 102/DA-6000 mass spectrometer/data system.

Preparation of ligands and complexes
The Schiff bases were prepared by refluxing a mixture of equimolar amounts of aldehydes (such as salicylaldehyde and vanilline) with corresponding amines (such as 2-aminopyridine, o-toluidine, aniline, 2-aminophenol, 3-nitrophenol and anthranilic acid) in methanolic medium on water bath for 4 h. The ligand, 2-(o-hydroxyphenyl)-benzoxazole (pboxH) and 2-mercaptobenzimidazole (mbzH) were prepared by literature method 11,12. The general method of preparation of complexes along with ligands used during the course of present investigations are shown in Scheme 1.

To a suspension of Schiff base, sapH (0.95 g, 4.8 mmol) in ethanol (~40 ml), a solution of CrCl 3.6H 2O (0.639g, 2.4 mmol) in ethanol (~30 ml) was added followed by immediate addition of anhydrous sodium acetate (0.39 g, 4.8 mmol) in hot ethanol (~20 ml). The reaction mixture was refluxed for ~4 h on a water bath and then filtered while hot to remove the precipitated sodium chloride and acetic acid. The green filtrate on concentration and cooling to ~5°C overnight yielded a green crystalline compound. It was filtered, washed with ethanol and dried over fused


To obtain the desired product, \([\text{Cr}(\text{sap})_2(\text{H}_2\text{O})_2]\text{Cl} (0.81g, 68\% \text{ yield})\). Similar procedure was adopted for the preparation of other chromium (III) complexes. The synthetic and analytical details are collected in Table 1.

**Results and discussion**

The complexes of chromium (III) have been prepared by the addition of ethanolic solution of chromium (III) chloride (hydrated) with the corresponding ligands followed by immediate

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**Table 1—Synthetic, analytical and melting point data of various mixed ligand complexes of chromium (III)**

<table>
<thead>
<tr>
<th>Complexes yield (g, %)</th>
<th>Colour</th>
<th>Melting pt (°C)</th>
<th>Found (Calc.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr}(\text{sap})_2(\text{H}_2\text{O})_2]\text{Cl} (0.81g, 68% \text{ yield}))</td>
<td>Yellowish green</td>
<td>9.92</td>
<td>6.72</td>
</tr>
<tr>
<td>([\text{Cr}(\text{o-smab})_2(\text{H}_2\text{O})_2]\text{Cl} (0.68g, 60% \text{ yield}))</td>
<td>Green</td>
<td>9.41</td>
<td>6.39</td>
</tr>
<tr>
<td>([\text{Cr}(\text{pm-smab})_2(\text{H}_2\text{O})_2]\text{Cl} (0.66g, 64% \text{ yield}))</td>
<td>Green</td>
<td>9.36</td>
<td>6.43</td>
</tr>
<tr>
<td>([\text{Cr}(\text{smab})_2(\text{H}_2\text{O})_2]\text{Cl} (0.81g, 67% \text{ yield}))</td>
<td>Light green</td>
<td>9.95</td>
<td>6.72</td>
</tr>
<tr>
<td>([\text{Cr}(\text{saph})_2(\text{H}_2\text{O})_2]\text{Cl} (0.77g, 72% \text{ yield}))</td>
<td>Reddish brown</td>
<td>9.29</td>
<td>6.23</td>
</tr>
<tr>
<td>([\text{Cr}(\text{sab})_2(\text{H}_2\text{O})_2]\text{Cl} (0.81g, 67% \text{ yield}))</td>
<td>Yellowish brown</td>
<td>8.26</td>
<td>5.46</td>
</tr>
<tr>
<td>([\text{Cr}(\text{aa})_2(\text{H}_2\text{O})_2]\text{Cl} (0.99g, 75% \text{ yield}))</td>
<td>Whitish brown</td>
<td>8.29</td>
<td>5.65</td>
</tr>
<tr>
<td>([\text{Cr}(\text{aa})_2(\text{H}_2\text{O})_2]\text{Cl} (0.99g, 75% \text{ yield}))</td>
<td>Dark green</td>
<td>7.69</td>
<td>5.15</td>
</tr>
<tr>
<td>([\text{Cr}(\text{aa})_2(\text{H}_2\text{O})_2]\text{Cl} (0.70g, 70% \text{ yield}))</td>
<td>Brown</td>
<td>9.33</td>
<td>6.29</td>
</tr>
<tr>
<td>([\text{Cr}(\text{aa})_2(\text{H}_2\text{O})_2]\text{Cl} (1.15g, 78% \text{ yield}))</td>
<td>Ash green</td>
<td>12.09</td>
<td>8.21</td>
</tr>
</tbody>
</table>

