Abstract

Acyclic linear analogues, 28-H₄35, 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 H₂9, H₄34 and H₄35 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 H₂9.

The mononuclear lanthanide(III) complexes of H₂9 and H₂30 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 H₃32 and H₃33, 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$30 and H$_3$36. The increased ligand to lanthanide charge ratio allowed for the formation of stable praseodymium(III) and neodymium(III) complexes of H$_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$17 to hydrolysis and the high reactivity of the secondary amine sites were used to the fullest advantage to make novel multiply-charged mononuclear lanthanide(III) macrocyclic complexes, H$_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.