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Role of diluent in the unusual extraction of Am³⁺ and Eu³⁺ ions with benzene-centered tripodal diglycolamides: local structure studies using luminescence spectroscopy and XAS†

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Two benzene-centered tripodal diglycolamide ligands (**L_I** and **L_{II}**) were used for the extraction of Am³⁺ and Eu³⁺ from nitric acid solutions into a diluent medium of *n*-dodecane modified with various amounts of isodecanol. The ligands showed preferential extraction of Eu³⁺ over Am³⁺ in most cases. While the extraction of the Am³⁺ ion was not much affected (with a slight increase) over the entire range of diluent compositions in the case of **L_I**, a gradual decline in the extraction of the Eu³⁺ ion suggested a reversal in the separation trend with Am³⁺ being preferentially extracted with a solution of **L_I** in pure isodecanol. On the other hand, a sharp decline was seen for the extraction of both Am³⁺ and Eu³⁺ in the entire range of diluents containing various fractions of isodecanol when **L_{II}** was used. The unusual extraction was attributed to the difference in the complexation behaviour of **L_I** and **L_{II}**, which was explained on the basis of photoluminescence (PL) spectroscopy as well as XAS studies. The PL studies suggested absence of any inner-sphere water molecules from the lifetime data, while the splitting of emission peaks and asymmetry ratio values gave an idea about the complex geometry. On the other hand, the XAS studies gave information about the bonding in the coordination complexes.

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Introduction

The complex chemistry of diglycolamide (DGA) ligands with lanthanide (Ln)/actinide (An) metal ion extraction is quite fascinating.^{1–7} Although they are quite similar to malonamides/glutaramides (Fig. 1) as both have two amide groups for complexation, the ‘ether’ linkage present at the centre of the DGA makes it a stronger complexing agent and, hence, extracting agent.^{8–13} In the case of the normal DGA ligands such as TODGA (*N,N,N',N'*-tetra-*n*-octyldiglycolamide, Fig. 2), the ease of extraction of the actinide ions has been reported as: Am³⁺ > Pu⁴⁺ >> UO₂²⁺,^{1,5} which is entirely different from the trend seen with other ligands, *i.e.*, Pu⁴⁺ > UO₂²⁺ > Am³⁺.^{5,6,14,15} While the

latter trend is universal and is based on their residual charge,¹⁶ there has been no easy way to explain the trend observed for TODGA.^{6,17,18} Zhu *et al.* observed a unique selectivity while studying the extraction of a large number of metal ions. They found that metal ions with an ionic size close to 100 pm were preferentially extracted irrespective of their oxidation state.¹⁹ This could also explain the unusually high extraction of Sr²⁺ with TODGA, though it is not very significantly extracted with other analogous extractants.^{17,19,20} It has been proposed that two TODGA molecules ‘self-assemble’ to resemble an 18-crown-6-like structure, which is a well-known extractant for alkali and alkaline earth metal ions. A more concrete explanation has been given by Jensen *et al.* and others,^{21,22} suggesting the formation of a reverse micellar structure involving 3–4 TODGA molecules facilitating the extraction of metal ions of a given size (as observed by Zhu *et al.*¹⁹). The resulting three-dimensional cavity does not favour the extraction of uranyl ions, which have a peculiar structure with two axial ‘O’ atoms and binding being possible at the equatorial plane alone. As the reverse micelle or ‘self-assembly’ formation requires the diluent to be non-polar, the whole phenomenon is controlled by the choice of diluent. This has been amply exploited by synthesizing DGA-functionalized calix[4]arenes,²³ or tripodals,^{3,24–29}

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Fig. 1 Structural formulae of (a) malonamide and (b) glutaramide.

which indeed gave very high extraction efficiencies for lanthanide and trivalent actinide ions.

Amongst the tripodal ligands, benzene-centred tripodal diglycolamide (abbreviated as Benz-T-DGA) ligands have been found to be highly efficient for the extraction of the trivalent $\text{Ln}^{3+}/\text{Am}^{3+}$ ions.^{26,29,30} Previously, we have reported the interesting separation behaviour of Am^{3+} and Eu^{3+} ions with the Benz-T-DGA ligands **L_I** and **L_{II}**²⁶ (Fig. 2). However, it was observed that the nature of the extracted complexes was quite different for both ligands.²⁶ This was assumed to be primarily determined by the structure of the ligands and, to a lesser extent, by the diluent medium. There has been no systematic study reported on this interesting aspect that can possibly explain the differences in the complex stoichiometry reported previously.

The objective of the present study is to verify the above hypothesis and to gain insight into the structural aspects of the two Benz-T-DGA ligands at various diluent compositions involving a non-polar (*n*-dodecane) and a polar (isodecanol) solvent. The extraction behaviour of trivalent lanthanide and actinide ions was investigated using Eu^{3+} and Am^{3+} as the representative ions. Photoluminescence (PL) and X-ray absorption spectroscopy (XAS) were used to gain structural insight into the binding of these two ligands with the Eu^{3+} ion. The Am^{3+} ion was not used for these studies in view of the high radioactive dose due to the ²⁴¹Am radionuclide. Furthermore, structural studies using single-crystal XRD were not possible in view of

our inability to isolate single crystals, since pasty masses were invariably obtained during umpteen attempts.

