Synthesis and characterization of lanthanide complexes of 2-acetylaminothiazole

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A few lanthanide complexes of 2-acetylaminothiazole of the type \([\text{Ln(acamth)}_2\text{Cl}_2]\) [where \(\text{Ln} = \text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}, \text{Tb(III)} \) or \(\text{Dy(III)}\)] have been synthesized and characterized by infrared, electronic, emission, magnetic susceptibility, molar conductance and X-ray powder data. It is observed from the IR spectra that ring nitrogen and carbonyl oxygen interact with lanthanide ions. The electronic spectra and molar conductivity suggest coordination number six around the metal ions.

A number of metal complexes of 2-acetylaminothiazole have been earlier reported. In the present note we report for the first time the synthesis and characterization of the complexes of \(\text{La(III)}, \text{Pr(III)}, \text{Nd(III)}, \text{Sm(III)}, \text{Eu(III)}, \text{Gd(III)}, \text{Tb(III)} \) and \(\text{Dy(III)}\) with 2-acetylaminothiazole (acamth, I).

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{C} & \quad \text{H}_3
\end{align*}
\]

Experimental

The lanthanide(III) chlorides (Indian Rare Earths Limited, Kerala, India) were used as obtained. 2-Acetylaminothiazole was prepared by following the procedure reported elsewhere. The solvents were purified using standard procedures.

Preparation of complexes

Dichloro bis(2-acetylaminothiazole)metal(III) chloride \([\text{Ln(acamth)}_2\text{Cl}_2]\) were prepared by mixing together anhydrous ethanolic solutions of the appropriate lanthanide chloride (1 mmol in 10 cm\(^3\)) and 2-acetylaminothiazole (2 mmol in 30 cm\(^3\)) and refluxing the mixture for \(\sim 4\) h. The reaction solution was concentrated to \(\sim 5\) ml and acetonitrile was added. A gummy solid was obtained which, after macerating with acetonitrile several times yielded crystalline complexes. The powdered complexes were filtered and washed with a mixture of acetonitrile and ethanol and dried in vacuo.

The metals, after destroying the organic matter by successive treatment with aqua regia and \(\text{H}_2\text{SO}_4\), were determined volumetrically by EDTA titration using xylene orange indicator. Chloride and sulphur were determined gravimetrically as \(\text{AgCl}\) and \(\text{BaSO}_4\), respectively. The molar conductance of \(10^{-3}\) \(M\) solutions of the complexes in ethanol was measured at room temperature on a WTW conductivity meter. The magnetic susceptibility measurements were carried out on a Cahn Faraday electrobalance using \(\text{Hg[Co(NCS)]}_4\) calibrant. The electronic absorption spectra were recorded on a Cary-2390 and Shimadzu-160A spectrophotometers. The infrared spectra were obtained in KBr discs on a Jasco FT/IR-5300 spectrophotometer. The emission spectra of solid complexes were recorded on Perkin-Elmer MPF-44B fluorescence spectrophotometer. The X-ray powder diffraction pattern was obtained on a Rigaku Geigerflex D/MAX-III X-ray diffractometer using CuK\(_{a}\) radiation. The indexing of X-ray powder lines was done by Ito's method.

Results and discussion

The analytical data (Table 1) show that acamth forms 2:1 adduct complexes of the formula \([\text{Ln(acamth)}_2\text{Cl}_2]\). The reaction of lanthanide chlorides with the ligand in 1:3 and 1:1 molar ratios also yielded the complexes having 2:1 metal-thiazole ratio. The complexes are soluble in methanol, ethanol, DMSO and DMF, but insoluble in water and other organic solvents like chloroform, acetone, acetonitrile, dichloromethane, carbontetrachloride and ether. The complexes melt in the range 128 to 164°C except \(\text{La(III)}\) and \(\text{Pr(III)}\) complexes which decomposes at 135°C and 215°C, respectively. The molar conductance values are commensurate with 1:1 electrolytic behaviour of the complexes. The lanthanum(III) complex is diamagnetic, while room temperature magnetic susceptibilities of all other complexes except those of \(\text{Sm(III)}\) and \(\text{Eu(III)}\) show a little deviation from Van Vleck values, indicating slight participation...
NOTES

