Synthesis, reactions and physico-chemical characterisation of iron(III) complexes containing substituted benzoxazole and various Schiff base moieties

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Some new complexes of iron (III) of the type \([\mu-Cl]_2Fe_2[\eta^2-(phbox)]_2\) (I) and \([\mu-Cl]_2Fe[\eta^2-(phbox)]\) (2) [where \(H_{\text{phbox}}=2-(o\text{-hydroxyphenyl})\text{-benzoxazole}\), have been synthesised by the interactions of iron(III) chloride with the corresponding ligand \((H_{\text{phbox}})\) in 1:2 and 1:1 molar ratio(s) in hot ethanol as reaction medium. The complex 1 has been further treated with various sodium salts of Schiff bases (sb) [Na(o-smab), Na(p-smab) and Na(sap)], alkoxo-Na(OPr\text{\textsubscript{i}}), aryloxo-Na(OAr) and tetrasopropoxyaluminate \([Na_2Al(OPr\text{\textsubscript{i}})\text{\textsubscript{4}}]\) in 1:1 molar ratio (in THF-benzene medium) to produce derivatives of the type: \([sb]Fe[\eta^2-(phbox)]\) (3), (4) and (5), \([\mu-OPr\text{\textsubscript{j}}]_2Fe[\eta^2-(phbox)]\) (6) \([\mu-OAr\text{\textsubscript{j}}]_2Fe[\eta^2-(phbox)]\) (7) and \([\mu-OPr\text{\textsubscript{j}}]_2Al(OPr\text{\textsubscript{i}})_2Fe[\eta^2-(phbox)]\) (8). All these derivatives have been characterised by elemental analysis, spectral (IR, UV-vis and FAB-mass) and magnetic susceptibility measurements. On the basis of these studies, most plausible structures for the iron(III) complexes have been suggested.

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There is a great deal of interest in the synthesis and characterisation of transition metal complexes of substituted benzoxazole/benzimidazole ligand due to their biological and pharmacological activities.\textsuperscript{1,3} Studies on the coordination behaviour of these ligands have been carried out mainly with cationic metal ions.\textsuperscript{4-7} However, only limited attention\textsuperscript{6,8} has been paid to studying the chemistry of monochloro complexes of later 3d transition metals involving benzimidazole and benzoxazole moieties, possibly due to their insoluble, non-volatile and polymeric nature, though they are useful precursors for the synthesis of new class of hydrocarbon soluble mixed ligand poly metallic (bi- and ter-) complexes of 3d transition metals.\textsuperscript{9,13}

We therefore, report herein the synthesis, reactions and characterisation (by the means of IR, UV-vis, FAB-mass and magnetic studies) of the new complexes of iron(III).

Experimental

All experiments were carried out in moisture free atmosphere. Solvents were dried by the standard procedures.\textsuperscript{13} Iron was determined by atomic absorption spectroscopy using GBC-932AA. Aluminium isopropoxide was prepared and analysed as reported earlier\textsuperscript{14,15} and chloride present in the complexes was estimated by Volhard's method.\textsuperscript{15} Isopropyl alcohol was determined by chromate oxidimetric method.\textsuperscript{16} Elemental analyses (C, H, N) were carried out on Heraeus Carlo Erba 1108 analysis at RSIC, CDRI Lucknow, IR (4000-200 cm\textsuperscript{-1}) and electronic spectra were recorded on Perkin-Elmer grating and Pye-Unicam model 557/SP. 8-100 spectrophotometers. Magnetic susceptibility was measured on Gouy-balance using Hg \([\text{Co(NCS)}\text{\textsubscript{2}}]\) as standard. FAB-mass spectra of iron(III) complexes were recorded on JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6kV, 10 mA) as the FAB-gas.