Results and discussion

Liquid-liquid extraction studies

The liquid-liquid extraction of the metal ions Eu^{3+} and Am^{3+} has previously been evaluated with **L_I** and **L_{II}** (1 mM) dissolved in 5% isodecanol (IDA) + 95% *n*-dodecane (*n*-dd).²⁶ The maximum separation factor ($\text{SF} = D_{\text{Eu}}/D_{\text{Am}}$) between Eu^{3+} and Am^{3+} was achieved at 1 M HNO_3 .

The effect of phase modifiers (in the present case a long-chain alcohol, *i.e.*, IDA) on the separation factor using **L_I**/**L_{II}** was not reported. The distribution ratios of Eu^{3+} and Am^{3+} were studied at 1 M HNO_3 with 0.7 mM **L_I**/**L_{II}** dissolved in different IDA concentrations (5–100% v/v) in *n*-dd. The two ligands behave differently with various IDA concentrations (Fig. 3). For **L_{II}** there is a regular decrease in the distribution ratios of both Eu^{3+} and Am^{3+} with increasing IDA content maintaining a constant SF of $\sim 4.3 \pm 0.2$ (within error limits). Brigham *et al.* have also shown that, using TODGA, the SF between Nd^{3+} and Pr^{3+} remains comparable even after the addition of 30% IDA in Isopar™ L Fluid (an approximately C_{12} isoparaffinic hydrocarbon).³¹

The distribution ratios of Eu^{3+} and Am^{3+} for **L_I** behave differently with increasing IDA content in *n*-dd, namely the D_{Eu} decreases and the D_{Am} increases (with a small positive slope, except at 100% IDA) (Fig. 3). The SF decreases with a crossover point ($\text{SF} \approx 1$) at 70% IDA + 30% *n*-dd and its reversal is at > 70% IDA + 30% *n*-dd (Fig. 3). The separation factor of **L_I** (14.61) is higher than that of **L_{II}** (4.45) at 5% IDA + 95% *n*-dd in 1 M HNO_3 .²⁶ The difference in the extraction behaviour of the two ligands with the IDA variation can be understood by speciation of the extracted Eu^{3+} -**L_I**/**L_{II}** complexes in the organic phase. Leoncini *et al.* have shown the extraction of 1 : 1 and 1 : 2

Fig. 2 Structural formulae of several (tripodal) DGA ligands along with the Benz-T-DGA ligands **L_I** and **L_{II}** used in the present study.

Fig. 3 Variation in the distribution ratios of Am^{3+} and Eu^{3+} with $\text{L}_\text{I}/\text{L}_\text{II}$ dissolved in different IDA concentrations (v/v) in *n*-dd; [ligand]: 0.7 mM; $[\text{HNO}_3]$: 1 M.

complexes for $\text{Eu}^{3+}\text{-L}_\text{I}$ and $\text{Eu}^{3+}\text{-L}_\text{II}$, respectively, in the 5% IDA + 95% *n*-dd mixture.²⁶ However, any discussion about this deviating behaviour is missing. A recent study by Brigham *et al.* has demonstrated that the stoichiometry of the extracted $\text{Ln}^{3+}\text{-TODGA}$ complex does not change upon the addition of 30% of a phase modifier.³¹

The previous study showed that, despite the overall lipophilicity of the $\text{Eu}^{3+}\text{-L}_\text{II}$ (1 : 2) complex being higher than that of the $\text{Eu}^{3+}\text{-L}_\text{I}$ (1 : 1) complex, L_II shows poor extraction of $\text{Ln}^{3+}/\text{An}^{3+}$ ions compared with L_I . The higher extraction of Am^{3+} by L_I was explained by the free energy of extraction (ΔG_ext) using theoretical studies.²⁶ Although a detailed solvent extraction was performed, the role of the preorganisation of the ligands received only limited attention.²⁶

The overall ΔG_ext (eqn (1)) is composed of several individual ΔG factors (eqn (1)) such as the free energy of ligand preorganisation in the organic phase (ΔG_preorg), the free energy of complexation (ΔG_comp), and the free energy of solvation (ΔG_sol) of the ML_n ($n = 1\text{--}2$) complex in the organic medium. All the above ΔG values are associated with the respective enthalpy and entropy changes in the process. For example, the

$$\Delta G_\text{ext} = \Delta G_\text{preorg} + \Delta G_\text{comp} + \Delta G_\text{sol} \quad (1)$$

organisation of ligands before metal ion complexation is an energy-intensive step and may also be not entropically favoured. The ΔG_comp value may also vary with the physical/chemical properties of the solvent for a given metal ion and ligand. The ΔG_sol will be unfavourable for ML_n complexes with a higher n value as it requires more disruption of the organic medium to accommodate its large size, which is an energy-intensive process.³² The overall extraction of the ML_n complex in any solvent depends on the intricate interplay between these factors.

