## Abstract

Acyclic linear analogues, **28**-$H_4$**35**, were successfully prepared by direct alkylation of the corresponding alkyl amines. The initial investigation, using FAB MS spectroscopy, showed a preference for dialkylated (**28c**) and the trialkylated (**28b**) products.

Compounds H**29**, $H_4$**34** and $H_4$**35** respectively were observed in the mass spectra but no isolatable compounds were forthcoming. However, there was much success in the template synthesis of the lanthanide(III) complexes of H**29**.

The mononuclear lanthanide(III) complexes of H**29** and $H_2$**30** showed high stability under FAB MS conditions. NMR spectroscopic studies revealed that in these cyclohexyl derivatives, the attached cyclohexyl arm(s) would orientate themselves in such a way that their hydroxyl groups were directed toward the ethereal backbone, allowing for the formation of hydrogen bonds between the O-H and N-H groups. Also, the ability of the lanthanide(III) ions to select a particular isomer for binding was highlighted, providing that the attached substituents were oriented in a manner which influenced strong bonding. NMR and mass spectroscopic studies of $H_3$**32** and $H_3$**33**, revealed that the tricyclohexyl alkylamines were poor binders of lanthanide(III) ions, presumably because of co-ordination preference factors.

Luminescent studies on the complexes of $H_2$**27** and $H_2$**30**, showed the chelating ligand, $H_2$**27**, to be a good sensitizer for $Tb^{3+}$ and $Eu^{3+}$ emissions and that $H_2$**30** formed well-defined mononuclear lanthanide(III) complexes. The light-harvesting properties of the tosyl groups in $H_2$**27** were the most probable source of luminescence intensity enhancement.

The macrocyclic(16C5) compound, $H_3$**37**, was successfully synthesized by the condensation of compounds, $H_2$**30** and **H36**. The increased ligand to lanthanide charge ratio allowed for the formation of stable praseodymium(III) and neodymium(III) complexes of $H_3$**37**, with the former showing good stability under FAB MS conditions. $^1$H NMR spectroscopic studies revealed that the praseodymium(III) metal ion perches on the cavity of chelate $H_3$**37**. The magnitude of the shifts seen, especially for the $CH_2$-N, phenolic OH, ethereal oxygens and the hydroxyl groups, indicated that they were all directly bonded to the metal ion.

The known vulnerability of the imine (C=N) bond of $H_2$**17** to hydrolysis and the high reactivity of the secondary amine sites were used to the fullest advantage to make novel multiply-charged mononuclear lanthanide(III) macroacyclic complexes, $H_4$**38** and $H_2$**39.** This was achieved by the systematic modification of the macrocyclic complexes of $H_2$**17**, using propylene oxide and ethylbromoacetate. The successful synthesis of a stable, novel europium(III) dinuclear complex of $H_3$**38**, strongly indicated that hydrolysis of the imine (C=N) bond will not result in the automatic loss of a metal ion;

providing the chelating ligand possesses good metal binding donor groups. The luminescence studies on this complex showed enhanced luminescence, temperature independent behaviour over that of the europium(III) complex of $H_2$**17** as expected from the emission quenching effects of the four N-H groups in $H_2$**17**, on the europium(III) emission.