

ABSTRACT

A combinatorial system has been generated from which novel polynuclear rare earth complexes have been isolated in crystalline form. This system is comprised of a library of Schiff's bases, and another library of oxo/hydroxo rare earth aggregates.

Condensation reactions between the dialdehyde, 2,6-diformyl-p-cresol (HL), and the short chain diamine, 1,2-diamino ethane (2), have produced the combinatorial library of cyclic and acyclic Schiff's bases. Rare earth salt hydrolysis in the presence of small quantities of water resulted in the combinatorial library of rare earth oxo/hydroxo aggregates. The combination of both libraries has facilitated recognition processes between their respective members, which has led to the self assembly of novel rare earth complexes.

Four novel polynuclear complex series and two uncomplexed ligands have been isolated by manipulation of the conditions of the multi-library system to promote crystal formation. These include the first example of a series of double helical tetranuclear rare earth complexes, two macrocyclic dinuclear systems, one acyclic dinuclear system, a [2+2] macrocyclic ligand and a bis(benzimidazolyl) ligand. The complexes were characterized by single crystal X-Ray diffraction, elemental analyses and infrared spectroscopy.

The electronic properties of the complexes were investigated by means of luminescence spectroscopic and decay dynamical studies.

The novel double helical series of tetranuclear rare earth complexes,

$[\text{Ln}_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_4\text{-L}^3)_2][\text{CF}_3\text{SO}_3]_2$, ($\text{Ln} = \text{Eu} - \text{Lu}, \text{Y}$), were isolated in crystalline form from the multi-library system at pH 7 in about 35% yield.

Crystals of $[\text{Eu}_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_4\text{-L}^3)_2][\text{CF}_3\text{SO}_3]_2$ give bright red luminescence at room temperature (296 K) and at 77 K when the $^5\text{D}_0$ state of Eu^{3+} is excited directly (with visible radiation of 579 or 589 nm) or indirectly (via the ligand with ultraviolet radiation of 370 nm).

Luminescence decay dynamical studies carried out on crystalline complexes of $[(\text{Eu}_x\text{Ln}_{1-x})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_4\text{-L}^3)_2][\text{CF}_3\text{SO}_3]_2$, where ($\text{Ln} = \text{Sm}, \text{Dy}$ and Yb) indicate that intramolecular interactions leading to quenching of europium(III) emission by hetero Ln^{3+} ions are quite strong. The efficiency with which the heterometals are coupled within the complexes is most likely facilitated by the simultaneous interaction of the acyclic ligands with all four metal ions. Significant intermolecular interactions were observed only for the $[(\text{Eu}_x\text{Dy}_{1-x})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_4\text{-L}^3)_2][\text{CF}_3\text{SO}_3]_2$ complexes.

In the case of $[(\text{Eu}_x\text{Yb}_{1-x})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_4\text{-L}^3)_2][\text{CF}_3\text{SO}_3]_2$, the Yb^{3+} ($^2\text{F}_{5/2} \leftarrow ^2\text{F}_{7/2}$) absorption couples with the stretching vibrations of carbonyl and imino groups, and additional low energy vibrations of approximately

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100 cm^{-1} , to cooperatively quench Eu^{3+} emission. The coupling constants, which describe the strength of the intramolecular interactions between Eu^{3+} ions and the hetero rare earth ions Dy^{3+} , Sm^{3+} and Yb^{3+} were determined to be 1.2×10^{-51} , 9.3×10^{-53} and $5.5 \times 10^{-52} \text{ m}^6 \text{ s}^{-1}$ respectively.

Two novel macrocyclic dinuclear series, $[\text{Ln}_2\text{H}_4\text{L}^2(\text{Br})_2(\text{CH}_3\text{OH})_6][\text{Br}]_4$ where $\text{Ln} = \text{La} - \text{Lu}, \text{Y}$, and $[\text{Ln}_2\text{H}_4\text{L}^2(\text{X})_z(\text{S})_{8-z}][\text{CF}_3\text{SO}_3]_{6-z}$ for $\text{Ln} = \text{La} - \text{Gd}$, where $\text{X} = \text{CF}_3\text{SO}_3$ or Cl , $\text{S} = \text{CH}_3\text{OH}$ or H_2O , $z = 2 - 6$, were isolated from the library at pH 4 in about 32 and 11% yields respectively. The metal ions' coordination spheres in the $[\text{Ln}_2\text{H}_4\text{L}^2(\text{Br})_2(\text{CH}_3\text{OH})_6][\text{Br}]_4$ complexes were consistent throughout the series. In complexes of the type $[\text{Ln}_2\text{H}_4\text{L}^2(\text{X})_z(\text{S})_{8-z}][\text{CF}_3\text{SO}_3]_{6-z}$ however, the metal ions' coordination environments varied from structure to structure depending on the reaction conditions and counter-anions present. Ligands such as water, alcohols, triflates and halides exchanged coordination sites readily, while chelate H_4L^2 was consistent in its coordination. As such, no luminescence studies were carried out on this series because the results so obtained would have been inconclusive.