The difference in both the extraction and the speciation of the extracted complexes of $\text{Ln}^{3+}/\text{An}^{3+}$ by L_I and L_II can be understood considering the above free energies. Theoretical studies²⁶ clearly show the preorganisation of L_I before extraction

Fig. 4 Cartoon showing (a) preorganisation of L_I and (b) planar L_II . (The theoretical optimised structures for L_I and L_II are taken from ref. 26)

due to the presence of ethyl groups at alternate positions of the benzene ring in L_I , whereas they are missing in L_II (Fig. 4). This gives an edge to L_I over L_II for $\text{Ln}^{3+}/\text{An}^{3+}$ extraction (assuming that other factors remain constant) as any free energy penalty to ΔG_ext due to ΔG_preorg is minimised for L_I compared with that of L_II . This is also reflected in the higher D_M ($\text{M} = \text{Eu}, \text{Am}$) value with L_I , possibly due to the formation of an 'inclusion' complex where the metal ion gets inside the cone (top cartoon of Fig. 4), thereby forcing the dehydration of the metal ion leading to a more lipophilic extracted species. The expected higher lipophilicity of the 1 : 2 ML_II ($\text{M} = \text{Eu}^{3+}$ or Am^{3+}) complex compared with that of the 1 : 1 ML_I complex becomes actually more hydrophilic due to the lower possibility of dehydration. Also, due to its large size, dissolution or solvation requires more disruption of the solvent phase, and hence, is energetically not favourable. This suppresses any positive contribution of a higher lipophilicity to the $D_\text{Eu/Am}$ values in the case of L_II .

The formation of a 1 : 1 ML_I complex in the case of L_I can also be understood from its preorganised structure considering two factors. First, the coordination numbers (CNs) of the metal ions are satisfied by complexation with three preorganised chains of L_I giving a 1 : 1 complex. Second, due to the steric restriction imposed by the preorganised structure, which makes it difficult to arrange two preorganised L_I molecules in a 1 : 2 fashion for complexation (Fig. 5).

However, for the non-preorganised L_II ligand,²⁶ the preorganisation of L_II in such a way that all three chains can coordinate to a metal ion seems energetically more difficult than bringing two L_II molecules together for complexation, hence, a 1 : 2 stoichiometry may be favoured. A similar coordination in 1 : 2 fashion in 5% IDA + 95% *n*-dd has also been observed for the multiple DGA ligands T9CODGA and T12C4DGA (Fig. 2).^{2,24}

The addition of phase modifiers leads to a change in the physical/chemical parameters of the solvent, such as water or acid uptake, polarity *etc.*, which can also influence the extraction of $\text{Ln}^{3+}/\text{An}^{3+}$ with a given ligand.^{33,34} For both ligands the acid and water uptake appeared to be very much similar (Table 1). This seems logical, as the extraction of both acid

Fig. 5 Cartoon showing the hindered approach of L_I for the formation of a 1:1 complex leading to 1:1 complex formation (top) and the easier approach of two L_{II} molecules towards a metal ion leading to 1:2 ML_{II} complex formation (bottom); M (blue sphere): Eu^{3+} or Am^{3+} .

Table 1 Water and acid extraction by L_I and L_{II} dissolved in n -dd with various IDA contents, $[HNO_3]$: 1 M

IDA (v/v, %)	Water uptake (%)		Acid uptake (M)	
	L_I	L_{II}	L_I	L_{II}
5	<0.05	<0.05	<0.01	<0.01
20	0.14 ± 0.03	0.12 ± 0.01	0.06 ± 0.01	0.07 ± 0.02
50	0.73 ± 0.04	0.77 ± 0.05	0.10 ± 0.02	0.13 ± 0.01
100	2.24 ± 0.03	2.21 ± 0.02	0.22 ± 0.03	0.20 ± 0.02

and water is only dependent on the IDA content in the organic phase due to the very low concentration of the ligand (<1 mM) employed. Consequently, other physical/chemical properties of the solvent system, such as viscosity, dielectric constant, density, *etc.*, can be assumed to be identical for both L_I and L_{II} . Hence, to understand the Eu^{3+} extraction trends in the case of L_I and L_{II} upon increasing the IDA content in n -dd, we need to focus on the state of L_I and L_{II} in the solvent phase before complexation and changes it must undergo for the complexation. Since L_I is relatively more preorganised compared with L_{II} in the pure solvent, it requires minimum changes in its structure to form Eu^{3+}/Am^{3+} - L_I 1:1 complexes and hence, $D_{Eu/Am}$ with L_I does not change drastically upon IDA variation. However, for L_{II} , the free ligand has more interaction with the solvent molecules due to its more open structure, and hence, bringing two L_{II} molecules for 1:2 Eu^{3+}/Am^{3+} - L_{II} complex is more dependent on the solvent changes. This leads to a substantial decrease in $D_{Eu/Am}$ with L_{II} on IDA variation. The other factor for the poor $D_{Eu/Am}$ value of L_{II} may be the poor solubility/solvation of the larger 1:2 Eu^{3+}/Am^{3+} - L_{II} complex with the increasing alcohol content in the alkane due to the increasing viscosity/density of the system.³⁵ Alcohols are known to form different structural units in an aliphatic solvent with different solvation properties; more details can be found in the literature.^{36,37}

