Substituted Salicylaldimine Complexes of Aluminium

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Reactions of monobasic bidentate N-(p-fluorophenyl)- and N-(p-chlorophenyl)-salicylaldimines with aluminium isopropoxide in anhydrous benzene in different molar ratios yield complexes of the types Al(OPr')₃(SB)ₙ (where n = 1, 2 or 3 and SBH represents the ligand molecule). The resulting complexes are coloured solids, non-electrolytes and monomeric in nature. Their IR and PMR spectral data are presented in support of the proposed structures.

The preparation and characterisation of aluminium complexes of ONO, ONS and ONNO donors have earlier been reported from these laboratories 1-3. Aluminium complexes of substituted salicylaldimines (ON donor) have now been prepared and characterised (IR and PMR). Exchange reactions of diisopropoxy and monoisopropoxy aluminium complexes with t-butanol have also been studied.

All the chemicals used were of BDH or equivalent quality. Aluminium isopropoxide was prepared by the method reported earlier 4. All the reactions were carried out under strictly anhydrous conditions.

N-(p-Fluorophenyl)-(I)- and N-(p-chlorophenyl)-(II)-salicylaldimines were prepared by condensing one mol of salicylaldehyde with one mol of p-fluoro- and p-chloro-anilines respectively in absolute ethanol and purified by recrystallization from absolute ethanol.

Compound (I) was obtained as a yellow crystalline solid, yield 80%, m.p. 72° (Found: C, 71.32; H, 4.92; N, 6.05. C₁₃H₁₀NOF requires C, 72.65; H, 4.65; N, 6.51%).

Compound (II) was also obtained as a yellow solid, yield 86%, m.p. 88° (Found: C, 66.21; H, 4.14; N, 5.82. C₁₃H₁₀NOCl requires C, 67.38; H, 4.11; N, 6.02%).

Complexes with aluminium isopropoxide were prepared as follows:

Aluminium isopropoxide (0.54-0.94 g) and the ligand (0.98-1.83 g) were dissolved in anhydrous benzene (~ 70 ml) and the mixture refluxed under an efficient fractionating column on an oil-bath at 110-120°C for several hours. The isopropanol collected in the azeotrope was estimated. When the reaction mixture attained the boiling temperature of benzene (g0°C), the solvent was removed under reduced pressure and the resulting complex was obtained as a coloured solid (Table 1).

The exchange reactions of diisopropoxy and monoisopropoxy aluminium complexes carried

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Table 1—Reactions of Aluminium Isopropoxide with Monobasic Bidentate Schiff Bases (I and II)

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Al(OPr')₃ (g)</th>
<th>Ligand (g)</th>
<th>Molar ratio</th>
<th>Refluxing time (hr)</th>
<th>Compd formed, colour</th>
<th>Found (Calc.)</th>
<th>Mol. wt found (calc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.94</td>
<td>C₁₃H₁₀ONF</td>
<td>1:1</td>
<td>8</td>
<td>(C₁₃H₁₀ONF)₂Al(OPr')₂ light yellow solid, 1.48</td>
<td>0.26 (0.27) 7.42 (7.52) 3.79 (3.89)</td>
<td>352 (359)</td>
</tr>
<tr>
<td>2</td>
<td>0.64</td>
<td>C₁₃H₁₀ONF</td>
<td>1:2</td>
<td>11</td>
<td>(C₁₃H₁₀ONF)₂Al(OPr') yellow solid, 1.45</td>
<td>0.35 (0.37) 5.28 (5.25) 5.40 (5.44)</td>
<td>520 (514)</td>
</tr>
<tr>
<td>3</td>
<td>0.54</td>
<td>C₁₃H₁₀ONF</td>
<td>1:3</td>
<td>18</td>
<td>(C₁₃H₁₀ONF)₃Al deep yellow solid, 1.60</td>
<td>0.46 (0.47) 4.07 (4.03) 6.19 (6.27)</td>
<td>680 (669)</td>
</tr>
<tr>
<td>4</td>
<td>0.98</td>
<td>C₁₃H₁₀ONCl</td>
<td>1:1</td>
<td>8</td>
<td>(C₁₃H₁₀ONCl)Al(OPr')₂ light yellow solid, 1.62</td>
<td>0.28 (0.28) 7.09 (7.18) 3.70 (3.72)</td>
<td>382 (375)</td>
</tr>
<tr>
<td>5</td>
<td>0.55</td>
<td>C₁₃H₁₀ONCl</td>
<td>1:2</td>
<td>12</td>
<td>(C₁₃H₁₀ONCl)₂Al(OPr') yellow solid, 1.32</td>
<td>0.31 (0.32) 4.97 (4.93) 5.04 (5.11)</td>
<td>538 (546)</td>
</tr>
<tr>
<td>6</td>
<td>0.54</td>
<td>C₁₃H₁₀ONCl</td>
<td>1:3</td>
<td>18</td>
<td>(C₁₃H₁₀ONCl)₃Al deep yellow, 1.55</td>
<td>0.46 (0.47) 3.69 (3.75) 5.89 (5.84)</td>
<td>708 (717)</td>
</tr>
</tbody>
</table>

