Schiff Base Derivatives of Lanthanons
Synthesis of La(III) Pr(III) and Nd(III) Derivatives of Ethylenediamine Bis-2,4-pentanedione

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The 1:1 and 2:3 molar reactions of La(III), Pr(III) and Nd(III) isopropoxides with the bifunctional tetradentate Schiff base, ethylenediamine bis-2,4-pentanedione \( [\text{AA}_2(CH_2)_2]^2 \) have been investigated in the medium of dry benzene.

\[
\text{Ln}(O-i-C_3H_7) [\text{AA}_2(CH_2)_2]^2 \quad (\text{where, } \text{Ln} = \text{La(III)}, \text{Pr(III)} \text{ or Nd(III)}) \text{ and } \text{AA}_2(CH_2)_2^{-2} \text{ anion of the corresponding Schiff base, } \text{AA}_2(CH_2)_2H_2 \text{ type of compounds have been obtained in almost quantitative yields and in a state of sufficient purity. The 1:1 derivatives have been shown to undergo exchange reactions with an excess of tetr-butyl alcohol leading to the formation of } \text{Ln}(O-t-am-C_4H_9) [\text{AA}_2(CH_2)_2]^2 \text{ (where, } \text{Ln} = \text{La(III)}, \text{Pr(III)} \text{ or Nd(III)}) \text{ type of derivatives. The ebullioscopic determination of molecular weights shows that the 1:1 derivatives are dimeric, whereas 2:3 derivatives are monomeric in boiling benzene. On the basis of elemental analysis, exchange reactions, molecular weight determinations and IR spectra, plausible structures for the resulting 1:1 and 2:3 complexes have been indicated.}
\]

Martell et al.\(^1\) have reported Cu(II), Ni(II), Co(II), Pd(II) and Pt(II) complexes with the bifunctional tetradentate Schiff base, ethylenediamine bis-2,4-pentanedione. Recently Dutt et al.\(^2\) have synthesized complexes of the composition, \([\text{Ln}]=\text{La}, \text{Ce}, \text{Pr}, \text{Nd} \text{ and Sm; } \text{enac} \text{ = ethylenediamine bis-2,4-pentanedione and } x = \text{Cl}^{-}, \text{NO}_3^{-} \text{ and SCN}^{-} \text{ and } [\text{Ln}_2(\text{enac})_2]_3^2 \text{ (where, } \text{Ln} = \text{Gd}, \text{Dy}, \text{Er and Y and } x = \text{Cl}^{-} \text{ and } \text{NO}_3^{-} \text{). In these derivatives, molecules and not the anions, of the Schiff base are coordinated with the metal ions. During the course of the present investigations, a convenient method for the synthesis of derivatives of the composition, } \text{Ln}(O-i-C_3H_7) [\text{AA}_2(CH_2)_2]^2 \text{ and } \text{Ln}_2[\text{AA}_2(CH_2)_2]^3 \text{ (where, } \text{Ln} = \text{La(III)}, \text{Pr(III)}, \text{ or Nd(III)} \text{ and } \text{AA}_2(CH_2)_2^{-2} \text{ the anion of the Schiff base, ethylenediamine bis-2,4-pentanedione } \text{AA}_2(CH_2)_2H_2 \text{ has been reported.}

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**Experimental**

Adequate precautions were taken to exclude moisture at all stages of the reactions and all glass apparatus fitted with standard Quickfit interchangeable joints was used.

**Materials:** Lanthanum, praseodymium and neodymium isopropoxides were prepared by the sodium alkoxide\(^3\) method and analysed before use.

- **La(III) isopropoxide**
  - Found: La 43.70, O-i-C_3H_7 55.80
  - Calcd: La 43.94, O-i-C_3H_7 55.06
  - Mol. wt. found 345.0, calcd 345.0

- **Pr(III) isopropoxide**
  - Found: Pr 44.40, O-i-C_3H_7 55.40
  - Calcd: Pr 44.21, O-i-C_3H_7 55.06
  - Mol. wt. found 348.0, calcd 348.0

- **Nd(III) isopropoxide**
  - Found: Nd 44.50, O-i-C_3H_7 55.20
  - Calcd: Nd 44.87, O-i-C_3H_7 55.13
  - Mol. wt. found 324, calcd 324

Schiff base, ethylenediamine bis-2,4-pentanedione was prepared by the condensation of 2,4-pen-
tanedione and ethylenediamine as reported in the literature and analysed before use.

