

Inorganic Chemistry

Combined Experimental and Density Functional Theoretical Studies of Am³⁺ and Eu³⁺ Extraction and Complexation with Different Nitrilotriacetamide (NTA) DerivativesArunasis Bhattacharyya,^[a] Prasanta K. Mohapatra,^{*[a]} Avinash S. Kanekar,^[a] Kun Dai,^[b] Richard J. M. Egberink,^[b] Jurriaan Huskens,^[b] and Willem Verboom^[b]

N,N,N',N'',N'''-hexaalkylnitrilotriacetamide (HRNTA) derivatives were found to be promising for the separation of trivalent actinides from lanthanides, which is a burning topic in the back end of the nuclear fuel cycle. In the present work, separation of Am³⁺ from Eu³⁺ was studied using the *N,N,N',N'',N'''*-hexa-2-ethylhexylnitrilotriacetamide (H2EHNTA) derivative and the role of the diluent medium to control the extractable complex was demonstrated. The effect of alkyl chain length and branching in the alkyl chain of different HRNTA (R = methyl, *n*-butyl, *n*-

hexyl, *n*-dodecyl and 2-ethylhexyl) derivatives on their complexation with Eu³⁺ were investigated using steady-state and time-resolved luminescence studies. Different species formed at different ligand to metal ratios were identified from the luminescence titration experiments and their lifetime values measured. The experimental results were corroborated with the help of density functional theoretical (DFT) calculations on Am³⁺ and Eu³⁺ complexes of HRNTA derivatives with varying alkyl chain length and branching.

Introduction

Nuclear energy is fast becoming to be the most viable option in view of the dwindling fossil fuel resources and the ever-increasing energy demands. There are debates all over the world about the expansion of the nuclear energy, especially after the Fukushima accident. The backend engineering including waste management is, however, very important regardless of world continuation or exiting of utilization of nuclear energy. The major drawback of the wide implementation of the nuclear energy is the long term radiotoxicity of some of the byproducts of the fission reaction which include the long-lived actinides *viz.* Am, Cm, also known as the minor actinides, which mainly exist in their trivalent states [1]. A large number of ligands have been evaluated for the separation of these minor actinides from the high level nuclear waste solutions, but those are unable to distinguish between the trivalent actinides and lanthanides because of the similar chemical interactions of the trivalent actinides and lanthanides with the 'O' donor ligands proposed for the actinide partitioning from high level waste.^[1,2] The separation of these minor actinides from lanthanides is, however, essential prior to their transmutation in high flux reactors because of the large neutron absorption cross section of some of the lanthanide

isotopes.^[3] A large number of soft (S, N) donor-based ligands have been evaluated because of the preference of these ligands for the trivalent actinides over the lanthanides. Various classes of soft donor ligands have their own limitations and advantages.^[4-8] Mixed soft-hard donor ligands have been explored and found to be promising for this An/Ln separation.^[9-13] Hexaalkylnitrilotriacetamides (HRNTA, Figure 1) represent a class of mixed 'N','O' donor ligands, where the 'N' atoms present at the centre of the ligand structure can also participate along with the carbonyl 'O' atoms of the amide groups. *N,N,N',N'',N'''*-hexa-*n*-octylnitrilotriacetamide (HONTA) was explored in detail by Sasaki et al. for An/Ln separations.^[14]

Wang et al. studied the separation of Am³⁺ and Eu³⁺ using HONTA in the presence of several masking agents in the aqueous phase and observed that the separation factor improved significantly in the presence of *N,N,N',N'''*-tetraethyl-*N,N''*-ethidene bisdiglycolamide (TEE-BisDGA).^[15] The alkyl groups present in the three amidic 'N' atoms may affect the complexation behaviour of the NTA derivatives significantly. They, therefore, systematically investigated the complexation and extraction behavior of Am³⁺ and Eu³⁺ with HRNTA

[a] Dr. A. Bhattacharyya, Dr. P. K. Mohapatra, A. S. Kanekar
Radiochemistry Division, Bhabha Atomic Research Centre, Trombay,
Mumbai-400085, India
E-mail: mpatra@barc.gov.in

[b] K. Dai, R. J. M. Egberink, Prof. J. Huskens, Dr. W. Verboom
Laboratory of Molecular Nanofabrication, MESA+ Institute for Nano-
technology, University of Twente, P.O. Box 217, 7500 AE Enschede, The
Netherlands

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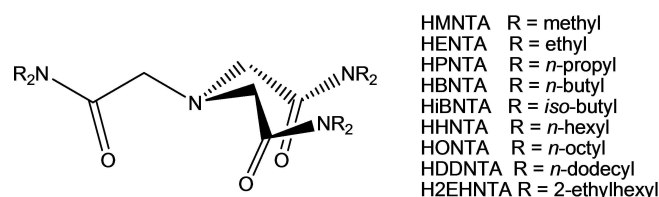


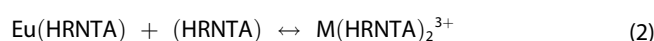
Figure 1. Schematic structure of *N,N,N',N'',N'''*-hexaalkylnitrilotriacetamides (HRNTA).