The addition of IDA increases the overall polarity of the organic phase, which may facilitate the solubility of the

relatively polar metal-ligand solvate in the organic phase^{38–43} and, hence, favour the extraction of the trivalent Ln^{3+}/An^{3+} by L_I compared with L_{II} . Typically, the extraction of Am^{3+} increased upon increasing the IDA content in n -dd, suggesting a better solvation of the Am^{3+} - L_I solvate compared with that in pure n -dd. A higher D_{Am} in polar 1-octanol compared with n -dd was also observed by Sasaki *et al.* in the case of TODGA.⁶ As mentioned above, the extraction of Eu^{3+} was different from that of Am^{3+} with L_I . The decrease in D_{Eu} may be due to the poor solubility of the Eu^{3+} - L_I solvate in IDA + n -dd mixtures, as also suggested by Brigham *et al.*³¹ for Ln^{3+} extraction by TODGA. There may be other reasons for the difference in the extraction profiles of Eu^{3+} and Am^{3+} by L_I with various IDA + n -dd mixtures, which require further investigations.

The interaction between the extractant (L_I/L_{II}) and IDA in the modified solvent system also plays an important role in determining the overall extraction profile of Ln^{3+}/An^{3+} , as seen by Deepika *et al.* for Am^{3+} extraction by branched DGA ligands in 1-decanol + n -dd mixtures.⁴⁴

To obtain further insight into the parameters that determine the formation and the structural aspects of the extracted Ln^{3+}/An^{3+} - L ($L = L_I, L_{II}$) complexes, photoluminescence (PL) and X-ray absorption spectroscopy (XAS) studies were performed.

Photoluminescence (PL) studies

From the PL spectra of the extracted Eu^{3+} - L ($L = L_I, L_{II}$) complexes in IDA + n -dd mixtures, the coordination and symmetry around the Eu^{3+} ion in the first coordination sphere can be deduced. The excitation spectra give important information about ligand-to-metal charge transfer (LMCT), which can be correlated with the effective interaction between the metal ion and the ligand orbitals.^{45–47}

The Eu^{3+} emission spectrum shows various transitions from the 5D_0 to 7F_J ($J = 1–4$) level and the splitting can be used to gain information about the point group around the Eu^{3+} ion in a given complex. The $^5D_0 \rightarrow ^7F_2$ transition at ~ 614 nm is an electric dipole transition and is sensitive to the local coordination around the Eu^{3+} ion, whereas the $^5D_0 \rightarrow ^7F_1$ transition at 589 nm is a magnetic dipole in nature and does not change much with local coordination around the Eu^{3+} ion. The ratio of the two transitions, the $^5D_0 \rightarrow ^7F_2$ transition (~ 614 nm) to the $^5D_0 \rightarrow ^7F_1$ (589 nm) transition, also known as the asymmetry ratio (AR), reveals the overall asymmetry around the Eu^{3+} ion in the given complex.^{47,48} The decay lifetime of the Eu^{3+} ion is dependent on its hydration sphere and, hence, is used for the determination of the number of water molecules in the primary sphere of the Eu^{3+} ion in any complex. A linear relationship (eqn (2)) between the lifetime and the number of associated water molecules (N_{H_2O}) in the primary sphere is given by Choppin and Peterman:⁴⁹

$$N_{H_2O} = 1.05/\tau \text{ (ms)} - 0.7 \quad (2)$$

The measurement of the excitation spectra at different λ_{em} values can be used for detecting different Eu^{3+} species in solution. For a single species, the excitation spectra look identical, whereas if more than one species is present, differences in the peak heights, positions or integrated intensity ratios may be observed.⁴⁷

Fig. 6 Excitation spectra of extracted (a) $\text{Eu}^{3+}\text{-L}_\text{I}$ and (b) $\text{Eu}^{3+}\text{-L}_\text{II}$ complexes as a function of various IDA contents in $n\text{-dd}$; $[\text{HNO}_3]$: 1 M.

The excitation spectra of Eu-L_I at λ_em of 612 nm and 617 nm appear identical, pointing to the presence of only one type of complex. The excitation spectra show a prominent LMCT band around 277 nm along with other characteristic excitation peaks due to the f-f transitions of Eu^{3+} (Fig. 6). The overall intensities of the excitation spectra decrease due to the lowering of the D_Eu values (*vide supra*) upon increasing the IDA content in $n\text{-dd}$. The excitation spectra of all the studied Eu-L_I samples were normalised to the intensity of the 395 nm band, and a regular decrease in the LMCT band intensity was observed with increasing IDA content in $n\text{-dd}$ (Fig. 6a). The intensity of the LMCT band can be taken as a representation of the metal-ligand interaction.⁴⁷ The LMCT bands increase with better energy level matching and a closer approach of the ligand towards the metal ion. The regular decrease in the LMCT band for the Eu-L_I complex suggests weakening of the interaction between them as also evident from a decrease in D_Eu upon increasing the IDA content in $n\text{-dd}$.