Preparation of ligands
The ligand \(2-(o\text{-hydroxyphenyl})\text{-benzoxazole (H}_{\text{phbox}})\), salicylidene-2-methyl-1-aminobenzene \((o\text{-smab})\), salicylidene-4-methyl-1-aminobenzene \((p\text{-smab})\), salicylidene-2-aminopyridine \((sapJ\text{-1})\) were synthesised as reported already.\textsuperscript{17,19} Sodium salts of Schiff bases 2-aminophenolate and sodium tetraalkoxoaluminate were prepared by known procedures.\textsuperscript{20}

Monochloro complexes of iron(III) \([\mu-Cl]_2Fe[\eta^2-(phbox)]_2\) (1)

A freshly prepared aqueous ethanolic solution (50% ethanol, \(-50 \text{ cm}^3\)) of iron(III) chloride (1.270 g, 4.7 mmol) was added dropwise to pre-stirred hot ethanol (\(-75 \text{ cm}^3\)) solution containing \(2-(o\text{-hydroxyphenyl})\text{-benzoxazole (1.974 g, 9.4 mmol})\) which produced a brown coloured precipitate. Dropwise addition of required dilute solution of sodium acetate with continuous stirring afforded brown coloured solid after complete precipitation. It was digested on water.
bath for about ~1 h. The complex so obtained was filtered, washed thrice with aqueous ethanol and dried at ~120°C under reduced pressure to afford \([(\mu\text{-Cl})_2\text{Fe}_2\{\text{pbox}\}_4]\) (1), a brownish black powdered solid (2.156 g, 90%).

Reactions of \([(\mu\text{-Cl})_2\text{Fe}_2\{\text{pbox}\}_4]\)

To a stirred hot brownish black suspension of monochloro-\([2\text{-}(\text{o-hydroxyphenyl})\text{-benzimidazolato iron(III)}\) \((0.98 \text{ g}, 1.92 \text{ mmol})\) in THF \((-30^\circ\text{C})\) was added sodium salt of salicylidene-2-methyl-1-aminobenzene \((0.448 \text{ g}, 1.92 \text{ mmol})\) in equimolar ratio. The reaction mixture was refluxed for ~2 h, so that the solution changed from dark brown to reddish brown. The separated NaCl \((0.11 \text{ g}, 1.90 \text{ mmol})\) was removed by filtration and excess of solvent removed by distillation followed by reduction under reduced pressure to afford solid product \([(\text{osmab})\text{Fe}(\text{pbox})_2]\) (3), which was purified by recrystallisation from benzene/THF mixture to give light brown powdered solid \((1.18 \text{ g}, 85\%)\).

Similar procedure was adopted to prepare the complex (2) and other derivatives (4), (5), (6), (7) and (8). The details for these reactions with analytical data are given in Table 1.

Results and discussion

The chloro complexes of iron(III) \([(\mu\text{-Cl})_2\text{Fe}_2\{\text{pbox}\}_4]\) and \([(\text{Cl})\text{Fe}(\text{pbox})_2]\) have been synthesised using a hot ethanol solution of \([2\text{-}(\text{o-hydroxyphenyl})\text{-benzoxazole}\) with an aqueous ethanol solution of iron(III) chloride in 2:1 and 1:1 molar ratio(s) followed by the addition of dilute solution of sodium acetate. The complexes are brown coloured solid, which have been purified by repeated washing with ethanol and finally dried at ~120°C under reduced pressure, and are formed by:

\[
\text{FeCl}_3\cdot6\text{H}_2\text{O}+2\text{Hopbox} \xrightarrow{(\text{i}) \text{Hot ethanol, stirred under reduced pressure at } -120^\circ\text{C}} \left[(\text{Cl})\text{Fe(pbox)}_2\right]+6\text{HCl}+6\text{H}_2\text{O} \tag{1}
\]

\[
\text{FeCl}_3\cdot6\text{H}_2\text{O}+\text{Hopbz} \xrightarrow{(\text{i}) \text{Hot ethanol, stirred under reduced pressure at } -120^\circ\text{C}} \left[(\text{Cl})\text{Fe(pbox)}_2\right]+4\text{HCl}+6\text{H}_2\text{O} \tag{2}
\]

The complexes are coloured solid and are found to be insoluble in most of the common organic solvents (such as \(\text{C}_6\text{H}_6, \text{CCl}_4, \text{n-hexane, etc.}\)). These complexes have been purified by recrystallisation in THF-benzene mixture.