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774
out by refluxing with an excess of t-butanol in the presence of dry benzene. The resulting compounds were dried in vacuo and analysed (Table 2).

The apparatus and instruments used for conductance measurements, molecular weight determinations and IR and PMR spectral studies were the same as reported in our previous communication.  

Aluminium isopropoxide reacts with the substituted monobasic bidentate Schiff bases (I and II) in 1:1, 1:2 and 1:3 molar ratios in refluxing benzene resulting in the successive replacement of the three isopropoxy groups with the formation of complexes of the types (ON)Al(OPri)2, (ON)2Al(OPri) and Al(ON). The reactions, which are quite facile and could be completed within 10-14 hr of refluxing, led to the formation of these complexes in almost quantitative yields.

All the complexes, isolated as light coloured solids, are monomeric and non-electrolyte in nature as revealed by their molecular weight determinations in benzene and molar conductances in DMF. All the 1:1, 1:2 and 1:3 complexes are soluble in common organic solvents and except 1:3 complexes, 1:1 and 1:2 complexes are susceptible to moisture. Further, the mono- and di-isopropoxy aluminium complexes undergo alcohol interchange reactions when refluxed with an excess of t-butanol, causing replacement of one and two isopropoxy groups respectively. These butoxy complexes like the parent compounds are also hexa-coordinated environments, respectively.

The IR spectra of both the aldimines (I and II) exhibit νOH or νNH as broad bands in the region 3320-3260 cm⁻¹ due to the intermolecular as well as intramolecular H-bonding. These bands, completely disappear in the corresponding aluminium complexes, indicating chelation of the central aluminium atom by the oxygen as well as nitrogen atoms of the donor system ON. The free ligand bands in the region 1630-1605 cm⁻¹ due to νC=N are shifted to the lower frequency region on complexation (Δν = 20 cm⁻¹) indicating the coordination of azomethine nitrogen to the central metal atom.

The νC–O (phenolic) modes of I and II, appearing at ~1280 cm⁻¹ are shifted to the higher frequency (~1300 cm⁻¹) in the complexes indicating coordination of the phenolic oxygen to the metal atom after deprotonation. The new bands in the spectra of complexes at 760-610 cm⁻¹ can be assigned to νAl–O and νAl–N modes.

The PMR spectrum of the ligand (I) in DMSO-d6 displays the phenolic proton at δ 12.10. In the corresponding 1:1, 1:2 and 1:3 complexes, this signal disappears indicating coordination of oxygen to the aluminium after its deprotonation. However, the azomethine proton singlet of the free ligand appearing at δ 8.75 undergoes downfield shift in 1:1, 1:2 and 1:3 complexes, which it appears at δ 8.85, 8.90 and 8.98, respectively. The aromatic protons in the ligand (I) and its corresponding 1:1, 1:2 and 1:3 complexes appear as a multiplet in the region δ 7.15-6.90. The methyl and methine protons of the isopropoxy groups in 1:2 and 1:1 complexes appear as a doublet at δ 2.1a and multiplet at δ 4.1 respectively. These signals are absent in the spectrum of the free ligand (I).

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References

775