ABSTRACT

Luminescence, spectroscopic and lanthanide(III) ion complexation selectivity studies of dilaanthanide macrocyclic complexes of a Schiff base chelate XVIII, Ln$_2$XVIII(NO$_3$)$_2$.H$_2$O (XVIII = C$_{36}$H$_{38}$N$_4$O$_6$) derived from the condensation of 2,6-diformyl-p-cresol and 3,6-dioxa-1,8-octanediamine are reported. XVIII is a strong light absorber and efficiently sensitizes Ln(III) emission. Dy$^{3+}$ and Tb$^{3+}$ emission is sensitized by the ligand singlet state, whereas Sm$^{3+}$ and Eu$^{3+}$ emission is sensitized by the an ill-defined state denoted as S/T* . Eu$^{3+}$ emission exhibits unusual non-radiative thermalized quenching behaviour at T > 110 K with a thermal barrier of about 2300 cm$^{-1}$.

![Structure of XVIII](image)

The dependence of the multiphonon relaxation rate on the energy gap was displayed clearly in the non-quenched lifetimes of the Sm$^{3+}$, Dy$^{3+}$, Eu$^{3+}$ and Tb$^{3+}$ complexes of XVIII which are 13, 15, 890 and 1600 µs respectively; the corresponding energy gaps are ≈7,500, 8,000, 12,000 and 14,500 cm$^{-1}$. The non-radiative relaxation processes at 77 K follow the
energy gap law with $B = 2 \times 10^8 \text{s}^{-1}$ and $\alpha = 10^{-3} \text{cm}$. With $\Delta E < 7000 \text{cm}^{-1}$ emission is very weak.

Homodinuclear complexes of Sm$^{3+}$ and Dy$^{3+}$ feature strong Sm$^{3+}$-Sm$^{3+}$ and Dy$^{3+}$-Dy$^{3+}$ interactions (in terms of energy transfer), dipole-dipole coupling constants of both being $\approx 1.02 \times 10^{-5}$ m$^6$ s$^{-1}$. Tb$^{3+}$-Tb$^{3+}$ and Eu$^{3+}$-Eu$^{3+}$ interactions are not observed. The above results have been published in the *Journal of Physical Chemistry*, 1992, 96, 7021.

Heterodinlanthanide molecules are identified by the dramatically short lifetimes of their Eu$^{3+}$ and Tb$^{3+}$ complexes. The lifetimes of Eu$^{3+}$ in Eu$^{3+}$-Dy$^{3+}$ and Eu$^{3+}$-Sm$^{3+}$ heteropairs are 6 and 120 $\mu$s respectively, and more importantly these short lifetimes reflect Eu$^{3+}$-Ln$^{3+}$ electronic interactions (dipole-dipole coupling constants are $6.8 \times 10^5$ and $2.9 \times 10^6$ m$^6$ s$^{-1}$ respectively).

Molecular recognition events are evident in the formation process of crystalline LnTbXVIII(NO$_3$)$_4$.H$_2$O and LnEuXVIII(NO$_3$)$_4$.H$_2$O complexes. From the relationship between the concentration of Eu$^{3+}$ and Tb$^{3+}$ in the mother reaction mixture and the concentration of Eu$^{3+}$ and Tb$^{3+}$ incorporated in the crystalline products, it is evident that there is a preference for the formation of Ln-Eu than Ln-Tb heteropairs. Also, in both cases, the cation discrimination index, $I_b$ (the ratio of probabilities of Ln$^{3+}$(1) and Ln$^{3+}$(2)
incorporation into the crystalline compounds) shows a preference for the larger lanthanide cations. These results indicate the formation of heteropaired molecules which were then confirmed by photophysical studies of \((Sm_{1.6}Eu_{x})_{2}XVIII(NO_3)_4\cdot H_2O\) and \((Pr_{1.6}Tb_{x})_{2}XVIII(NO_3)_4\cdot H_2O\) complexes. Two distinct microscopic environments were revealed for \(Eu^{3+}\) and \(Tb^{3+}\) in \((Sm_{1.6}Eu_{x})_{2}XVIII(NO_3)_4\cdot H_2O\) and \((Pr_{1.6}Tb_{x})_{2}XVIII(NO_3)_4\cdot H_2O\) and these were attributed to \(Ln_2XVIII(NO_3)_4\cdot H_2O\) (\(Ln = Eu\) or \(Tb\)) homopaired (slow component) and heteropaired molecules \(SmEuXVIII(NO_3)_4\cdot H_2O\) and \(PrTbXVIII(NO_3)_4\cdot H_2O\) (fast component). The lifetimes of \(Sm-Eu\) and \(Pr-Tb\) heteropairs are 120 \(\mu s\) and \(= 79 \mu s\) respectively, which yield dipole-dipole coupling constants of ca. \(2.9 \times 10^{-33}\) and \(4.7 \times 10^{-33}\) \(m^8 s^{-1}\) respectively. For the \(Eu/Sm\) system, the "cation pairing selectivity" constants (the ratio of \(Eu-Eu\) to \(Eu-Sm\)) were 1 : 1.5 (expected 1 : 2 for random pairing) which indicates that molecular recognition mechanisms are operating in the ion pairing processes leading to the formation of the homo- and heterodinuclear complexes of XVIII. A report on this work has been published in the *Journal of the Chemical Society, Dalton Transactions*, 1993, 1719.

