Synthesis and characterization of mixed-ligand fluoro complexes of manganese (III) containing amino acid as co-ligands

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A few mixed-ligand fluoromanganate (III) complexes of the type \( A[Mn\ L_2\ F_4]3H_2O \) (where \( L = \) alanine or valine, \( A = Na, K \) or \( NH_4 \)) containing amino acid as co-ligands have been synthesised and characterized by elemental analyses, infrared, electronic spectroscopic studies, room, temperature magnetic susceptibility and in some cases pyrolytic studies. The newly synthesised complexes are found to have a distorted octahedral structure.

Manganese can adopt a wide variety of oxidation states, and this ability is certainly related to the redox function of the metal ion in biological systems. The tripotitive state of the metal requires a special attention not only because of its biochemical relevance in diverse redox functions but also because it is difficult to stabilize it in aqueous medium and many of its complexes exhibit unusual magnetic and structural features. Recent reports indicate that strong acidic ligands like fluoride has a pronounced stabilizing effect on manganese (III) both in solution as well as in solid state, and coordination of fluoride also introduces antiferromagnetism in fluoro manganates. Thus chemistry of mixed ligand fluoro-manganates(III) would be interesting as the idea of ligand additivity predicts their properties to be different from those of the corresponding binary complexes. In view of the increasing interest in metal amino acid systems due to their potentials as bio-mimetic model and considering the stabilizing effect of fluoride ion on manganese(III) especially in aqueous medium, it was therefore considered worthwhile to explore the possibility of synthesising mixed-ligand fluoro complexes of manganese(III) containing amino acid as co-ligands from aqueous medium. The present note describes the synthesis and structural assessment of new mixed-ligand fluoro complexes of manganese (III) containing alanine or valine as co-ligands.

Experimental

The chemicals used were all reagent grade products. The compound MnO(OH) was prepared by the oxidation of Mn(OH)\(_2\) with \( H_2O_2 \). Infrared spectra were recorded on a Perkin Elmer model 983 spectrophotometer. The reflectance spectra of the compounds were recorded against MgO using Carl-Zeis Jena VSU 2-p instrument. The Gouy method was used to measure the magnetic susceptibility of the complexes with \( Hg[Co(NCS)_4] \) as the standard.

Synthesis of the complexes

Synthesis of mixed-ligand fluoro complexes, of the type \( A[Mn\ L_2\ F_4]3H_2O \) (\( L = \) alanine or valine; \( A = Na, K \) or \( NH_4 \))

General procedure

An amount of 0.89g (10.11 mmol) of freshly prepared MnO(OH) was dissolved in 2.0 cm\(^3\) (40.0 mmol) of 40% HF with continuous stirring, keeping the molar ratio as 1:4. The solution was stirred for ca 10 min followed by the addition of 1.80 g (20.22 mmol) of alanine/2.36 g (20.22 mmol) of valine keeping MnO(OH) to amino acid (alanine or valine) ratio at 1:2 and the resulting solution was stirred for a further period of ca 15 min. To the resulting mixture was added a specific amount of \( A_2CO_3 \) (\( A = Na, K, NH_4 \)) with stirring keeping the MnO(OH) : \( A_2CO_3 \) ratio at 1:0.5. The reaction mixture was then concentrated over a steam bath followed by a slow addition of acetone, whereupon pink micro-crystalline product was precipitated out. The compounds were collected by filtration, washed three to four times with small amount of acetone and dried \textit{in vacuo} over conc. \( H_2SO_4 \).

Manganese was estimated by the literature method. The fluoride contents of the compounds were determined by volhard’s method. Sodium and potassium were determined by the method reported in literature. Carbon, Hydrogen and Nitrogen were estimated by micro-analytical methods.