**Ethylenediamine bis-2,4-pentanedione**

\[ C_{12}H_{20}O_2N_2 \]

Found: N 12.58 C 64.14 H 8.85,  
Caled: N 12.50 C 64.28 H 8.92.

Benzene (B.D.H.) was first refluxed over sodium wire for several hours and then distilled azeotropically with absolute alcohol. Isopropanol (B.D.H.) was refluxed over sodium metal and then distilled over aluminium isopropoxide.

**Synthesis of La(III), Pr(III) and Nd(III) Schiff base complexes**

The reactions of La(III), Pr(III) and Nd(III) isopropoxides and ethylenediamine bis-2,4-pentanedione in 1:1 and 2:3 molar ratios were carried out in anhydrous benzene. The contents were refluxed and the isopropanol liberated in the reaction was collected azeotropically with benzene using the same experimental technique as reported earlier. After removing the volatile solvent over pump, the products were finally dried under reduced pressure (40-60 °C/0.5 mm). The details of their syntheses and physical properties are recorded in Table I.

**Exchange reactions**

The exchange reactions of mono-isopropoxy lanthanon Schiff base derivatives with tert-butyl alcohol were carried out in anhydrous benzene. The isopropanol-benzene azeotrope was collected slowly and the course of reaction assured by estimating the isopropanol liberated in the reaction. The volatile fraction was removed and the product finally dried under reduced pressure. The details of these reactions are recorded in Table II.

**Analytical methods and physical measurements**

Lanthanum, praseodymium and neodymium were determined by complexometric titration with EDTA using Eriochrome Black T as the indicator.

Nitrogen was estimated by Kjeldahl's method and the isopropanol by oxidation method using normal potassium dichromate solution in 12.5% sulphuric acid.

Molecular weights were determined in boiling benzene by means of semi-micro ebulliometer (Gallenkamp) using thermistor sensing.

Infrared spectra were recorded in the region, 4000–400 cm⁻¹ as nujol mulls using a Perkin Elmer model 337 grating infrared spectrophotometer (Table III).

**Results and Discussion**

The formation of mono-isopropoxy lanthanon Schiff base and bis-lanthanon tris-Schiff base derivatives, the products 1:1 and 2:3 molar reactions, respectively, can be represented by the following general equations:

<table>
<thead>
<tr>
<th>Ln(O–i-C₃H₇)₃</th>
<th>Schiff base</th>
<th>Molar flux – ratio</th>
<th>Product and characteristics</th>
<th>Isopropanol in the azeotrope</th>
<th>Analysis [%]</th>
<th>Molecular weight</th>
<th>Molecular association</th>
</tr>
</thead>
<tbody>
<tr>
<td>La(O–i-C₃H₇)₃</td>
<td>C₁₂H₂₀O₂N₂</td>
<td>1:1</td>
<td>16</td>
<td>La(O–i-C₃H₇) (C₁₂H₁₈O₂N₂)</td>
<td>0.19 (0.19)</td>
<td>33.16 (33.07)</td>
<td>6.59 (6.66)</td>
</tr>
<tr>
<td>La(O–i-C₃H₇)₃</td>
<td>[0.52]</td>
<td>0.37</td>
<td></td>
<td>Light yellow solid, soluble in benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pr(O–i-C₃H₇)₃</td>
<td>C₁₂H₂₀O₂N₂</td>
<td>2:3</td>
<td>30</td>
<td>Pr₂(O–i-C₃H₇) (C₁₂H₁₆O₂N₂)</td>
<td>0.28 (0.29)</td>
<td>29.36 (29.41)</td>
<td>8.90 (8.89)</td>
</tr>
<tr>
<td>Nd(O–i-C₃H₇)₃</td>
<td>C₁₂H₂₀O₂N₂</td>
<td>1:1</td>
<td>16</td>
<td>Nd(O–i-C₃H₇) (C₁₂H₁₆O₂N₂)</td>
<td>0.26 (0.27)</td>
<td>33.88 (33.90)</td>
<td>6.62 (6.58)</td>
</tr>
<tr>
<td>Nd(O–i-C₃H₇)₃</td>
<td>[0.74]</td>
<td>0.51</td>
<td></td>
<td>Yellow solid, sparingly soluble in benzene</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nd(O–i-C₃H₇)₃</td>
<td>C₁₂H₂₀O₂N₂</td>
<td>2:3</td>
<td>30</td>
<td>Nd₂(O–i-C₃H₇) (C₁₂H₁₆O₂N₂)</td>
<td>0.35 (0.36)</td>
<td>30.24 (30.18)</td>
<td>8.80 (8.71)</td>
</tr>
</tbody>
</table>
Table II. Reactions of isopropoxy Schiff base derivatives of Ln(III) with tert-butyl alcohol.