The monochloro iron(III) complexes have been treated with sodium salt of Schiff bases \([\text{Na(osmab)}, \text{Na(p-smab)}\) and \(\text{Na(sap)}\), to produce mixed ligand complexes such as \([\text{(osmab)}\text{Fe}(\text{pbox})_2]\) (3), \([\text{(p-smab)}\text{Fe}(\text{pbox})_2]\) (4), and \([\text{(sap)}\text{Fe}(\text{pbox})_2]\) (5), which can be shown as:

\[
\left[(\text{pbox})_2\text{Fe(Cl)}\right]+\text{Na(sap)} \xrightarrow{\text{STIRRED/REFLUXED}} \left[(\text{pbox})_2\text{Fe(sap)}\right]+\text{NaCl} \tag{6}
\]

\[
\left[(\text{pbox})_2\text{Fe(Cl)}\right]+\text{Na(OAr)} \xrightarrow{\text{STIRRED/REFLUXED}} \left[(\text{pbox})_2\text{Fe(OAr)}\right]+\text{NaCl} \tag{7}
\]

Further, iron(III) complex (1) has been treated with sodium tetraisopropoxyaluminium, \([\text{Na}[\text{Al(OPr)}_3]_2]\), to produce new alkoxo bridged (bimetallic) complex of the type \([\mu\text{-OPr}_2]_2\text{Al(OPr)}_2\text{Fe}(\text{pbox})_2\) (8).

\[
\left[(\text{pbox})_2\text{Fe(Al(OPr)}_3_2\right]+\text{NaCl} \xrightarrow{\text{STIRRED/REFLUXED}} \left[(\text{pbox})_2\text{Fe(Al(OPr)}_3_2\right]+\text{NaCl} \tag{8}
\]

All these mixed ligand complexes are coloured solid and found to be soluble in common organic solvents. These complexes have been purified by recrystallisation in THF-benzene mixture. Synthetic and analytical details of all these derivatives are given in Table 1.
Table 1 — Synthetic and analytical details for iron(III) complexes containing benzoxazole and different moieties

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Reactants (g, mmol)</th>
<th>Product (g, % yield)</th>
<th>Found (Calc.) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1</td>
<td>FeCl₃·6H₂O (1.270,4.7) + Hopbox (1.98,9.4)</td>
<td>[(μ-Cl₂)Fe₂[N₂⁺(pbox)]₄ (1)</td>
<td>60.2</td>
</tr>
<tr>
<td>2</td>
<td>FeCl₃·6H₂O (0.846,3.2) + Hopbox (0.57,3.2)</td>
<td>[(Cl)₂Fe₂[N₂⁺(pbox)] (2)</td>
<td>46.9</td>
</tr>
<tr>
<td>3</td>
<td>[(μ-Cl₂)Fe₂[N₂⁺(pbox)]₄ + Na(o-smab) (0.93,1.02)</td>
<td>[(o-smab)Fe₂[N₂⁺(pbox)]₂ (3)</td>
<td>69.6</td>
</tr>
<tr>
<td>4</td>
<td>[(μ-Cl₂)Fe₂[N₂⁺(pbox)]₄ + Na(p-smab) (0.89,1.75)</td>
<td>[(p-smab)Fe₂[N₂⁺(pbox)]₂ (4)</td>
<td>69.9</td>
</tr>
<tr>
<td>5</td>
<td>[(μ-Cl₂)Fe₂[N₂⁺(pbox)]₄ + Na(sap) (0.87,1.96)</td>
<td>[(sap)Fe₂[N₂⁺(pbox)] (5)</td>
<td>68.0</td>
</tr>
<tr>
<td>6</td>
<td>[(μ-Cl₂)Fe₂[N₂⁺(pbox)]₄ + Na(OPri) (0.94,1.95)</td>
<td>[(μ-OPri)₂Fe₂[N₂⁺(pbox)]₄ (6)</td>
<td>64.7</td>
</tr>
<tr>
<td>7</td>
<td>[(μ-Cl₂)Fe₂[N₂⁺(pbox)]₄ + Na(OAr) (0.98,1.92)</td>
<td>[(μ-OAr)₂Fe₂[N₂⁺(pbox)]₄ (7)</td>
<td>65.0</td>
</tr>
<tr>
<td>8</td>
<td>[(μ-Cl₂)Fe₂[N₂⁺(pbox)]₄ + Na(Al(OPri)) (0.87,1.78)</td>
<td>[(μ-OPri)₂(Al(OPri)₂)Fe₂[N₂⁺(pbox)]₄ (8)</td>
<td>56.0</td>
</tr>
</tbody>
</table>

