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, $H_4\mathbf{L^1}$ (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 $[H_x\mathbf{L^1}]^{x-4}$ (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 ($H_4\mathbf{L^1}$) results in mononuclear complexes $[LnH_4\mathbf{L^1}(H_2O)][Ln(NO_3)_6]$ (**8**, Ln = La, Pr) and $[LnH_4\mathbf{L^1}(H_2O)](ClO_4)_3.X$ (**9**; Ln = Pr, Eu – Tb; X = solvent based component). Sequential deprotonation of the alcoholic groups of $H_4\mathbf{L^1}$ results in dimeric complexes $[GdH_2\mathbf{L^1}(H_2O)]_2(NO_3)_2$ (**10**) and $[YbH_2\mathbf{L^1}]_2(ClO_4)_2$ (**11**),

tetranuclear clusters $[(LnH_2\mathbf{L^1})\{Ln(NO_3)_2(\mu_3\text{-}OH)\}_2(NO_3)(LnH\mathbf{L^1})]$ (**12**, Ln = La, Pr), and pentanuclear nanoclusters $[(Ln\mathbf{L^1})_2\{Ln(NO_3)_2\}_3(\mu_5\text{-}OH)]$ (**13**, Ln = Pr – Ho, Y).

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