The excitation spectra of the Eu-L_II complexes exhibit a similar decrease in the LMCT band upon increasing IDA content (Fig. S1, ESI†). The intensity of the LMCT band drops

significantly when going from 5% IDA to 10% IDA + $n\text{-dd}$ mixtures (Fig. 6b), while very poor data were obtained with 20% or higher IDA content (Fig. S1, ESI†). The steep decrease in the LMCT band suggests very poor or no interaction between L_II and Eu^{3+} in the 20% IDA + 80% $n\text{-dd}$ mixture, which was also reflected in the abrupt decrease in the D_Eu value under these conditions. It is noted that the relative LMCT intensity of the Eu-L_II complex is higher than that of the Eu-L_I complex at 5% IDA + 95% $n\text{-dd}$. This indicates a closer approach of L_II towards the metal ion than L_I , which is also observed in the EXAFS results (*vide infra*). This closer approach is visualised in Fig. 5, where two molecules of L_II are approaching and they can get close without encountering any steric hindrance, whereas for L_I the maximum approach of the coordination sites is restricted by the steric strain produced in the preorganised L_I structure.

The effect of increasing the IDA content on the D_M value also suggests more interaction of L_II with the IDA molecules, which is evident from its open structure, whereas for L_I , the approach of IDA is restricted due to its closed preorganised structure. At the lowest volume fraction of IDA in $n\text{-dd}$, the structure of L_I can be visualised as all the coordinating sites (carbonyl and ethereal oxygens) pointing towards the interior of the large cone made of the DGA arms. With increasing IDA, one can imagine that some of the coordinating sites flip outside due to the increasing polarity of the solvent. Even in the extreme situation with all the coordinating sites bending outwards towards the solvent (outside of the cone) in pure isodecanol, for complexation with trivalent ions they just need to rotate back. Such flipping may not be too energy intensive. However, in the case of L_II , the situation is very different and any small change in the solvent polarity will affect its solvation and complexation ability. This is directly reflected in the substantial decrease in the D_M values upon increasing the IDA content in $n\text{-dd}$. However, once the complex is formed, it shows more LMCT, suggesting a better interaction of L_II with the metal ion compared with L_I .

The emission spectra of the Eu-L complexes were recorded at λ_ex = 395 nm and at the LMCT band peak maxima. The emission spectra show characteristic peaks for Eu^{3+} for the $^5\text{D}_0$ to $^7\text{F}_j$ ($j = 1\text{--}4$) transitions. The emission spectra recorded at the LMCT and 394 nm are similar, confirming the presence of single species for both L_I and L_II . The emission spectra of the extracted Eu-L_I complex are superimposable with those of increasing IDA content in $n\text{-dd}$, suggesting minimal or no change in the local environment around coordinated Eu^{3+} caused by IDA additions (Fig. 7a). The emission spectra of Eu-L_II with IDA variations are difficult to compare at higher IDA content (due to poor signal/noise ratio), except for 10% IDA + 90% $n\text{-dd}$ (Fig. 7b).

The emission spectra of Eu-L_II at 5% and 10% IDA + $n\text{-dd}$ are very similar (Fig. 7b) and point to a similar local environment of Eu^{3+} ion in both cases. The much weaker or undetectable fluorescence emission of Eu-L_II from organic solvents containing a high IDA concentration is mainly caused by the much lower Eu(III) concentration in the organic phase due to the very poor D_Eu value. To overcome this, and to gain better

Fig. 7 Emission spectra of extracted (a) $\text{Eu}^{3+}\text{-L}_\text{I}$ and (b) $\text{Eu}^{3+}\text{-L}_\text{II}$ complexes as a function of various IDA contents in *n*-dd; $[\text{HNO}_3]$: 1 M. (c) Comparison of the emission spectra of Eu-L_II extracts in 5% IDA + 95% *n*-dodecane ($[\text{L}_\text{II}]$: 0.7 mM) and 100% IDA ($[\text{L}_\text{II}]$: 5 mM); λ_{ex} : 394 nm, $[\text{HNO}_3]$: 1 M. (d) Comparison of the emission spectra of Eu-L_I extracts in 5% IDA + 95% *n*-dodecane and 100% IDA; λ_{ex} : 394 nm, $[\text{HNO}_3]$: 1 M. (e) Comparison of the emission spectra of Eu-L_II extracts in 5% IDA + 95% *n*-dodecane (1 M HNO_3) and 75% IDA + 25% *n*-dodecane (3 M HNO_3); λ_{ex} : 394 nm, $[\text{L}_\text{II}]$: 0.7 mM. (f) Comparison of the emission spectra of Eu-L_I and Eu-L_II complexes in 100% IDA; λ_{ex} : 394 nm; [ligand]: 5 mM; $[\text{HNO}_3]$: 1 M.