Luminescence from the $^5\text{D}_0$ energy level of Eu^{3+} in crystals of $\text{Eu}_2\text{H}_4\text{L}^2(\text{Br})_2(\text{CH}_3\text{OH})_6[\text{Br}]_4$ exhibits temperature dependence and there is no emission at room temperature. When excited by light of 577 nm at 77 K however, bright red emission is seen. Interactions between europium(III)

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Crystals of $[\text{Eu}_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_4\text{-L}^3)]_2[\text{CF}_3\text{SO}_3]_2$ give bright red luminescence at room temperature (296 K) and at 77 K when the $^5\text{D}_0$ state of Eu^{3+} is excited directly (with visible radiation of 579 or 589 nm) or indirectly (via the ligand with ultraviolet radiation of 370 nm).

Luminescence decay dynamical studies carried out on crystalline complexes of $[(\text{Eu}_x\text{Ln}_{1-x})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_4\text{-L}^3)]_2[\text{CF}_3\text{SO}_3]_2$, where ($\text{Ln} = \text{Sm}, \text{Dy}$ and Yb) indicate that intramolecular interactions leading to quenching of europium(III) emission by hetero Ln^{3+} ions are quite strong. The efficiency with which the heterometals are coupled within the complexes is most likely facilitated by the simultaneous interaction of the acyclic ligands with all four metal ions. Significant intermolecular interactions were observed only for the $[(\text{Eu}_x\text{Dy}_{1-x})_4(\mu_4\text{-O})(\mu_2\text{-OH})_2(\mu_4\text{-L}^3)]_2[\text{CF}_3\text{SO}_3]_2$ complexes.

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100 cm⁻¹, to cooperatively quench Eu³⁺ emission. The coupling constants, which describe the strength of the intramolecular interactions between Eu³⁺ ions and the hetero rare earth ions Dy³⁺, Sm³⁺ and Yb³⁺ were determined to be 1.2×10^{-51} , 9.3×10^{-53} and 5.5×10^{-52} m⁶ s⁻¹ respectively.

Two novel macrocyclic dinuclear series, [Ln₂H₄L²(Br)₂(CH₃OH)₆][Br]₄ where Ln = La - Lu, Y, and [Ln₂H₄L²(X)_z(S)_{8-z}][CF₃SO₃]_{6-z} for Ln = La - Gd, where X = CF₃SO₃ or Cl, S = CH₃OH or H₂O, Z = 2 - 6, were isolated from the library at pH 4 in about 32 and 11% yields respectively. The metal ions' coordination spheres in the [Ln₂H₄L²(Br)₂(CH₃OH)₆][Br]₄ complexes were consistent throughout the series. In complexes of the type [Ln₂H₄L²(X)_z(S)_{8-z}][CF₃SO₃]_{6-z} however, the metal ions' coordination environments varied from structure to structure depending on the reaction conditions and counter-anions present. Ligands such as water, alcohols, triflates and halides exchanged coordination sites readily, while chelate H₄L² was consistent in its coordination. As such, no luminescence studies were carried out on this series because the results so obtained would have been inconclusive.

Luminescence from the ⁵D₀ energy level of Eu³⁺ in crystals of Eu₂H₄L²(Br)₂(CH₃OH)₆][Br]₄ exhibits temperature dependence and there is no emission at room temperature. When excited by light of 577 nm at 77 K however, bright red emission is seen. Interactions between europium(III)

and dysprosium(III) were weak and resulted in no effective quenching of europium(III) emission. Dipole - dipole interactions in the $\text{Eu}^{3+}/\text{Nd}^{3+}$ and $\text{Eu}^{3+}/\text{Tm}^{3+}$ systems seem to have occurred intermolecularly across distances of $\sim 8.5 \text{ \AA}$, rather than across the large intramolecular separation of $9.6 \text{ \AA}$. The strengths of these interactions are described by coupling constants of 7.9×10^{-51} and $2.5 \times 10^{-51} \text{ m}^6 \text{ s}^{-1}$ respectively.

Crystals of the acyclic dinuclear complex series $\text{Ln}_2(\text{L}^4)_3(\text{CF}_3\text{SO}_3)_3$, where $\text{Ln} = \text{La} - \text{Dy}$, were isolated in about 75% yield in the presence of excess 1,2-diaminoethane. $\text{Eu}_2(\text{L}^4)_3(\text{CF}_3\text{SO}_3)_3$ complexes exhibit temperature dependent luminescence behaviour since they produce red emission at 77 K when the $^5\text{D}_0$ state of Eu^{3+} is excited directly (with visible radiation of 579 nm), or indirectly (via the ligand with ultraviolet radiation of 400 nm), but are not emissive at 296 K.

The following are the ligands which participated in the molecular recognition processes that led to the formation of the polynuclear complexes isolated in this study.

