Synthesis and characterisation of saccharide complexes of La(III) ion

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A series of ten La(III)-saccharide complexes have been synthesised with eight different monosaccharides (D-glucose, D-fructose, D-galactose, D-mannose, L-sorbose, D-arabinose, D-ribose and D-xylose) and two disaccharides (D-maltose and D-altrose), and characterised by analytical, spectral and electrochemical techniques. $^{13}$C NMR spectra reveal interesting binding modes of saccharide molecules towards La(III).

In view of the growing interest in the coordination chemistry of lanthanide metal ions, we have taken up the task of developing lanthanide-saccharide chemistry. In continuation with our ongoing efforts in the field of metal ion-saccharide chemistry, herein we report the synthesis and characterisation of La(III)-saccharide complexes of simple mono- and disaccharides.

Experimental

The solvents were purified, dried and distilled immediately before use by adapting routine procedures. Hydrated La(III)-chloride was prepared from La$_2$O$_3$ using a literature procedure. Absorption spectra (Shimadzu UV-2101 spectrophotometer), FTIR spectra (in KBr, Impact 400 Nicolet FTIR spectrometer), C,H,N analyses (Carlo-Erba elemental analyzer), La and Na (Labtam Plasmalab 8440 analyser), CD spectra (JASCO J-600 spectropolarimeter), thermal analysis (Shimadzu DT-30 thermal analyzer), NMR spectra (Bruker Avance DRX500 spectrometer) were all measured. All the solution characterizations were performed with freshly prepared aqueous.

La-D-Glucose, 1

Disodium salt of D-glucose was prepared by the addition of sodium to a methanolic suspension of D-glucose, where the flask is placed in an ice-salt bath, followed by stirring for 3-4 h, in mol ratio of 2:1 (Na:saccharide) for monosaccharides, and 4:1 for disaccharides. To this, in situ generated sodium salt, LaCl$_3$·6H$_2$O (0.245 g, 1 mmol, dissolved in 5 mL of MeOH) was added dropwise and the resulting suspension was allowed to stir for further 2 h to develop an off-white solid. The solid thus formed was isolated, and purified by washing with 10% water-methanol mixture and finally with acetone, and then drying in vacuo to obtain colourless solid in 45% yield. All the other saccharide complexes, 2-10 were synthesized in a similar manner and the products were isolated in 50-75% yield.

Results and discussion

All the La(III)-saccharide complexes were found to be soluble only in warm water and not in any common organic solvents. These are moderately hygroscopic in nature and absorb moisture over a period of 4 to 5 days in open air, but the extent of hygroscopicity is found to be somewhat less when compared to that of the transition metal saccharide complexes. All the complexes were subjected to elemental analysis and molar conductivity measurements in order to establish their compositions. The corresponding data is listed in Table 1 and is in good agreement with the proposed formulae for the compounds.

The DTA and TGA data of the complexes were recorded in the temperature range 25-700°C, under N$_2$ atmosphere, which exhibited generally 5-7 steps of degradation. An endothermic weight loss was observed in the range 50-120°C and this corresponds to loss of solvent molecules. After this initial weight loss, an exothermic process started at around 200°C. The pyrolysis of the saccharide molecules occur within 200-450°C with the liberation of CO$_2$, CO and H$_2$O at different stages, all of which were found to be exothermic in nature. Finally, the degradation completed at around 500°C leaving behind some residue whose weight did not change until the final temperature of 700°C was attained. The end product of such thermal degradation of lanthanide(III)
complexes was found to be generally the oxide La₂O₃ (ref. 3).

FTIR spectra of La(III)-saccharide complexes, 1-10 were measured in KBr matrix in the range, 400-4000 cm⁻¹. The spectra exhibited a pattern similar to those observed earlier in case of lanthanide-metal ion-saccharide complexes². Comparison of the FTIR spectra of complexes with the corresponding free ligands revealed formation of these complexes. The absence of sharp signals in the spectra of the complexes, otherwise present in the spectra of free saccharide molecule, indicate the interaction of the saccharide moiety with the metal ion as well as the presence of ion-dipole interactions involving Na⁺. Though the spectra were broad, the ranges of the frequencies for the stretching vibrations of OH, CH, CC, CO, OCH and CCH could be identified in the complexes. A broad band observed around 3400 cm⁻¹ is attributable to OH stretching frequencies arising from the saccharide moieties, methanol and water molecules. The skeletal vibrations of C-H, C-C and C-O have appeared as broad bands at around 2850, 1600 and 1400 cm⁻¹, respectively. The bending vibrations of O-C-H and C-C-H have also been observed at around 1050 cm⁻¹.