Novel dilanthanide complexes of XXII and XXIII were prepared in an attempt to remove the labile imine bonds, \(>C=N\), while still retaining the good luminescent characteristics of XVIII. An *in situ* reduction of a methanolic solution of 2,6-diformyl-p-cresol, 3,6-dioxa-1,8-octanediolamine and the lanthanide nitrate with sodium borohydride or sodium
cyanoborohydride lead to the formation of new complexes of XXIII, Ln$_2$XXIII(NO$_3$)$_4$ (characterised by $^{13}$C CP-MAS) or a mixture of isostructural compounds, Ln$_2$XXII(NO$_3$)$_4$, 1.2CH$_3$OH and [La(NO$_3$)$_2$(B(OCH$_3$)$_4$)(CH$_3$OH)$_2$].

The structure of these novel tetramethoxyborate complexes was determined by x-ray crystallography and featured an interesting long polymeric chain motif. The structure of this complex was published in *Inorganic Chemistry*, 1993, 32, 1442. Reduction of the preformed ligand XVIII with NaBH$_4$ followed by the addition of the lanthanide cations resulted in the formation of pure crystals (paralleloipeda) of complexes of an asymmetric imino-amine ligand, XXII. The structure was established by FT-
IR, $^{13}$C CP-MAS and x-ray crystallography. Concentrated and doped terbium samples of XXII, $\text{Tb}_2\text{XXII(NO}_3)_4 \cdot 1.2\text{CH}_3\text{OH}$ and $(\text{La}_{0.97}\text{Tb}_{0.03})_2\text{XXII(NO}_3)_4 \cdot 1.2\text{CH}_3\text{OH}$ respectively, exhibit strong Tb$^{3+}$ emission sensitized by the singlet state of XXII at both 77 and 295 K. Since no Tb$^{3+}$-Tb$^{3+}$ self-quenching or N-H trapping effects were found, complexes of XXII are potentially good luminescent diagnostic agents.

In the dilute terbium sample, $(\text{La}_{0.97}\text{Tb}_{0.03})_2\text{XXII(NO}_3)_4 \cdot 1.2\text{CH}_3\text{OH}$, unusual thermal equilibration of the ligand singlet/triplet (S/T$^+$) state and Tb$^{3+}$ (6$^D_J$) occurs at room temperature. Energy back transfer (metal-to-ligand) occurs at a rate of $\approx 71,000$ s$^{-1}$ and the ligand-to-metal energy transfer rate at $\approx 43,600$ s$^{-1}$. A similar behaviour is displayed by the dilute terbium/lanthanum sample of XVIII, $(\text{La}_{0.98}\text{Tb}_{0.02})_2\text{XVIII(NO}_3)_4 \cdot \text{H}_2\text{O}$ which when excited at room temperature at 337 nm a non-exponential decay is observed ($k_1 = 333,300$ s$^{-1}$ and $k_2 = 142,900$ s$^{-1}$) and at 77 K an excitation build-up ($\approx 32$ µs) and a decay rate of $\approx 900$ s$^{-1}$. A report of this work was published in Inorganic Chemistry, 1994, 33, 1382.