Results and discussion

The problem associated with the synthesis of manganese (III) compounds from aqueous medium is the
Table 1 — Analytical data of mixed-ligand fluoro complexes of Mn(III)

<table>
<thead>
<tr>
<th>Compound (yield, %)</th>
<th>Magnetic moment at 300K, µB</th>
<th>A or N</th>
<th>Mv</th>
<th>F</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄[Mn(ala)₂F₄].3H₂O (89)</td>
<td>5.0</td>
<td>-</td>
<td>14.39</td>
<td>19.98</td>
<td>19.01</td>
<td>6.86</td>
<td>11.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(14.43)</td>
<td>(19.95)</td>
<td>(18.92)</td>
<td>(6.82)</td>
<td>(11.02)</td>
</tr>
<tr>
<td>K[Mn(ala)₂F₄].3H₂O (87)</td>
<td>4.9</td>
<td>9.90</td>
<td>13.76</td>
<td>18.62</td>
<td>18.01</td>
<td>5.65</td>
<td>6.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(9.70)</td>
<td>(13.68)</td>
<td>(18.90)</td>
<td>(17.91)</td>
<td>(5.47)</td>
</tr>
<tr>
<td>Na[Mn(ala)₂F₄].3H₂O (80)</td>
<td>-</td>
<td>5.99</td>
<td>14.22</td>
<td>19.75</td>
<td>18.69</td>
<td>5.76</td>
<td>7.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(5.96)</td>
<td>(14.25)</td>
<td>(19.69)</td>
<td>(18.65)</td>
<td>(5.69)</td>
</tr>
<tr>
<td>NH₄[Mn(val)₂F₄].3H₂O (92)</td>
<td>4.6</td>
<td>-</td>
<td>12.78</td>
<td>17.20</td>
<td>27.43</td>
<td>6.65</td>
<td>9.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(12.59)</td>
<td>(17.39)</td>
<td>(27.46)</td>
<td>(6.55)</td>
<td>(9.61)</td>
</tr>
<tr>
<td>K[Mn(val)₂F₄].3H₂O (90)</td>
<td>-</td>
<td>8.85</td>
<td>12.21</td>
<td>16.80</td>
<td>26.31</td>
<td>6.45</td>
<td>6.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(8.52)</td>
<td>(12.01)</td>
<td>(16.59)</td>
<td>(26.20)</td>
<td>(6.55)</td>
</tr>
<tr>
<td>Na[Mn(val)₂F₄].3H₂O (85)</td>
<td>4.7</td>
<td>5.22</td>
<td>12.68</td>
<td>17.90</td>
<td>27.10</td>
<td>6.83</td>
<td>6.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(5.20)</td>
<td>(12.44)</td>
<td>(17.19)</td>
<td>(27.15)</td>
<td>(6.79)</td>
</tr>
</tbody>
</table>

Tendency of the metal ion to disproportionate to manganese(IV) and manganese(II)\(^2\). However, in view of the recent results\(^4\)-\(^10\) it was anticipated that this problem can be encountered if the reaction is carried out in highly acidic medium in the presence of fluoride ions, as it has pronounced stabilizing effect on manganese(III). For the synthesis of mixed-ligand fluoro-manganates(III) complexes containing alanine(ala) or valine(val) as the co-ligands, freshly prepared MnO(OH) was allowed to react with 40% HF and the corresponding amino acid maintaining the ratio of Mn:F: amino acid at 1:4:2. Alkali-metal and ammonium carbonate was used as the source of counter cations instead of alkali-metal or ammonium fluoride. An excess amount of fluoride was avoided in order to suppress the formation of MnF\(_5^{2-}\) instead of the desired compounds. The compounds were precipitated by the slow addition of acetone to the concentrated reaction mixture. The compounds synthesised in this way were found to be pink-microcrystalline product of composition A[MnL\(_2\)F\(_4\)].3H\(_2\)O (L = alanine or valine; A = Na, K or NH\(_4\)). (Analytical data given in Table 1).

All the newly synthesised compounds are stable in the absence of moisture and can be stored for a prolong period in sealed polythene bags. The stability of the compounds can be ascertained by periodic estimation of manganese and recording their infrared spectra. However, the compounds undergo slow decomposition in water, and they are practically insoluble in common organic solvents precluding their molar conductance measurements.