Aqueous solution absorption spectra for all the complexes were recorded in the range, 190-900 nm. The complexes exhibited no peaks in the visible region owing to f⁰ electronic configuration of La(III) ion. In the UV region (190-400 nm), broad bands were observed mainly in the ranges, 255-270 nm (1010-2360 L.M⁻¹.cm⁻¹), 327-330 nm (210-870 L.M⁻¹.cm⁻¹) and 350-375 nm (120-690 L.M⁻¹.cm⁻¹). The spectra of the complexes are shown in Fig. 1. Solid state reflectance spectra exhibited broad bands in these ranges consistent with that observed in the solution absorption studies.

The sign of CD spectra was found to be similar to that observed with the transition metal saccharides as well as the rare earth metal ion-saccharide complexes reported earlier¹,². Though the Cotton effect is not so prominent in these complexes when compared to that observed in case of Ce(III)-, Pr(III)- and Nd(III)- saccharide complexes, the sign of the CD spectra was found to be similar to that observed for the other cases, among any given saccharide type.

¹H and ¹³C NMR spectra of the complexes were measured in D₂O. While the proton NMR spectra of these complexes are not very informative due to the bunching of signals in 3.2-4.2 ppm region, the ¹³C NMR spectra are highly informative, and have been used extensively in deriving the metal ion binding

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**Table 1—Characterization data of 1-10 complexes.**

<table>
<thead>
<tr>
<th>Comp. No.</th>
<th>Composition and formula</th>
<th>Found (Calcd.), %</th>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C₁₄H₃₂LaNaO₁₆ Na[La(gl)c₃(H₂O)₂] .2CH₃OH</td>
<td>28.14 (27.20)</td>
<td>5.53 (5.22)</td>
<td>3.71 (3.72)</td>
<td>23.35 (22.47)</td>
</tr>
<tr>
<td>2</td>
<td>C₁₄H₃₂LaNaO₁₆ Na[La(fru-c₃(H₂O)₂] .2CH₃OH .CH₃COCH₃</td>
<td>30.44 (30.19)</td>
<td>5.42 (5.66)</td>
<td>3.77 (3.40)</td>
<td>19.57 (20.54)</td>
</tr>
<tr>
<td>3</td>
<td>C₁₉H₄₀LaNaO₁₅ Na[La(gal-b₂(H₂O)₃] .CH₃OH .2CH₃COCH₃</td>
<td>31.53 (31.68)</td>
<td>5.34 (5.60)</td>
<td>4.04 (3.19)</td>
<td>19.95 (19.28)</td>
</tr>
<tr>
<td>4</td>
<td>C₂₀H₄₀LaNaO₁₅ Na[La(man-b₂(H₂O)₃] .2CH₃OH .2CH₃COCH₃</td>
<td>30.64 (32.71)</td>
<td>5.86 (6.04)</td>
<td>3.74 (3.13)</td>
<td>18.78 (18.91)</td>
</tr>
<tr>
<td>5</td>
<td>C₁₆H₃₄LaNaO₁₆ Na[La(sor-b₂(H₂O)₃] .2CH₃OH .CH₃COCH₃</td>
<td>30.44 (29.83)</td>
<td>5.36 (5.32)</td>
<td>3.35 (3.57)</td>
<td>21.56 (21.52)</td>
</tr>
<tr>
<td>6</td>
<td>C₁₉H₃₄LaNaO₁₃ Na[La(ar-a₂(H₂O)₂] .H₂O</td>
<td>23.75 (23.35)</td>
<td>3.99 (4.28)</td>
<td>4.01 (4.49)</td>
<td>26.54 (27.13)</td>
</tr>
<tr>
<td>7</td>
<td>C₁₃H₃₂LaNaO₁₅ Na[La(rib-b₂(H₂O)₂] .2CH₃OH .CH₃COCH₃</td>
<td>29.97 (29.23)</td>
<td>5.22 (5.56)</td>
<td>3.85 (3.73)</td>
<td>23.24 (22.54)</td>
</tr>
<tr>
<td>8</td>
<td>C₁₃H₃₂LaNaO₁₅ Na[La(xy-b₂(H₂O)₂] .2CH₃OH .CH₃COCH₃</td>
<td>28.79 (29.23)</td>
<td>5.14 (5.56)</td>
<td>3.02 (3.73)</td>
<td>22.11 (22.54)</td>
</tr>
<tr>
<td>9</td>
<td>C₁₃H₃₂LaNaO₁₆ Na[La(mal-b₂(H₂O)₂] .2CH₃OH .2CH₃OH</td>
<td>28.04 (27.20)</td>
<td>5.06 (5.22)</td>
<td>3.13 (3.72)</td>
<td>21.60 (22.47)</td>
</tr>
<tr>
<td>10</td>
<td>C₁₄H₃₂LaNaO₁₆ Na[La(lac-b₂(H₂O)₂] .2CH₃OH .2CH₃OH</td>
<td>27.30 (27.20)</td>
<td>5.12 (5.22)</td>
<td>3.16 (3.72)</td>
<td>23.46 (22.47)</td>
</tr>
</tbody>
</table>
characteristics of the saccharides, used in the present study.

