ABSTRACT

A detailed study of the formation, structure, and luminescence characteristics of novel tetramethoxyborate complexes, $[\{Na\}\{(\mathbf{sal})_3Ln(B(OCH_3)_4)Ln(\mathbf{sal})_3\}]_n$ **11** (Ln = Nd – Lu, Y) (**sal** = $C_7H_5O_2^-$), revealed that although these systems are structurally one-dimensional, their metal-metal electronic interactions and concomitant excitation energy transport are not. Strong Eu^{3+} - Eu^{3+} electronic interactions result in multi-dimensional energy migration across Eu^{3+}- Eu^{3+} distances as large as 7.2 Å, and at temperatures as low as 8 K. These strong coupling interactions result in a dynamic excitation energy transport regime, with a coupling constant between Eu^{3+}- Dy^{3+} hetero-pairs of *ca.* 4 x 10^{-52} m^6 s^{-1} (a dominant dipole-dipole interaction is assumed). In addition, europium(III) luminescence from **11** (Ln = Eu_xGd_{x-1}, x = 0.06 – 0.21; Eu_xDy_{x-1}, x = 0.03 – 0.24; $Eu_{0.04}Y_{0.96}$) reveals the presence of defect Eu^{3+} sites, possibly resulting from the swapping

of regular Eu^{3+} and Na^{+} positions. Further, a lanthanide(III) cation discrimination study revealed that system **11** has a preference for the smaller lanthanides(III) ions. This is substantiated by the cation discrimination index, I_D, of ≈ 1.3 (in favour of Dy^{3+} over Eu^{3+}), for the mixed lanthanide system $[\{Na\}\{(\mathbf{sal})_3Dy_{1-x}Eu_x(B(OCH_3)_4)Dy_{1-x}Eu_x(\mathbf{sal})_3\}]_n$.

A fast atom bombardment mass spectrometry (FAB MS) study of the crystalline $Ln(CH_3COO)_3.nH_2O$ (Ln = Gd, n = 4 (**12**); Ln = Y, n = 3 (**14**)) was done to explore the possibility of generating ligated clusters of lanthanide(III) ions from the interaction between the hypoco-ordinate cation, $[LnO]^+$, and acetate species generated from **12** and **14** in the gaseous phase. Indeed, novel lanthanide(III) oxoacetate clusters were formed, all of which conformed to the general formula, $[(Ln_xO_y)(CH_3COO)_{3x-(2y+1)}]^+$, **13** (Ln = Gd, Y). The formation chemistry of these complexes, and hence the behaviour of the hypoco-ordinate $[LnO]^+$ species

in the presence of co-ordinating ligands such as CH_3COO^-, was studied in detail. This study revealed a remarkable dependence of cluster size on oxygen content, therefore indicating the importance of oxygen for the stabilisation of metal-rich clusters. In addition, the larger gadolinium(III) ion proved to be a better oxoacetate cluster former than the smaller yttrium(III) ion. This demonstrates that cationic size factors, inherent in the lanthanide ion contraction, need to be considered in the design and development of synthetic protocols for the assembly of stable polynuclear lanthanide(III) cluster complexes.

In further investigating the formation and stability of polynuclear lanthanide(III) complexes and their metal-metal interactions, the dendritic amines, **15** – **17**, were functionalised in an attempt to introduce light absorbing ligand sites capable of trapping multiple lanthanide(III) ions and sensitising metal ion emission. Solid state studies of the diaminium tetra-phthalimido perchlorate salt (**30**) and solution ^1H NMR studies of the tetra-phthalimide (**20**) and its di-

phthalate derivative (**29**), and the octa-phthalimide (**21**), revealed the presence of extensive inter- and intra-molecular pi-pi interactions. Further, the dendritic phthalimides, **20** and **21**, the octa-phthalamate, **23**, and the mono-protonated octa-phthalimide, **31**, were proven to be good binders of lanthanide(III) ions, and efficient sensitisers of their emission. Although the larger dendritic phthalimide, **21**, and its derivative, **31**, formed di- and possibly quinta-nuclear lanthanide(III) complexes, the smaller dendritic phthalimide, **20**, formed mono-nuclear complexes. Luminescent decay dynamical studies of the lanthanide(III) complexes of **20** (Ln = Eu, $Eu_{0.05}Gd_{0.95}$, and Tb) were consistent with the encapsulation of the lanthanide(III) ion by two dendritic ligands. This encapsulation could result in the isolation of each lanthanide(III) ion from the other, thereby precluding metal-metal interactions. The tetra- and octa-phthalimides, **20** (Ln = Tb) and **31** (Ln = Tb), exhibit remarkable temperature independent bright green emission, while the octa-phthalamate complex, **23** (Ln = Eu), substantiate the

claims of Barrett *et al* on the ability of the phthalamate chromophore to sensitise intense temperature independent europium(III) emission.

Finally, in an attempt to increase the versatility, solubility, and 'metal sponge-like' characteristics of the dendrimers, the dendritic Schiff's bases, **24** – **26**, were synthesised. **25** was subsequently reduced to **27**, followed by acetylation to form **28**. The results from these synthetic reactions showed that a large number of dendritic systems capable of binding multiple lanthanide(III) ions, may be obtained through relatively simple chemical transformations.

Overall, diverse polynuclear lanthanide(III) complexes, from the linear systems to the complex clusters of lanthanide(III) ions, have successfully been synthesised. Most of these complexes exhibit intense metal-metal coupling interactions and sensitised lanthanide(III) emission. In addition, these novel polynuclear complexes have all demonstrated

the importance of crystal packing, cation size, structural dimensionality, chromophore type, and impurities, on the formation and stability of polynuclear lanthanide(III) complexes, and metal-metal interactions featured in them.