<table>
<thead>
<tr>
<th>Compound</th>
<th>tert- Butyl alcohol (in excess) [g]</th>
<th>Product and characteristics</th>
<th>Isopropanol in the azeotrope</th>
<th>Analysis [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Found (Calcd.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>La</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>N</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>F ound (Calcd.)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(Calcd.)</td>
<td></td>
</tr>
<tr>
<td>La(O-i-C₃H₇) (C₁₂H₁₈O₂N₂)</td>
<td>3.20 [0.72]</td>
<td>Light yellow solid, sparingly soluble in benzene</td>
<td>0.10 (0.10)</td>
<td>32.06 (32.00)</td>
</tr>
<tr>
<td>Pr(O-i-C₃H₇) (C₁₂H₁₈O₂N₂)</td>
<td>3.62 [0.68]</td>
<td>Yellow solid, sparingly soluble in benzene</td>
<td>0.09 (0.09)</td>
<td>32.32 (32.29)</td>
</tr>
<tr>
<td>Nd(O-i-C₃H₇) (C₁₂H₁₈O₂N₂)</td>
<td>2.90 [0.76]</td>
<td>Yellow solid, sparingly soluble in benzene</td>
<td>0.11 (0.11)</td>
<td>32.88 (32.81)</td>
</tr>
</tbody>
</table>

Table III. Infrared frequencies [in cm⁻¹] of Schiff bases and complexes of La(III), Pr(III) and Nd(III).

<table>
<thead>
<tr>
<th>Compound</th>
<th>C = N stretching</th>
<th>O-i-C₃H₇ stretching</th>
<th>Ring deformation + Ln-O stretching</th>
<th>CH₃ stretching</th>
<th>C-H out of plane deformation + Ln-O stretching</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₂H₂₅O₂N₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>La(O-i-C₃H₇) (C₁₂H₁₈O₂N₂)</td>
<td>1608</td>
<td>—</td>
<td>1112</td>
<td>660</td>
<td>938</td>
</tr>
<tr>
<td>La₂(C₁₂H₁₈O₂N₂)₃</td>
<td>1606</td>
<td>—</td>
<td>1118</td>
<td>660</td>
<td>936</td>
</tr>
<tr>
<td>Pr₂(C₁₂H₁₈O₂N₂)₃</td>
<td>1605</td>
<td>—</td>
<td>1118</td>
<td>660</td>
<td>935</td>
</tr>
<tr>
<td>Nd₂(C₁₂H₁₈O₂N₂)₃</td>
<td>1605</td>
<td>—</td>
<td>1118</td>
<td>660</td>
<td>935</td>
</tr>
</tbody>
</table>

\[
\text{Ln(O-i-C₃H₇)₃} + \text{AA₂(CH₂)₂H₂} \rightarrow \\
\text{Ln(O-i-C₃H₇)[AA₂(CH₂)₂] + 2-i-C₃H₇OH}
\]

\[
2 \text{Ln(O-i-C₃H₇)₃} + 3 \text{AA₂(CH₂)₂H₂} \rightarrow \\
\text{Ln₂[AA₂(CH₂)₂]₃ + 6-i-C₃H₇OH}
\]

(where, Ln = La(III), Pr(III) or Nd(III)).

