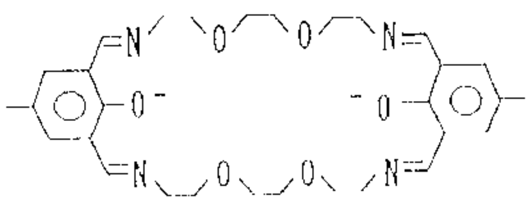
ABSTRACT

Luminescence, spectroscopic and lanthanide(III) ion complexation selectivity studies of dilanthanide macrocyclic complexes of a Schiff base chelate **XVIII**, Ln_2**XVIII**$(NO_3)_4.H_2O$ (**XVIII** = $C_{30}H_{38}N_4O_6$) 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}.



XVIII

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

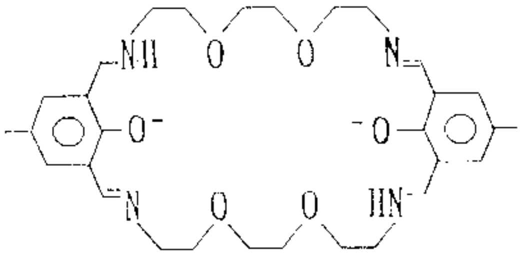
Homodinuclear complexes of Sm^{3+} and Dy^{3+} feature strong Sm^{3+}–Sm^{3+} and Dy^{3+}-Dy^{3+} interactions (in terms of energy transfer), dipole-dipole coupling constants of both being $\approx 1.02 \times 10^{-50}$ m^6 s^{-1}. Tb^{3+}-Tb^{3+} and Eu^{3+}-Eu^{3+} interactions are not observed. The above results have been published in the *Journal of Physical Chemistry*, **1992**, 96, 7021.

Heterodilanthanide 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 μs respectively, and more importantly these short lifetimes reflect Eu^{3+}-Ln^{3+} electronic interactions (dipole-dipole coupling constants are 6.8×10^{-52} and 2.9×10^{-53} m^6 s^{-1} respectively).

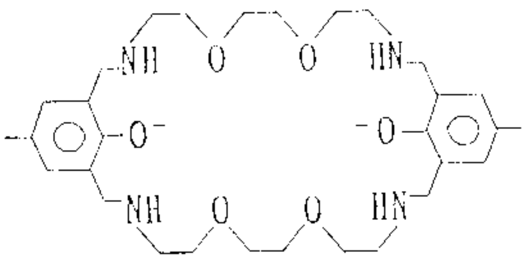
Molecular recognition events are evident in the formation process of crystalline LnTb**XVIII**$(NO_3)_4.H_2O$ and LnEu**XVIII**$(NO_3)_4.H_2O$ complexes. From the relationship between the concentration of Eu^{3+} and Tb^{3+} in the mother reaction mixture and the concentration of Eu^{3+} and Tb^{3+} 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_D (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 $(Sm_{1-x}Eu_x)_2$**XVIII**$(NO_3)_4.H_2O$ and $(Pr_{1-x}Tb_x)_2$**XVIII**$(NO_3)_4.H_2O$ complexes. Two distinct microscopic environments were revealed for Eu^{3+} and Tb^{3+} in $(Sm_{1-x}Eu_x)_2$**XVIII**$(NO_3)_4.H_2O$ and $(Pr_{1-x}Tb_x)_2$**XVIII**$(NO_3)_4.H_2O$ and these were attributed to Ln_2**XVIII**$(NO_3)_4.H_2O$ (Ln = Eu or Tb) homopaired (slow component) and heteropaired molecules SmEu**XVIII**$(NO_3)_4.H_2O$ and PrTb**XVIII**$(NO_3)_4.H_2O$ (fast component). The lifetimes of Sm-Eu and Pr-Tb heteropairs are 120 μs and $\approx$ 79 μs respectively, which yield dipole-dipole coupling constants of ca. 2.9×10^{-53} and 4.7×10^{-53} $m^6 s^{-1}$ 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 *insitu* reduction of a methanolic solution of 2,6-diformyl-p-cresol, 3,6-dioxa-1,8-octanediamine 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**$(NO_3)_4.1.2CH_3OH$ and $[La(NO_3)_2(B(OCH_3)_4)(CH_3OH)_2]$.



XXII



XXIII

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 (parallelopipeda) 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**, Tb_2**XXII**$(NO_3)_4.1.2CH_3OH$ and $(La_{0.97}Tb_{0.03})_2$**XXII**$(NO_3)_4.1.2CH_3OH$ 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, $(La_{0.97}Tb_{0.03})_2$**XXII**$(NO_3)_4.1.2CH_3OH$, unusual thermal equilibration of the ligand singlet/triplet (S/T*) state and Tb^{3+} ($^5D_4$) 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**, $(La_{0.998}Tb_{0.002})_2$**XVIII**$(NO_3)_4.H_2O$ 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*.