The room temperature (300 K) magnetic susceptibility measurements of the complexes exhibit magnetic moment values of A[Mn(val)\(_2\)F\(_4\)].3H\(_2\)O and A[Mn(ala)\(_2\)F\(_4\)].3H\(_2\)O and (A = Na, K or NH\(_4\)) in the range 4.6- 4.7 \(\mu\)B and 5.0 \(\mu\)B respectively. These values are normal as expected for a high spin \(d^4\) system of Mn(III) ion. The slightly lower magnetic moment values in case of valine complexes indicate that there exists a possibility of weak antiferromagnetic interactions to be operative between continuous Mn(II) ions in the crystal lattice.

The electronic (reflectance) spectrum of alanine complexes exhibit bands at ca 13.831, ca 19.436 and at ca 24.906 cm\(^{-1}\) assigned to \(^5\)A \(_{1g} \rightarrow \ ^5\)A \(_{1g}\), \(^5\)B \(_{2g} \rightarrow \ ^5\)E \(_{g}\) and \(^5\)B \(_{2g} \rightarrow \ ^5\)E \(_{g}\) modes of transitions respectively, whereas the corresponding valine complexes exhibit at ca 14.705, ca 21.739 and at ca 24.154 cm\(^{-1}\) respectively. The spectral pattern suggests an appreciable splitting of \(^5\)E \(_{g}\) ground state of manganese (III) and suggest that the newly synthesised complexes have distorted octahedral structures\(^{15}\). The magnetic moment values and electronic spectral band positions unequivocally suggest the presence of high-spin Mn(III) in each of the complexes reported herein.

The significant features of the infrared spectra of A[MnL\(_2\)F\(_4\)].3H\(_2\)O (L = alanine or valine; A = Na, K or NH\(_4\)) display patterns typical of coordinated amino acid\(^{16}\) and coordinated fluoride ligand\(^{17}\). The (COO\(^-\)) frequency of amino acid are effected by coordination as well as by intermolecular interactions, with the increase in antisymmetric (O-C-O) stretching frequency while the symmetric ones are shifted to lower values\(^{16}\). The \(\nu\) (COO\(^-\)) in the present case occur at ca 1589 and 1410 cm\(^{-1}\) and are assigned \(\nu\) \(_{s\text{ym}}\) (COO\(^-\)) and \(\nu\) \(_{as\text{ym}}\) (COO\(^-\)) modes of vibrations of amino acid. The appearance of two additional bands at ca 1618 and at
ca 1531 cm⁻¹ attributed to δ(NH₃⁺) and δ₂ (NH₃⁺) modes of vibration of the zwitterionic form of amino acid. These values agree well with reported ones in the literature. The appearance of these bands and absence of any bands at ca 480 and ca 350 cm⁻¹ due to ν(Mn-N) and δ(Mn-N) lend support to the proposition that in the present case both alanine and valine are present in their zwitterionic form -

\[(\text{NH}_3^+ \cdot \text{CH} \cdot \text{COO}^-)\]

and coordinated to the metal centre through their carboxylic oxygen atom in unidentate fashion. The coordination of fluoride ligand was ascertained from observation of band at ca 412 cm⁻¹ assigned to ν(Mn-F). Two additional bands at ca 3460 and ca 1635 cm⁻¹ resemble in their shapes and positions to that of ν(O-H) and δ(H-O-H) modes of lattice water.

The results of pyrolytic studies of Na[Mn(valF)₄]. 3H₂O shows that compound begin to lose weight at ca 100°C and loses one molecule of water at 110°C followed by the loss of two molecules between 150-160°C. The compound on being further heated to 200-220°C suffered loss of three molecules of HF per molecule of the product. The origin of HF may be due to the abstraction of three H from NH₃⁺ moiety of the amino acid by fluoride ligands. The thermal studies therefore clearly suggest the presence of uncoordinated water molecules and supports the formulation of the compounds.

Fluoride assisted stabilization of manganese (III) has been demonstrated by synthesising mixed ligand fluoromanganate (III) complexes with amino acid as co-ligand from aqueous medium. The newly synthesised complexes have distorted octahedral structure and there exist a finite possibility of weak antiferromagnetic interaction to be operative through Mn...F...Mn...chain in the crystal lattice.

Acknowledgement

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References


17. Reference 29, pp 324.