insight into the structural aspects of the extracted complex with IDA variation, one needs to improve the D_{Eu} value in the L_II case. The extraction of Eu(III) into the organic phase can be increased either by increasing the feed acidity or by employing a higher ligand concentration. It is interesting to compare the emission spectrum of Eu-L_II at 5% IDA + *n*-dodecane with that of 100% IDA. We have increased the concentration of L_II by 7 times, i.e., $[\text{L}_\text{II}]$ was 5 mM keeping the L_II -to-Eu concentration ratio as 10 and the respective emission and excitation spectra of the Eu-L_II extract were recorded. The excitation spectrum shows improved intensity, as expected, compared with that of 0.7 mM L_II due to the higher extraction of Eu(III) (Fig. S2, ESI[†]). The emission spectrum of the Eu-L_II complex was found to be different in 100% IDA compared with that of 5% IDA + *n*-dodecane (Fig. 7c), suggesting a difference in the two species. The spectrum of Eu-L_I in 100% IDA was also recorded under similar conditions ($[\text{L}_\text{I}]$ was 5 mM and the L_I -to-Eu concentration ratio was 10) and compared with the emission spectra at 5% IDA + 95% *n*-dodecane. For the Eu-L_I extracts, the emission spectra remain the same (Fig. 7d) but changes were seen for the Eu-L_II complex with IDA variation (Fig. 7c) suggesting more influence of solvent on the latter complex. One can think of changes in the Eu-L speciation when changing the concentration of ligands to such higher values. The emission spectrum of the Eu-L_I extract with L_I concentration as 5 mM and L_I to Eu concentration ratio as 10, and with L_I concentration as 0.7 mM (as control) in 1 M HNO_3 was compared, and the similarity of

the emission spectra (Fig. S3, ESI[†]) at these two ligand concentrations validates the adopted procedure.

The extraction of Eu(III) was also performed in 3 M HNO_3 with 0.7 mM L_II in 75% IDA + 25% *n*-dodecane (as poor emission was observed at 100% IDA) and the emission spectrum was recorded. The emission spectrum of the Eu-L_II extract was found to be different at different IDA concentrations (Fig. 7e), as also observed above. A similar experiment was also performed with L_I , and the two emission spectra recorded at different IDA concentrations were found to be superimposable (data not shown). The emission spectra of Eu-L_I and Eu-L_II were similar at 5% IDA + 95% *n*-dodecane (Fig. S4, ESI[†]) but differed significantly at 100% IDA (Fig. 7f). The luminescence studies suggested changes in the Eu-L_II emission spectra with IDA variation, and these changes in the structural arrangement may be responsible for the decrease in the D_{Eu} value with IDA for L_II , whereas minimum or no structural changes were observed for Eu-L_I complex with IDA variation, which is also reflected in its D_{Eu} values.

It is interesting to note that the excitation spectra of both Eu-L_I and Eu-L_II look similar except in the LMCT region (<310 nm) (Fig. S5, ESI[†]). The position of the emission lines is the same for the two complexes, but the relative intensities at 612 nm and 617 nm differ (Fig. S4, ESI[†]). The AR ratio in both Eu-L_I and Eu-L_II complexes are also comparable (Table 2). The photophysical properties of these complexes, along with those of some other DGA ligands, are tabulated in Table 2. The decay

Table 2 Decay lifetime (τ (ms)), number of inner-sphere water molecules ($N_{\text{H}_2\text{O}}$) and AR of the extracted Eu^{3+} complexes from IDA + n -dd mixtures with different DGAs. (The structures of the ligands included here are given in Fig. 2)

Ligand	τ (ms)	$N_{\text{H}_2\text{O}}$	AR	Ref.
L_I^a	1.56 ± 0.06^b	−0.04	2.77 ± 0.45	p.w.
L_II^a	1.25 ± 0.11^b	0.14	2.78 ± 0.49	p.w.
TREN-G1-DGA ^c	1.527	0.25	2.20	50
T12C4ODGA ^c	1.92	0	2.07	2
T9C3ODGA ^c	1.18	0.19	—	24
TODGA ^c	2.07	−0.03	1.96	50
T2EHDGA ^c	1.63	0.20	2.53	50

^a Average value of decay lifetime from 5–100% IDA + n -dd. ^b 1 M HNO_3 .

^c 3 M HNO_3 , 5% IDA + n -dd.

lifetime values at different IDA amounts in n -dd for both Eu-L_I and Eu-L_II are given in the ESI† (Table S1).

The absence of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ transition in all the extracted complexes suggests that they have a higher symmetry than the point groups C_{nv} , C_n or C_s . The $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition was split into at least two peaks for all the complexes.⁴⁷ This suggests that the predominant point group around the Eu^{3+} ion may be D_2 , D_3 , D_{2d} or S_4 .

