

ABSTRACT

Mononuclear and polynuclear lanthanide(III) complexes of 1,4,7,10-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane (H_4L) were synthesized in the presence of 1-azirideneethanol. The complexes were structurally characterized using single crystal X-ray diffraction. Luminescence spectroscopy and decay dynamics were used to determine the electronic interactions.

The hexanuclear complexes,

$[Ln_6(\mu_3-OH)_4(\mu_3-HL)_3(CF_3SO_3)_3](CF_3SO_3)_2 \cdot S \cdot nH_2O$ (**I**, $Ln = Pr, Sm - Tb$, $S =$ ethanol or 1-butanol and $n = 0-3$),

$[Ln_6(\mu_3-OH)_3(\mu_2-H_2L)_2(\mu_3-HL)(\mu_2-L)(ClO_4)(H_2O)](ClO_4)_3(EtOH)_2$ (**II**, $Ln = Pr$ and Nd), and $[Pr_6(\mu_6-O)(\mu_3-OH)_8(H_2O)_{22}(ClO_4)_2]6ClO_4 \cdot 4H_2O$ (**III**) and the mononuclear complexes $[LnH_2L]CF_3SO_3 \cdot S$ (**6**, $S =$ ethanol), $[LnH_2L]NO_3 \cdot S$ (**7**, $Ln = S =$ water or ethanol), $[PrH_4L(H_2O)]Pr(NO_3)_6$ (**8**) and

$[NdH_4L(H_2O)](ClO_4)_3 \cdot H_2O$ (**9**) were prepared via template synthesis with 1-azirideneethanol. The complex formed depends on the lanthanide(III) anion, reaction stoichiometry, pH and solvent mixtures employed. The wing-spans of hexanuclear **I**, **II** and **III** are 1.38, 1.45 and 1.44 nm, respectively, which qualify them as small nanoclusters.

Hexanuclear **I**, $[\text{Ln}_6(\mu_3\text{-OH})_4(\mu_3\text{-HL})_3(\text{CF}_3\text{SO}_3)_3](\text{CF}_3\text{SO}_3)_2 \cdot n\text{H}_2\text{O}$ and $[\text{LnH}_2\text{L}]\text{CF}_3\text{SO}_3 \cdot \text{S}$ (**6**) were prepared under the same reaction conditions. Here the larger lanthanide(III) ions form the hexanuclear complex while the smaller ions form the mononuclear complex. The lanthanide contraction is therefore a determining factor in the formation of these complexes.

Luminescence studies of hexanuclear **I** shows the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ peak appearing as a doublet which suggests that there are two different Eu^{3+} environments. This conclusion is supported by the crystal structure which shows the Eu^{3+} ions in two different coordination sites, a distorted monocapped square antiprism with C_{4v} symmetry and a distorted bicapped trigonal prism. Competitive complexation studies reveal that the formation of the hexanuclear nanoclusters is selective towards the larger lanthanide(III) ions, with the exception of La^{3+} . The presence of both homo- and hetero-lanthanide complexes in the crystalline products when two lanthanide ions are reacted is also indicated.

Energy transport is diffusive and occurs within the intermediate regime. There are increased electronic coupling interactions between europium and samarium as a result of many-body energy transfer processes which is evident at high quencher concentration. These processes require two samarium absorptions to couple and quench one Eu^{3+} emission. In addition, energy transfer is intramolecular and there are no intermolecular interactions in hexanuclear **I**.

The complexes of hexanuclear **II**,

$[\text{Ln}_6(\mu_3\text{-OH})_3(\mu_2\text{-H}_x\text{L})_2(\mu_3\text{-H}_x\text{L})(\mu_2\text{-L})(\text{ClO}_4)(\text{H}_2\text{O})](\text{ClO}_4)_3\cdot\text{EtOH}$, have three different metal coordination sites; four are encapsulated by the macrocycle in a distorted monocapped square anti-prismatic coordination environment (site A), one is a seven coordinate monocapped trigonal prism (site B) and the other is an eight coordinate bicapped trigonal prism (site C).