Table 1 - Characterization data of Ln(III) complexes of acamth

<table>
<thead>
<tr>
<th>Complex</th>
<th>M.pt. (°C)</th>
<th>Found (Calcd.), %</th>
<th>μeff (BM)</th>
<th>Λm (ohm⁻¹cm⁻²mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M</td>
<td>Cl</td>
<td>S</td>
</tr>
<tr>
<td>[La(acamth)₂Cl₂]Cl</td>
<td>135³</td>
<td>26.3</td>
<td>20.0</td>
<td>12.0</td>
</tr>
<tr>
<td>52, White</td>
<td></td>
<td>(26.2)</td>
<td>(20.1)</td>
<td>(12.1)</td>
</tr>
<tr>
<td>[Pr(acamth)₂Cl₂]Cl</td>
<td>215³</td>
<td>26.6</td>
<td>20.1</td>
<td>12.1</td>
</tr>
<tr>
<td>59, Cream</td>
<td></td>
<td>(26.5)</td>
<td>(20.0)</td>
<td>(12.0)</td>
</tr>
<tr>
<td>[Nd(acamth)₂Cl₂]Cl</td>
<td>128-132</td>
<td>26.8</td>
<td>20.0</td>
<td>11.9</td>
</tr>
<tr>
<td>70, Light purple</td>
<td></td>
<td>(26.9)</td>
<td>(19.9)</td>
<td>(11.9)</td>
</tr>
<tr>
<td>[Sm(acamth)₂Cl₂]Cl</td>
<td>148-151</td>
<td>27.7</td>
<td>19.7</td>
<td>11.7</td>
</tr>
<tr>
<td>49, Cream</td>
<td></td>
<td>(27.8)</td>
<td>(19.7)</td>
<td>(11.8)</td>
</tr>
<tr>
<td>[Eu(acamth)₂Cl₂]Cl</td>
<td>150-153</td>
<td>28.1</td>
<td>19.5</td>
<td>11.8</td>
</tr>
<tr>
<td>72, Cream</td>
<td></td>
<td>(28.0)</td>
<td>(19.6)</td>
<td>(11.8)</td>
</tr>
<tr>
<td>[Gd(acamth)₂Cl₂]Cl</td>
<td>142-146</td>
<td>28.6</td>
<td>19.5</td>
<td>11.8</td>
</tr>
<tr>
<td>60, Cream</td>
<td></td>
<td>(28.7)</td>
<td>(19.4)</td>
<td>(11.7)</td>
</tr>
<tr>
<td>[Tb(acamth)₂Cl₂]Cl</td>
<td>161-164</td>
<td>28.8</td>
<td>19.4</td>
<td>11.7</td>
</tr>
<tr>
<td>45, Cream</td>
<td></td>
<td>(28.9)</td>
<td>(19.3)</td>
<td>(11.6)</td>
</tr>
<tr>
<td>[Dy(acamth)₂Cl₂]Cl</td>
<td>160-164</td>
<td>29.4</td>
<td>19.1</td>
<td>11.4</td>
</tr>
<tr>
<td>53, Cream</td>
<td></td>
<td>(29.3)</td>
<td>(19.2)</td>
<td>(11.5)</td>
</tr>
<tr>
<td>d - decomposed</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

of the 4f-electrons in bonding. The relatively high values obtained in case of Sm(III) and Eu(III) complexes is due to low J-J separation, which leads to thermal population of higher energy levels and show susceptibilities due to a first order Zeeman effect.

The electronic spectra of Pr(III), Nd(III) and Sm(III) complexes recorded in nujol mull were compared with those of aqueous metal nitrate solution. The spectral data and various parameters calculated are given in Table 2. The features of the hypersensitive transition $^4G_{5/2} \rightarrow ^2G_{7/2}$ in the neodymium(III) complex in nujol mull differ from that of the aquo metal ion. The hypersensitive band observed at 17301 cm⁻¹ in [Nd(acamth)₂Cl₂]Cl is observed at lower energy compared to aqua ion. The slight red shift clearly indicates interaction of metal ion with the ligand.