From the decay lifetimes it is clear that both the complexes are devoid of any water molecules ($N_{\text{H}_2\text{O}}$ in Table 2). The coordination number of 9 for Eu^{3+} must be satisfied by the coordinating sites on the DGA arms and also by the 'O' donors of the inner-sphere nitrate (NO_3^-) anions (for charge neutralization, each extracted species should contain three nitrate ions either in the inner- or outer-sphere). Assuming the most symmetric planar molecule with 9-coordination, having three groups of three atoms together in a symmetric arrangement, the point group will be D_{3h} . For this particular point group, the number of crystal field components for the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 0-4$) transitions in the luminescence spectra of the Eu^{3+} ion must be 0, 2, 1, and 3 for the $^5\text{D}_0 \rightarrow ^7\text{F}_0$, $^5\text{D}_0 \rightarrow ^7\text{F}_1$, $^5\text{D}_0 \rightarrow ^7\text{F}_2$ and $^5\text{D}_0 \rightarrow ^7\text{F}_4$ transitions, respectively.⁴⁷ However, the presence of more than one peak for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition in the luminescence spectra excludes the possibility of the D_{3h} point group. The next most probable point group that can be assigned for the Eu^{3+} -L complex is D_3 , which is also in line with the luminescence spectra of these complexes having two peaks for the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition. The classification of the exact point group is difficult based on the PL spectra at 298 K, due to the poor splitting of different peaks, and one needs to perform experiments at 77 K for better results. Nevertheless, the variation in the peak ratios at 612 nm and 617 nm in the Eu-L_I and Eu-L_II emission spectra (Fig. 7e) indicates a difference in the point/symmetry group for both the complexes.

XAS studies were done to gain more insight into the structures of the complexes.

EXAFS studies

The XAS data of the extracted Eu^{3+} complexes with $\text{L}_\text{I}/\text{L}_\text{II}$ dissolved in 5% IDA + 95% n -dd were recorded at the Eu L_3 edge along with Eu_2O_3 as the reference. The normalised EXAFS

Fig. 8 Normalised EXAFS spectra of the Eu-L_I (Eu(III)-TAE) and Eu-L_II (Eu(III)-TenCB) complexes at the Eu L_3 edge. The inset shows the normalised XANES spectra along with the reference Eu_2O_3 .

spectra of the Eu complexes and the XANES spectra are shown in Fig. 8. Comparison with the Eu_2O_3 standard showed that the complexes have a +3 oxidation state. The initial-guess structural parameters for fitting the EXAFS data of the ML_n [$\text{L} = \text{L}_\text{I}$ ($n = 1$) and L_II ($n = 2$)] complexes were taken from the DFT results.²⁶ The amorphous guess structure was assumed to initiate the data fitting, as no crystal structure was available. Data fitting and refinement of the bond lengths and other factors were done to reach the best fit for the two complexes.

The $\chi(R)$ versus R plots generated (Fourier transform range $k = 2.0-9.5 \text{ \AA}^{-1}$) for Eu-L_I (Eu1) and Eu-L_II (Eu3) from the $\mu(E)$ versus E spectra following the methodology described in the ESI† and the best fit to the experimental data are shown in Fig. 9. The first peak of the Eu-L_I sample at 1.8 Å is due to the contribution of two different oxygen coordination shells at a bond distance of 2.30 Å and 2.35 Å with a coordination number of 5.0 ± 0.4 . The second peak at 2.6 Å is fitted with the carbon and nitrogen coordination shells at 3.14 Å and 3.58 Å, respectively. The coordination numbers of 7.7 ± 1.4 and 3.3 ± 0.6

Fig. 9 Fourier-transformed EXAFS spectra of Eu-L_I (Eu1) and Eu-L_II (Eu3) at the Eu L_3 edge (scatter points) and the theoretical fit (solid lines).

Table 3 Best-fit parameters of the EXAFS data fitting for extracted Eu^{3+} – $\text{L}_\text{I}/\text{L}_\text{II}$ complexes in 5% IDA + 95% *n*-dd

Path	Parameter	Eu– L_I	Eu– L_II
Eu–O	R (Å)	2.30 ± 0.01	2.25 ± 0.01
	N	5.0 ± 0.40	4.8 ± 0.36
	σ^2	0.0056 ± 0.001	0.0022 ± 0.0008
Eu–O	R (Å)	2.35 ± 0.01	2.29 ± 0.01
	N	5.0 ± 0.40	4.8 ± 0.36
	σ^2	0.0056 ± 0.001	0.0022 ± 0.0008
Eu–C	R (Å)	3.14 ± 0.02	3.12 ± 0.01
	N	7.7 ± 1.4	7.0 ± 0.49
	σ^2	0.0043 ± 0.0025	0.0096 ± 0.0015
Eu–N	R (Å)	3.58 ± 0.01	3.57 ± 0.01
	N	3.3 ± 0.6	3.0 ± 0.21
	σ^2	0.0043 ± 0.0025	0.0096 ± 0.0015

were achieved from the best-fit data for the carbon and nitrogen shells, respectively. Like the Eu– L_I sample, the first peak of the Eu– L_II sample at 1.8 Å is a contribution of two oxygen coordination shells. However, the peak is shifted to a slightly lower distance when compared with the Eu– L_I sample. The closer interaction of L_II is also suggested by the higher LMCT intensity in the excitation spectra of the Eu– L_II complex compared with the Eu– L_I complex.

The second peak at 2.6 Å is again a contribution of the carbon and nitrogen coordination shells. From the EXAFS fitting results, the local structures of the two complexes look very similar (Table 3) with respect to the CN and bond distances on the other hand PL studies suggested difference in the geometrical arrangement of ligand around Eu in the two cases at 5% IDA + *n*-dodecane.

