ABSTRACT

An investigation of the molecular recognition factors that govern the aggregation of lanthanide(III) (Ln$^{3+}$) ions to form polynuclear complexes was undertaken utilising 1-aziridineethanol as a versatile source of a variety of chelates (see summary of reactions below). Based on mass spectrometry studies, the facile ring-opening cyclo-oligomerization of 1-aziridineethanol leads to the formation of at least twelve cyclic ligands (Series A), five of which are novel. The cyclo-oligomerization of four 1-aziridineethanol units is the most favourable process, leading to the formation of the 12-membered cyclen based macrocycle, $H_4L^1$ (1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraaza-cyclododecane), the metal complexes of which were isolated.

The coordinative unsaturation of the alkoxy sites of $[H_4L^1]^{x-}$ (where $x < 4$) and Ln(III) ions in coordination numbers less than nine are crucial factors in the formation of polynuclear lanthanide(III) complexes. The fully protonated ligand ($H_4L^1$) results in mononuclear complexes $[LnH_4L^1(H_2O)][Ln(NO_3)_3]$ (8, Ln = La, Pr) and $[LnH_4L^1(H_2O)](ClO_4)_2$.X (9; Ln = Pr, Eu – Tb; $X =$ solvent based component). Sequential deprotonation of the alcoholic groups of $H_4L^1$ results in dimeric complexes $[GdH_2L^1(H_2O)]_2(NO_3)_2$ (10) and $[YbH_2L^1]_2(ClO_4)_2$ (11),
tetranuclear clusters \[([\text{LnH}_2\text{L}^1]\{\text{Ln(NO}_3)_2\{\mu_3\text{-OH}\}\}_2\{\text{NO}_3\}\{\text{LnHL}^1\}])\] (12, \(\text{Ln} = \text{La, Pr}\)), and pentanuclear nanoclusters \[([\text{LnL}^1]\{\text{Ln(NO}_3)_2\}_2\{\mu_5\text{-OH}\}])\] (13, \(\text{Ln} = \text{Pr \_ Ho, Y}\)).

A summary of the syntheses and products is shown in the scheme below.