* a decomposed; b neither melted nor decomposed; c analysis for sulphur: Found = 15.0%; Calc. 15.18%
addition of hot ethanolic solution of anhydrous sodium acetate in 1:2:2 molar ratio. The reaction mixture was refluxed on water bath and then filtered while hot to remove the precipitated sodium chloride. The filtrate on concentration and cooling to 5°C overnight gave complexes of the type [Cr(L)(H₂O)₂]Cl, which can be represented as follows:

\[
\text{CrCl₃.6H₂O + 2sbH } \xrightarrow{(i) \text{ CH₃COOH}} \xrightarrow{(ii) \Delta - 4h} [\text{Cr(sb)(H₂O)}]\text{Cl + 2NaCl } \downarrow + 4\text{H₂O + 2CH₃COOH} \]
\[
\text{CrCl₃.6H₂O + 2pboxH } \xrightarrow{(i) \text{ CH₃COOH}} \xrightarrow{(ii) \Delta - 4h} [\text{Cr(pbox)(H₂O)}]\text{Cl + 2NaCl } \downarrow + 4\text{H₂O} \]
\[
\text{CrCl₃.6H₂O + 2mbzH } \xrightarrow{(i) \text{ CH₃COOH}} \xrightarrow{(ii) \Delta - 4h} [\text{Cr(mbz)(H₂O)}]\text{Cl + 2NaCl } \downarrow + 4\text{H₂O} \]

The complexes are coloured solids, soluble in DMSO and DMF, but insoluble in ether, benzene and chloroform.

Similar reactions of CrCl₃.6H₂O with the above ligands in hot pyridine yielded different reaction products and can be represented as follows:

\[
\text{CrCl₃.6H₂O + 2LH } \xrightarrow{(i) \text{ hot pyridine}} \xrightarrow{(ii) \sim 1g \text{ zinc dust}} [\text{Cr(L)(Py)}]\text{Cl.2H₂O + ZnCl₂ + 4H₂O} \]

where LH = salicylidene-2-aminopyridine(sapH), salicylidene-2-methyl-1-aminobenzene (o-smabH), salicylidene-4-methyl-1-aminobenzene (p-smabH), salicylidene-1-aminobenzene (sabH), salicylidene-2-amino phenol (saphH), salicylidene-2-nitroaniline (snabH), salicylidene-anthranilic acid (saaH), 2-(o-hydroxyphenyl)benzoxazole (pboxH) and 2-mercaptobenzimidazole (mbzH). These complexes are non-hygroscopic, air stable and green coloured solids. The purity of the complexes was checked by TLC. They are soluble in hot pyridine, DMSO and DMF, but insoluble in ether, benzene and chloroform. The complexes are thermally stable and do not melt or decompose up to 250°C. Molar conductance of the complexes (in DMSO) reveals their non-electrolytic nature. The synthesis and structures of the representative complexes are given in Scheme 1.