Conclusions

The extraction behaviour of Am^{3+} and Eu^{3+} appears to be quite interesting when carried out in diluent mixtures of *n*-dodecane with increasing isodecanol fractions. While L_II showed preferential Eu^{3+} ion extraction *vis-à-vis* the Am^{3+} ion with downward extraction profiles with increasing IDA content, the extraction trend in the case of L_I was quite unusual. Though Eu^{3+} ion extraction showed a decreasing trend with increasing IDA content, in the case of Am^{3+} the trend is opposite. At lower IDA contents (up to 20%), these changes were less steep, which changed to higher deviations at higher IDA content. While preferential extraction of Eu^{3+} ion was seen up to 70% IDA content, beyond that there was a reversal. This is a rather unusual observation for DGA ligands and is quite interesting.

Structural analysis of the extracted complexes by PL suggested inner-sphere binding by the DGA sites and nitrate ions, resulting in the complete replacement of all the inner-sphere water molecules. An attempt was made to determine the symmetry of the complexes from the observed splittings of the emission lines and asymmetry ratio values. The local structures of both the Eu^{3+} – L_I and Eu^{3+} – L_II complexes are similar with respect of CN and bond distance around Eu based on EXAFS, whereas, the PL studies shows difference in symmetry around the Eu in the two cases.

This study clearly demonstrates that the composition of the diluent plays an important role in the extraction behaviour of (DGA) ligands. This may be of interest for many other studies, since the attention is typically focused on the ligand design.

Experimental

Distribution ratio measurements

The distribution ratio of trivalent Ln/An was measured using liquid–liquid extraction experiments. The extraction studies were carried out by equilibrating equal volumes (usually 1 mL) of 0.7 mM ligand at different IDA concentrations (5–100% v/v) in *n*-dd and the aqueous phase containing the required radiotracer ($^{152,154}\text{Eu}$ or ^{241}Am). All the equilibrations were carried out in leak-tight Pyrex glass tubes (5 mL capacity), in a thermostatted water bath at 25 ± 0.1 °C. The time of equilibration was maintained at about 2 h or less after confirming the extraction kinetics (*vide supra*). Subsequently, the tubes were centrifuged at 5000 rpm for 5 min and 100 µL aliquots were taken out from both aqueous and organic phases for radiometric assay. The radiometric assay of ^{241}Am and $^{152,154}\text{Eu}$ was done using a well-type NaI(Tl) scintillation counter (Para Electronics) coupled with a multi-channel analyser (ECIL, India). The distribution ratio of the trivalent metal ions (D_M) was calculated as the ratio of counts per unit time per unit volume in the organic phase to that in the aqueous phase. Each liquid–liquid extraction experiment was carried out in triplicate and the accepted data were within the relative standard deviation of 5%.

Photoluminescence and EXAFS sample preparation

The organic samples for photoluminescence and EXAFS studies were prepared using liquid–liquid extraction. Equal volumes (~ 2 mL) of the aqueous phase (Eu^{3+} (10^{-4} M) in 1 M HNO_3) and the organic phase (0.7 mM $\text{L}_\text{I}/\text{L}_\text{II}$ with various IDA concentrations (5–100% v/v) in *n*-dd) were equilibrated for 2 h and the organic phase was separated by centrifugation at 5000 rpm for 5 min. The separated organic phase was used for photoluminescence and EXAFS studies. The EXAFS studies were carried out for Eu^{3+} – $\text{L}_\text{I}/\text{L}_\text{II}$ extracts in 5% IDA + 95% *n*-dd as, at the higher IDA concentration, the distribution ratio of Eu^{3+} becomes very poor (especially for L_II), giving rise to a very poor signal-to-noise ratio in the fluorescence mode EXAFS data collection and were hence omitted.

Photoluminescence studies

The emission and excitation spectra, and the decay lifetimes of the Eu^{3+} – $\text{L}_\text{I}/\text{L}_\text{II}$ extracts at different IDA concentrations (5–100% v/v) in *n*-dd were recorded/determined using a Quantamaster 400 (PTI-Horiba) unit with a 75 W Xe continuous lamp and a 15 W microsecond Xe flash lamp. The emission spectra were recorded at an excitation wavelength (λ_ex) of 394 nm ($^5\text{L}_6 \leftarrow ^7\text{F}_0$) in the wavelength range of 570–720 nm, whereas the excitation spectra were recorded in the wavelength region of 200–550 nm at an emission wavelength (λ_em) of 612 nm. The data acquisition as well as the analysis was carried out using Felix-GX

software. The decay lifetimes were recorded at $\lambda_{\text{ex}} = 394$ nm and $\lambda_{\text{em}} = 612$ nm. The decay curves were fitted iteratively using the in-built mono- and bi-exponential decay functions of the Felix-GX software provided with the instrument. It was found that the data can be best fitted using the mono-exponential decay fitting.

EXAFS studies

EXAFS measurements were carried out at the Energy-Scanning EXAFS beamline (BL-9) at the INDUS-2 Synchrotron Source (2.5 GeV, 200 mA) at the Raja Ramanna Centre for Advanced Technology (RRCAT), Indore, India. More information about the beamline and data analysis is given in the ESI.†

Conflicts of interest

There are no conflicts to declare.

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