Jørgensen attributed these shifts to the effect of crystal fields upon the interelectronic repulsion among the 4f electrons, i.e. to lowering of the interelectronic repulsion parameter ($\beta$) in the complex. The other parameters viz., bonding ($\beta^{1/2}$), covalency ($\eta$) and Sinha's parameter (%$\delta$) have also been calculated using literature procedures. These values indicate partial covalent bonding developing between the metal ion and the ligand. This is also supported by oscillator strength values ($P$) (Table 3). The spectral profiles of the neodymium complex have similar appearance in solid (nujol) and ethanolic solution. This indicates that the complex retains its identity in solution also. The spectral feature of the hypersensitive transition $^4I_{9/2} \rightarrow ^4G_{5/2}$ is consistent with coordination number six around the metal ion as reported by Karraker.

The IR spectrum of 2-acetylaminothiazole shows bands at 3414, 1685, 1570, 1500, 1470, 1369, 1232 and 659 cm⁻¹ which are assigned to $\nu(N-H)$, $\nu(C=O)$, amide II, $\nu(C=N)$ ring skeletal (I), ring skeletal (II), $\nu(C-N)_{exo}$, ring skeletal(III) and $\nu(C-S)$ respectively. The $\nu(C=O)$ and $\nu(N-H)$ are observed at 1630-1626 and 3410-3364 cm⁻¹ respectively in the spectra of the complexes. This gives a clue for bonding of acamth through the carbonyl oxygen. This is also supported by negative shifts in amide II (25-72 cm⁻¹) and $\nu(C-N)_{exo}$ (35-77 cm⁻¹) bands. The bonding through ring nitrogen is inferred from shifting of bands due to ring skeletal (I, II & III) to the lower frequencies 1460-1450, 1448-1400 and 1172-1168 cm⁻¹, respectively. The $\nu(C-S)$ does not show any change suggesting non-involvement of sulphur in bonding.

The study of emission $f-f$ spectra gives useful information concerning nature of the chromophore and geometry around lanthanide ions in the complexes. [Ln(acamth)₂Cl₂]Cl [Ln = Sm(III),...
Table 2 – Electronic spectral data of Pr(III), Nd(III) and Sm(III) complexes of acamth

<table>
<thead>
<tr>
<th>Complex</th>
<th>Band max. (cm⁻¹)</th>
<th>Assignments</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in nujol (solid)</td>
<td>in EtOH solution</td>
<td></td>
</tr>
<tr>
<td>[Pr(acamth)₂Cl₂]Cl_3</td>
<td>6389</td>
<td>²H₄ → ³F₅</td>
<td>( \beta = 0.9905 )</td>
</tr>
<tr>
<td></td>
<td>6849</td>
<td>→ ³F₄</td>
<td>( \delta = 0.9579 )</td>
</tr>
<tr>
<td></td>
<td>9727</td>
<td>→ ¹G₄</td>
<td>( \eta = 0.9790 )</td>
</tr>
<tr>
<td></td>
<td>16806</td>
<td>¹D₂</td>
<td>( \eta = 0.0688 )</td>
</tr>
<tr>
<td></td>
<td>20661</td>
<td>³P₀</td>
<td>( \eta = 0.0950 )</td>
</tr>
<tr>
<td></td>
<td>21276</td>
<td>³P₁</td>
<td>( \eta = 0.9905 )</td>
</tr>
<tr>
<td></td>
<td>22471</td>
<td>³P₂</td>
<td>( \eta = 0.9579 )</td>
</tr>
<tr>
<td>[Nd(acamth)₂Cl₂]Cl</td>
<td>11520</td>
<td>⁴L₉/₂ → ⁴F₃/₂</td>
<td>( \beta = 0.9930 )</td>
</tr>
<tr>
<td></td>
<td>12500</td>
<td>⁴F₃/₂</td>
<td>( \beta = 0.9930 )</td>
</tr>
<tr>
<td></td>
<td>13368</td>
<td>⁴F₅/₂</td>
<td>( \delta = 0.7013 )</td>
</tr>
<tr>
<td></td>
<td>13550</td>
<td>⁴S₃/₂</td>
<td>( \delta = 0.7013 )</td>
</tr>
<tr>
<td></td>
<td>14705</td>
<td>⁴F₂/₂</td>
<td>( \eta = 0.0837 )</td>
</tr>
<tr>
<td></td>
<td>15974</td>
<td>²H₁₁/₂</td>
<td>( \delta = 0.0590 )</td>
</tr>
<tr>
<td></td>
<td>17301</td>
<td>²G₁₀/₂</td>
<td>( \delta = 0.0590 )</td>
</tr>
<tr>
<td></td>
<td>19230</td>
<td>⁴G₉/₂</td>
<td>( \delta = 0.0590 )</td>
</tr>
<tr>
<td></td>
<td>21097</td>
<td>²G₆/₂</td>
<td>( \delta = 0.0590 )</td>
</tr>
<tr>
<td></td>
<td>23474</td>
<td>²D₅/₂</td>
<td>( \delta = 0.0590 )</td>
</tr>
<tr>
<td></td>
<td>28571</td>
<td>²D₁₀/₂</td>
<td>( \delta = 0.0590 )</td>
</tr>
<tr>
<td>[Sm(acamth)₂Cl₂]Cl</td>
<td>6493</td>
<td>⁶H₉/₂ → ⁶H₁₄/₂</td>
<td>( \beta = 0.9784 )</td>
</tr>
<tr>
<td></td>
<td>7042</td>
<td>⁶F₅/₂</td>
<td>( \beta = 0.9784 )</td>
</tr>
<tr>
<td></td>
<td>7905</td>
<td>⁶F₃/₂</td>
<td>( \delta = 0.1039 )</td>
</tr>
<tr>
<td></td>
<td>9276</td>
<td>⁶G₇/₂</td>
<td>( \delta = 2.0068 )</td>
</tr>
<tr>
<td></td>
<td>20491</td>
<td>⁴I₂/₂</td>
<td>( \eta = 0.1485 )</td>
</tr>
<tr>
<td></td>
<td>21505</td>
<td>⁴I₃/₂</td>
<td>( \eta = 0.1485 )</td>
</tr>
<tr>
<td></td>
<td>24752</td>
<td>⁴F₇/₂</td>
<td>( \eta = 0.1485 )</td>
</tr>
</tbody>
</table>