Complexation shifts ($\Delta \delta$ ppm = $\delta_{\text{complex}} - \delta_{\text{ligand}}$) were identified for different carbon centres from $^{13}$C NMR spectra, and the $\Delta \delta$ value for each type of carbon centre is plotted against the corresponding saccharide complexes, as shown in Fig. 2. In the spectra of free saccharides, the pyranose form was found to be the major species present in solution. In the spectra of complexes, only D-sorbitose complex (5) was found to be interacting in furanose conformation, while all other saccharides were found to be in pyranose conformation. It has been observed that C-3 and C-4 have suffered significant shifts among the hexose complexes (1-5). However, in case of 2 (La-D-fructose), both C-4 and C-5 showed higher complexation shifts. This indicates that in these complexes, the saccharide molecules are interacting with the metal ion predominantly through O-3, O-4, and O-4, O-5. Pentose complexes (6-8) showed large shifts in C-2, C-3 and C-4. Therefore, it is predicted that among O-2, O-3 and O-4, two are chelating to the metal ion either as O2-O3 pair or O3-O4 pair, through deprotonated hydroxyl moieties and the remaining one is interacting weakly as un-deprotonated -OH group. Disaccharide complexes (9 and 10) seem to be interacting as tridentate chelates, extending major coordination through O-3’, O-4’, O-3 for maltose (9) and O-3’, O-4’, O-1 for the lactose (10) complex. Additional interactions are extended by the saccharide moieties in the form of un-deprotonated hydroxyls (–OH groups) resulting in low magnitudes of $\Delta \delta$.

The binding modes of the saccharide molecules in these complexes were predicted based on $^{13}$C NMR spectral data. FTIR spectral pattern and solution absorption spectra have also supported the complexation between saccharides and La(III) ion.

The molar conductance measurements exhibited 1:1 electrolyte behaviour of the complexes (Table 1), and this has been further supported by the elemental analysis data. While thermal analysis revealed the stepwise degradation and the presence of solvent molecules in the compounds, CD spectral features revealed the relative orientations of the –OH groups in the complexes. Combining the results obtained from different spectral methods with those of the analytical ones, the compositions of the complexes are found to be Na[La(sacch)$_2$(H$_2$O)$_2$] in case of monosaccharide complexes (1-8) and
Fig. 3—Proposed structures of, (a), 1; (b), 5; (c), 6,7 or 8; (d), 10. Solid lines represent the binding through de-protonated hydroxyls and the dotted

Na[La(disacch)(OH)(H$_2$O)$_2$] in case of disaccharide complexes (9 and 10). These complexes are associated with solvent molecules (Table 1). Some representative structures of these complexes are shown in Fig. 3. All the complexes exhibited a coordination number of 8 around the metal ion, which is similar to that reported in the literature in case of La(III) complexes, where the La(III) ion adopts a bicapped trigonal prismatic geometry.

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References