**IR spectral studies**

The IR spectra of the ligand showed bands in range 1650-1630 cm⁻¹ which are attributed to ν(C=O) band. The band is shifted to lower frequency region 1618-1595 cm⁻¹ in all the chromium (III) complexes indicating that bonding is taking place through the azomethine nitrogen. The ν(C=O) (phenolic) stretching frequencies of the ligands were observed at 1728-1259 cm⁻¹ in the free ligands which get shifted to higher region 1265-1290 cm⁻¹ in the complexes. It is indicative of bonding through phenolic oxygen. The broad band appearing at ~1030 cm⁻¹ in the spectrum of the ligand has been assigned to -OCH₂ group. A broad band observed at ~3300 cm⁻¹ is indicative of NH group present in imidazole rings. This peak is almost unchanged in complex 10. However, ν(C=O) mode occurring at ~1610 cm⁻¹ in the complex indicates the coordination of ligand to chromium via their imidazole tertiary nitrogen. A broad band is observed in all the complexes in the range ~3450 cm⁻¹ due to νOH of the coordinated H₂O. This is supported by the appearance of an additional band in the range 840-800 cm⁻¹ for (O-H) rocking deformation. The new bands also appear in the range 750-710 cm⁻¹ which is not observed in the ligand spectrum. This band can be assigned to the wagging mode of the coordinated water. The complexes also showed medium to strong intensity bands in the region 570-535 cm⁻¹, 461-440 cm⁻¹ and 402 cm⁻¹ which can be attributed to ν(Cr-N), ν(Cr-O) and ν(Cr-S) bands respectively.

**Electronic and magnetic studies**

The electronic absorptive spectra of all the chromium(III) complexes were measured in DMSO. These spectra are quite similar to one another and may be interpreted on the basis of an octahedral environment around chromium(III) in these complexes. All these spectra exhibits three bands (Table 2) in the regions ~16200 cm⁻¹, ~22500 cm⁻¹ and ~32,400 cm⁻¹ assigned to \( ^{4}A_{2g} \rightarrow ^{4}T_{2g} (F) \) and \( ^{4}A_{2g} \rightarrow ^{4}T_{1g} (F) \) and \( ^{4}A_{2g} \rightarrow ^{4}T_{1g} (P) \).
transitions respectively in order of increasing energy. The various ligand field parameters have been evaluated for Cr(III) complexes. The value of the first spin allowed transition \( \nu_1 \) at \(~16200\text{cm}^{-1}\) is directly taken as 10Dq. The value of Racah parameters (B) has been calculated by the Underhill and Billing equation \[ \beta = v_3 + v_2 = 30\text{Dq}/5. \]

The covalency factor, \( \beta_{35} \) for spin allowed transition for these derivatives, i.e., ratio of value of Racah interelectronic repulsion parameter (B) for the complexes against that for the free Cr\(^{3+}\) ion \( (1030\text{ cm}^{-1}) \) is also given in Table 2.

The room temperature magnetic moment values \(^\text{16}\) (Table 2) observed, for chromium (III) complexes synthesized during the present course of investigations, are in the range 3.61-3.90 BM, and are close to theoretical spin only values \( (\mu_{\text{eff}} = 3.87\text{BM}) \) for Cr\(^{3+}\) \( (3d^3 \text{ system}) \).

**FAB-mass studies**

The FAB-mass\(^\text{11,17}\) spectrum of the chromium (III) complex \([\text{Cr}(\text{pbox})_2(\text{H}_2\text{O})_2]\text{Cl} \) \( 9 \) shows a characteristic molecular ion \( (M^+) \) peak at \( m/z = 543 \), which corresponds to the molecular weight of the complex for a monomeric structure. The mass spectrum shows multiple peaks representing successive degradation of the complex molecule by the formation of radical \( \text{C}_6\text{H}_4\text{O}^\cdot \). The fragmentation pattern showing the structure of the complex is given in Scheme 2. On the other hand, complex \([\text{Cr}(\text{mbz})_2(\text{H}_2\text{O})_2]\text{Cl} \) \( 10 \) shows a molecular ion peak at \( m/z = 386 \) suggesting the monomeric form of the complex. Successive fragmentation gives many more important peaks, due to the formation of \( \text{C}_1^\cdot \), \( \text{C}_6\text{H}_4\text{N}^\cdot \) and \( \text{CHN}^\cdot \) radicals.