The formation of these complexes may be ascribed to the polarized nature of the metal-oxygen bond (Ln⁶⁺-O⁶⁻-C) in the metal isopropoxides and the constant removal of the benzene-isopropanol azeotrope pushes the reaction to completion.

However, in the method reported by Dutt et al.,² Ln(NO₃)₃ • 6 H₂O salts are dissolved in the ethanolic medium. There is very little attraction between the aquo complex, [Ln(OH₂)₃]³⁺ and the solvated NO₃⁻ ion and the interaction with the Schiff base simply results in the displacement of the bonded water molecules and preserving the ionic nature of the complex.

The mono-isopropoxy lanthanon Schiff base derivatives are yellow crystalline solids and on heating appear to undergo decomposition. These have been found to be dimeric in boiling benzene, the dimerization possibly occurs through isopropoxy bridges. These may be structurally represented as indicated below (I):
The bis-lanthanon tris-Schiff base derivatives, the products of 2:3 molar reactions are almost of the same nature and found to be monomeric as shown by structure (2):

\[
\begin{align*}
\text{CH}_3 & - \text{C} = \text{C} - \text{CH}_3 \\
\text{N} & - \text{O} \\
\text{H}_3 & - \text{C} \\
\text{Ln} & \\
\text{N} & - \text{O} \\
\text{CH}_2 & - \text{C} - \text{C} - \text{C} - \text{CH}_3
\end{align*}
\]

(where, \( \text{Ln} = \text{La}(\text{III}), \text{Pr}(\text{III}) \) or \( \text{Nd}(\text{III}) \)).

In these newly synthesized lanthanon derivatives, the central lanthanon atom is expected to have hexacoordination environment as reported earlier also in the derivatives obtained by the ethylenediamine bis-salicylaldehyde\(^9\), 2,4-pentanedione\(^10\), methyl salicylate\(^11\) and glycols\(^12\).

Further, mono-isopropoxy lanthanon Schiff base derivatives, obtained by the interaction of lanthanon isopropoxides with the ethylenediamine bis-2,4-pentanedione, have been found to undergo exchange reactions with an excess of tert-butyl alcohol in the presence of benzene as shown by the following general equation:

\[
\text{Ln}(O-i-C_3H_7)[\text{AA}_2(CH_2)_2] + \text{tert}-\text{CH}_3\text{OH} \rightarrow \\
\text{Ln}(O-\text{tert}-C_4H_9)[\text{AA}_2(CH_2)_2] + i-C_3H_7\text{OH}
\]

(where \( \text{Ln} = \text{La}(\text{III}), \text{Pr}(\text{III}) \) or \( \text{Nd}(\text{III}) \) and \( \text{AA}_2(CH_2)_2 \) is the anion of the Schiff base, \( \text{AA}_2(CH_3)_2H_2 \)).

The resulting mono-butoxy lanthanon Schiff base derivatives are also non-volatile, yellow solids and sparingly soluble in benzene.

**Infrared spectra**

In the infrared spectra of ethylenediamine bis-2,4-pentanedione, no band is observed in the region, 3500–3150 cm\(^{-1}\). On account of strong O–H–N or O⋅H–N type of hydrogen bonding between enolic hydroxyl group and azomethine group, the stretching vibration of the enolic hydroxy group is lowered and overlaps with the νCH vibrations resulting in a broad band in the region, 3150–2795 cm\(^{-1}\). Henecka\(^16\) has, however reported that hydrogen bonding cannot occur in the 'anti' form and is only possible in the case of the 'syn' form.

A strong band appears at 1610 cm\(^{-1}\) in the Schiff bases and this may be ascribed to the νC=N modes. This is however, observed in almost the
same region in the case of Schiff base complexes as reported earlier also$^{17,18}$.

The metal-oxygen stretching bands in the resulting derivatives are expected below 400 cm$^{-1}$ and could not be observed on account of the limited range of the IR spectrophotometer used. The coupled stretching vibrations of Ln-O and C-CH$_3$ were noted at ~ 660 cm$^{-1}$ and the one at ~ 610 cm$^{-1}$


may be due to the CH-out-of-plane deformation coupled with Ln-O stretching modes$^{19,20}$.

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