Table 2 — IR spectral data of mixed complexes of iron(III) containing Schiff bases and substituted benzoxazole

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Complexes</th>
<th>νFe-Cl</th>
<th>νFe-N</th>
<th>νFe-O</th>
<th>νC-OPri (SH)</th>
<th>νC=N</th>
<th>ν(C-O) FeAlk oxy*</th>
<th>ν(Al-O)</th>
<th>µD(μ.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>[(μ-Cl₂)Fe₂[N₂⁺(pbox)]₄ (1)</td>
<td>312, 281</td>
<td>452</td>
<td>535</td>
<td>1272</td>
<td>1620</td>
<td>-</td>
<td>-</td>
<td>4.87</td>
</tr>
<tr>
<td>2</td>
<td>[(Cl)₂Fe₂[N₂⁺(pbox)] (2)</td>
<td>342, 335</td>
<td>463</td>
<td>547</td>
<td>1280</td>
<td>1618</td>
<td>-</td>
<td>-</td>
<td>5.87</td>
</tr>
<tr>
<td>3</td>
<td>[(o-smab)Fe₂[N₂⁺(pbox)]₂ (3)</td>
<td>-</td>
<td>450</td>
<td>552</td>
<td>1275</td>
<td>1603</td>
<td>-</td>
<td>-</td>
<td>5.82</td>
</tr>
<tr>
<td>4</td>
<td>[(p-smab)Fe₂[N₂⁺(pbox)]₂ (4)</td>
<td>-</td>
<td>456</td>
<td>543</td>
<td>1279</td>
<td>1618</td>
<td>-</td>
<td>-</td>
<td>5.85</td>
</tr>
<tr>
<td>5</td>
<td>[(sap)Fe₂[N₂⁺(pbox)] (5)</td>
<td>-</td>
<td>467</td>
<td>545</td>
<td>1267</td>
<td>1603</td>
<td>-</td>
<td>-</td>
<td>5.78</td>
</tr>
<tr>
<td>6</td>
<td>[(μ-OPri)₂Fe₂[N₂⁺(pbox)]₄ (6)</td>
<td>454</td>
<td>548</td>
<td>1280</td>
<td>1607</td>
<td>-</td>
<td>-</td>
<td>3.41</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>[(μ-OAr)₂Fe₂[N₂⁺(pbox)]₄ (7)</td>
<td>-</td>
<td>470</td>
<td>539</td>
<td>1272</td>
<td>1619</td>
<td>-</td>
<td>-</td>
<td>5.42</td>
</tr>
<tr>
<td>8</td>
<td>[(μ-OPri)₂(Al(OPri)₂)Fe₂[N₂⁺(pbox)]₄ (8)</td>
<td>465</td>
<td>555</td>
<td>1278</td>
<td>1614</td>
<td>1150</td>
<td>617</td>
<td>4.75</td>
<td></td>
</tr>
</tbody>
</table>