**Table 2**—Electronic and magnetic data of the chromium (III) complexes

<table>
<thead>
<tr>
<th>No.</th>
<th>Electronic transitions (cm(^{-1}))</th>
<th>10Dq ( (\text{cm}^{-1}) )</th>
<th>B ( (\text{cm}^{-1}) )</th>
<th>( \beta_{35} )</th>
<th>( \mu_{\text{eff}} ) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( ^4\text{A}<em>{2g} \rightarrow ^4\text{T}</em>{2g} ) ((F))</td>
<td>22817</td>
<td>35037</td>
<td>15995</td>
<td>670</td>
</tr>
<tr>
<td>2</td>
<td>( ^4\text{A}<em>{2g} \rightarrow ^4\text{T}</em>{2g} ) ((P))</td>
<td>23533</td>
<td>35482</td>
<td>16949</td>
<td>625</td>
</tr>
<tr>
<td>3</td>
<td>( ^4\text{T}<em>{2g}(F) \rightarrow ^4\text{T}</em>{2g}(P) )</td>
<td>23436</td>
<td>36200</td>
<td>16856</td>
<td>620</td>
</tr>
<tr>
<td>4</td>
<td>( ^4\text{T}<em>{2g}(F) \rightarrow ^4\text{T}</em>{2g}(P) )</td>
<td>22886</td>
<td>35441</td>
<td>16215</td>
<td>660</td>
</tr>
<tr>
<td>5</td>
<td>( ^4\text{T}<em>{2g}(F) \rightarrow ^4\text{T}</em>{2g}(P) )</td>
<td>22425</td>
<td>34270</td>
<td>15537</td>
<td>720</td>
</tr>
<tr>
<td>6</td>
<td>( ^4\text{T}<em>{2g}(F) \rightarrow ^4\text{T}</em>{2g}(P) )</td>
<td>23451</td>
<td>36965</td>
<td>16960</td>
<td>645</td>
</tr>
<tr>
<td>7</td>
<td>( ^4\text{T}<em>{2g}(F) \rightarrow ^4\text{T}</em>{2g}(P) )</td>
<td>22426</td>
<td>34894</td>
<td>15897</td>
<td>667</td>
</tr>
<tr>
<td>8</td>
<td>( ^4\text{T}<em>{2g}(F) \rightarrow ^4\text{T}</em>{2g}(P) )</td>
<td>23094</td>
<td>37230</td>
<td>17193</td>
<td>610</td>
</tr>
<tr>
<td>9</td>
<td>( ^4\text{T}<em>{2g}(F) \rightarrow ^4\text{T}</em>{2g}(P) )</td>
<td>23591</td>
<td>35722</td>
<td>16290</td>
<td>712</td>
</tr>
<tr>
<td>10</td>
<td>( ^4\text{T}<em>{2g}(F) \rightarrow ^4\text{T}</em>{2g}(P) )</td>
<td>23771</td>
<td>36729</td>
<td>16786</td>
<td>690</td>
</tr>
</tbody>
</table>

Fragmentation pattern \([\text{Cr}(\text{pbox})_2(\text{H}_2\text{O})_2]\text{Cl} \) (9) using FAB-mass spectrum

**Scheme 2**
which confirms the structure (Scheme 3) of the complex 10. These complexes show molecular ion peaks in good agreement with the structure suggested by elemental analysis, spectral and magnetic studies.

On the basis of the above elemental analysis and spectral studies, confirmed by FAB-mass spectra (9 and 10) showing characteristic molecular ion peak at their expected m/z value for their monomeric form, octahedral structure is proposed for these complexes. Definite structures of these fascinating Schiff base complexes in solid state would be possible only after X-ray crystallographic studies, which have not been successful so far.

Acknowledgement
Authors are grateful to IIT, Mumbai and CDRI, Lucknow for providing spectral and analytical data.

References