Luminescence data on the small complexes of series **II** are consistent with the presence of multiple Eu^{3+} sites with ($^5\text{D}_0 \leftarrow ^7\text{F}_0$) absorptions occurring at 569 nm, 573 nm and 577 nm. Cooperative effects are active in which the chemistry of the different coordination sites are selective toward specific lanthanide(III) ions. Luminescence data indicated that in series **II** the smaller lanthanide ions are preferentially encapsulated by the macrocycle (site A) while the larger ions go into the other coordination sites (B or C). The presence of homo- and hetero-lanthanide complexes is confirmed by decay curves for europium-dysprosium and other mixtures which constitutes fast decaying components due to quenching in hetero-complexes ($\text{Ln}_{6-x}\text{Eu}_x$) and single-exponential, slow decaying tails which deviate very marginally from the decay of the pure europium complex (Eu_6) due to quenching by hetero- ($\text{Ln}_{6-x}\text{Eu}_x$) and homo-complexes (Ln_6).

The presence of back energy transfer was postulated as a result of the relative

intensity of the ($^5D_0 \rightarrow ^7F_0$) peaks at different temperatures. This claim was supported by the behaviour of europium decay; at 77 K the decay rates are different when the sample is excited at different wavelengths, however at 297 K the decay rates are similar. This observation was also made for the europium-dysprosium and europium-samarium decays. Exciting at 77 K and 297 K, result in the excitation of different types of Eu^{3+} ions, i.e. europium ions in different coordination sites. At 297 K, irrespective of excitation wavelength, Eu^{3+} ions in all the different coordination sites are being excited. At 77 K exciting at 577 nm results predominantly in the excitation of europium ions encapsulated by the macrocycle (site A), at 532 nm all the different Eu^{3+} species are excited and exciting at 585 nm results in the decay of Eu^{3+} ions in the other sites (B or C).

Electronic coupling interactions between europium-dysprosium and europium-samarium are comparable to dinuclear lanthanide complexes^{33, 98} with no evidence of many-body processes or any other mechanism which could cause stronger or weaker interactions. Energy transfer occurs in the intermediate at 77 K and in the static regime at 298 K. Both intra- and inter-molecular transfer is present.

The electronic investigations in hexanuclear **I** and series **II** reveal different intensities of the coupling interactions because, while many-body processes are

active in hexanuclear **I** the coupling interactions in series **II** is comparable to that observed in dinuclear lanthanide complexes^{33, 98}. Energy transfer is intramolecular in hexanuclear **I** yet both intra- and inter-molecular in series **II**. The dynamics of energy transfer in these clusters are enigmatic. However it is clear that differences in coordination environment and the strengths of the dipoles interacting with the metal sites play a vital role in the energy transfer interactions.

All three clusters have unusually broad defect emission and absorption bands of unknown origin, upon which sharp Eu^{3+} peaks are superimposed. The similarity between these clusters is that they are hexanuclear and their structures are of nanometer dimensions. The luminescence of other polynuclear species (pentanuclear, tetranuclear and dinuclear)³¹⁻³⁸ have been reported, however none of these spectra feature the broad defect emission and absorption that are specific to our hexanuclear clusters. We propose that this anomaly may be due to the nano-sized dimensions of these clusters.

Two eight coordinate mononuclear complexes were synthesized, $[\text{LnH}_2\text{L}]\text{CF}_3\text{SO}_3\cdot\text{S}$ (**6**, $\text{Ln} = \text{Dy} - \text{Lu}$ and Y , $\text{S} = \text{solvent}$) and $[\text{LnH}_2\text{L}]\text{NO}_3\cdot\text{S}$ (**7**, $\text{Ln} = \text{Ho} - \text{Lu}$ and Y , $\text{S} = \text{solvent}$), from lanthanide(III) triflates and lanthanide(III) nitrates, respectively. The complexes were prepared under highly basic conditions resulting in deprotonation of the macrocycle, $[\text{H}_4\text{L}]$ to

$[\text{H}_2\text{L}]^{2-}$. The lanthanide(III) ions in these two structures are eight coordinate distorted square antiprisms.

Two additional mononuclear complexes were prepared,

$[\text{PrH}_4\text{L}(\text{H}_2\text{O})]\text{Pr}(\text{NO}_3)_6$ (**8**) and $[\text{NdH}_4\text{L}(\text{H}_2\text{O})](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ (**9**). The Pr^{3+} ions in **8** are in two different coordination environments, a distorted monocapped square antiprism in which the Pr^{3+} ion is encapsulated by the macrocycle and icosahedral in which the Pr^{3+} ion is coordinated to six bidentate nitrate anions.

The neodymium complex has the metal ion in a coordination environment of C_{4v} symmetry with a coordination polyhedron that can be described as a monocapped square antiprism.