* = terminal isopropoxy; b = bridging isopropoxy group
IR spectral studies

The characteristic IR bands (4000-200 cm\(^{-1}\)) for the free ligand, when compared with those of its iron(III) complexes, provide positive indications with regard to the bonding sites of the ligands. A negative shift observed for \(\nu_{C=\delta}\) band 1625 ±15 cm\(^{-1}\) in the spectrum of the free ligand to lower values 1600 ±30 cm\(^{-1}\) in its complexes is consistent with coordination of the azomethine nitrogen to the central Fe(III) ion\(^{21,22}\). The \(\nu_{C=\delta}\) (phenolic) stretching frequencies of the ligand were observed at 1248±10 cm\(^{-1}\) which get shifted to higher frequency region at 1275±20 cm\(^{-1}\), which is indicative of bonding through phenolic oxygen\(^{23-25}\). The characteristic frequencies for \(\nu_{C=\delta}/M\) observed in the

\[\begin{align*}
\text{Scheme 1}
\end{align*}\]
range 1050-980 cm⁻¹ indicate the presence of bridging isopropoxy group in the complex²⁶ (6). The isopropoxy-bridged bimetallic complex (8) frequency observed for metal alkoxide group ν(C=O)νc in the range 1160-1650 cm⁻¹ is assigned to terminal isopropoxy group and at 960-950 cm⁻¹ for bridging isopropoxy group²⁷. Beside these, a band observed at 610 ±7 cm⁻¹ has been assigned for ν(AlO). The complexes exhibited new bands in the region 560-280 cm⁻¹ which are attributed to ν(C=O)νc, ν(CH₃), ν(C=O)νc, and ν(Fe-O) frequency respectively²⁸. Also, the complex (1) showed characteristic strong band at around 280 ±5 cm⁻¹, which is characteristic for bridging chlorine (μ-Cl). Fe between two iron atoms.

**Electronic spectra**

The electronic spectral data of iron(III) complexes, (1, 3, 4, 5, 6, 7 and 8) showed characteristic bands in the region 12242±600, 19997±800 cm⁻¹ and 25760±200 cm⁻¹, which may arise due to "A₁→"T₁, (G) and "A₂→"T₁, (G) transitions expected for an octahedral iron(III) complex³¹. The complex [(Cl)FeCp² (pbox)] (2) exhibits bands at 17035 and at 21628, assigned to "A₁→"T₁ and charge transfer transitions respectively, suggesting T₃ geometry around iron(III).

**Magnetic studies**

The magnetic moments of the iron(III) complexes (Table 2) were determined in solid state at room temperature. All the dimeric iron(III) complexes (1, 6, 7 and 8) show slightly lower μₘ value indicative of interaction between two iron(III) centre bridged through chlorine, phenolic or alcoholic-oxygen forming dimeric complexes suggesting six co-ordinated geometry around iron(III)²⁵. The complex (2) showed magnetic moment 5.9 BM indicating tetrahedral geometry. Isopropoxy bridged complex [(μ-OPr)₂Al(OPr)₂Fe₂Cp²(pbox)]₂ (8) exhibited slightly lower value of magnetic moment (4.63 BM) than the spin only value for high spin iron(III) complexes.

**FAB-mass spectral studies**

The FAB-mass spectrum of the iron(III) complex [(μ-Cl)FeCp²(pbox)], (1) (Scheme 1) showed characteristic molecular ion M⁺ peak at m/z = 1018, which corresponds to the molecular weight of the complex for dimeric structure. The mass spectrum showing multi peaks representing successive degradation of the complex molecule by the formation of a monomer in the first phase, for which an ion peak was observed at 509 (m/z). Other important peaks were also observed due to the formation of various radicals, such as, chloride (Cl⁻), benzyne-oxy (C₆H₅O⁻) and C₆H₅O⁻. The fragmentation pattern showing the structure of the complex (2) is shown in Scheme 2. On the other hand, complex (2) showed a molecular ion peak at m/z = 336 which suggests the monomeric form of the complex, where successive degradation of molecule produced many more important peaks due to the formation of Cl⁻ and C₆H₅O⁻ radicals, which confirms the structure of the complex.

**Acknowledgement**

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References

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