Table 3 – Oscillator strength values for Pr(III) and Nd(III) complexes of acamth

<table>
<thead>
<tr>
<th>Complex</th>
<th>Spectral range</th>
<th>Assignments</th>
<th>Oscillator strengths (( P \times 10^6 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Pr(acamth)₂Cl₂]Cl</td>
<td>16366-17132</td>
<td>³H₄ → ¹D₂</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>20120-20790</td>
<td>³P₀</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>20790-21668</td>
<td>³P₁</td>
<td>2.88</td>
</tr>
<tr>
<td></td>
<td>21668-22634</td>
<td>³P₂</td>
<td>6.45</td>
</tr>
<tr>
<td>[Nd(acamth)₂Cl₂]Cl</td>
<td>11273-11695</td>
<td>⁴L₉/₂ → ⁴F₅/₂</td>
<td>3.56</td>
</tr>
<tr>
<td></td>
<td>12077-12809</td>
<td>⁴F₅/₂</td>
<td>18.68</td>
</tr>
<tr>
<td></td>
<td>13005-13781</td>
<td>⁴F₃/₂, ⁴S₃/₂</td>
<td>16.64</td>
</tr>
<tr>
<td></td>
<td>16677-17608</td>
<td>²G₇/₂, ⁴G₉/₂</td>
<td>11.89</td>
</tr>
<tr>
<td></td>
<td>18518-20120</td>
<td>⁴G₂/₂</td>
<td>6.45</td>
</tr>
<tr>
<td></td>
<td>27255-29463</td>
<td>⁴D₃/₂</td>
<td>6.28</td>
</tr>
</tbody>
</table>
Eu(III) and Tb(III) complexes do not fluoresce or fluoresce very weakly even at liquid nitrogen temperature. This may be due to internal quenching through strong coupling of the ions with the crystal forces. This may also be due to nature of the ligand which acts as effective 'sink' for tunnelling away of the energy and thus reducing the fluorescence yield drastically.

The presence of only a few weak lines in the powder pattern are indicative of amorphous nature of the ligand and the complex [La(acamth)$_2$Cl$_2$]Cl. No lines are common in the ligand and its complex showing that the complex is a new entity and not a mixture of the ligand and metal chloride.

Acknowledgement
The authors are thankful to the Head, Department of Chemistry, Banaras Hindu University, for providing laboratory facilities. We wish to thank Prof. S Lele, Department of Metallurgical Engineering, BHU for recording X-ray powder patterns and also to RSIC, Bose Institute, Calcutta, for recording emission spectra.

References