derivatives varying the alkyl groups starting from *n*-butyl to *n*-dodecyl, in order to evaluate the role of the alkyl chain length, and isobutyl, ethyl-phenyl, ethyl-*p*-Mephenyl, 2-ethylhexyl, to understand the role of branching on the complexation, extraction and separation behavior of Am³⁺ and Eu³⁺ using solvent extraction and steady-state luminescence studies.^[16] In all the solvent extraction studies the authors used methyl isobutyl ketone (MIBK) as the diluent medium, where they observed 1:1 complexes as the extractable species for the extraction of both Am³⁺ and Eu³⁺ from 0.1 M HNO₃ medium for all the HRNTA derivatives. Single-phase complexation studies in a methanol-water (1:1) mixture also showed the formation of only 1:1 complexes of Eu³⁺ for all the HRNTA derivatives.^[16] Sasaki et al.^[14] have also reported varying metal-ligand stoichiometries in the extracted complexes of HONTA in *n*-dodecane medium. Am³⁺ and Eu³⁺ were extracted as 1:2 and 1:1 complex, respectively, from 0.2 M HNO₃ medium, whereas both were extracted as 1:1 complex from 1 M HNO₃ medium. Our previous study^[17] on the complexation of Eu³⁺ with HONTA in methanol medium, however, indicated the formation of both 1:1 and 1:2 complexes and the corresponding solvent extraction studies in *n*-dodecane medium revealed that a 1:2 complex was extracted for both Am³⁺ and Eu³⁺ from 0.1 M HNO₃ medium, which is significantly different than the complexes reported by Wang et al. in the MIBK and methanol-water (1:1) mixture. Wang et al. also pointed out that the extractability of the NTA derivatives increased with increasing the alkyl chain length, whereas with increasing branching in the alkyl groups, the extraction of both the Am³⁺ and Eu³⁺ ions decreased.^[16] However, to the best of our knowledge, no detailed study is available to understand of the effect of the alkyl chain length and branching on the bonding of the NTA derivatives with the Am³⁺ and Eu³⁺ ions. It was, therefore, of interest to investigate the role of the alkyl chain length and the branching in the alkyl chain of HRNTA derivatives more systematically on their complexation behaviour towards trivalent actinides and lanthanides. Furthermore, the role of the diluent medium on the complexation and extraction behavior of Am³⁺ and Eu³⁺ was also required to be studied more systematically. In the present work, Eu³⁺ complexation of HRNTA derivatives having different straight chain alkyl groups, viz. methyl (HMNTA), *n*-butyl (HBNTA), *n*-hexyl (HHNTA), *n*-dodecyl (HDDNTA), was studied using steady-state and time-resolved luminescence spectroscopy. In order to study the effect of alkyl chain branching, the Eu³⁺ complexation was also studied with the 2-ethylhexyl derivative of HRNTA (termed as H2EHNTA). Two-phase liquid-liquid extraction of Am³⁺ and Eu³⁺ was also studied with H2EHNTA in different diluents. Kaneko et al. investigated the complexation of Am³⁺ and Eu³⁺ with HMNTA using DFT-based computational studies.^[18] To the best of our knowledge, however, no literature is available on DFT-based calculations where the complexation was studied with the HRNTA derivatives having alkyl groups of varying chain length and branching. In the present work, therefore, DFT calculations on the Am³⁺ and Eu³⁺ complexes of HRNTA derivatives of varying alkyl chain length and branching were performed in order to rationalize our experimental results.

Results and Discussion

Luminescence Studies: Eu³⁺ Complexation in Methanol Medium

Eu³⁺ complexation studies with the different NTA derivatives were carried out in methanol medium by following the change in the ⁵D₀→⁷F₄ transition peak in the wavelength range of 670–710 nm. The titration profiles observed (Figures S1–S5) clearly show that the spectral feature of the final complex in the case of the branched alkyl derivative of HRNTA (H2EHNTA) (Figure S5) is significantly different from that observed in the case of all other *n*-alkyl derivatives of HRNTA (HMNTA, HBNTA, HHNTA and HDDNTA) (Figures S1–S4). The fitting of the titration data, however, showed that in the case of all the HRNTA derivatives both 1:1 and 1:2 complexes were formed, and this observation was clearly in variance to that had been reported before.^[16] Based on our results the following two step complexation reactions can be proposed.



Predominantly 1:2 complex was seen from solvent extraction studies which was due to favourable partitioning of the complex vis-à-vis the 1:1 complex (vide infra). The formation constants (log β) of the 1:1 complexes were found to be in the range of 4.5 – 5. It was interesting to note here that H2EHNTA showed a higher tendency to form the 1:1 complex than the 1:2 complex with stepwise complexation constants of 4.96 and 2.13, respectively, whereas in the case of the other HRNTA derivatives, having *n*-alkyl groups, these values were found to be in the range of 4.5–4.9 and 3.3–4, respectively. Lower log β₂ value for H2ENTA was attributed to steric factors. Recently, Wang et al. have studied Eu³⁺ complexation with different HRNTA derivatives in methanol-water mixture and observed only 1:1 complex formation in all cases.^[16] This difference can be attributed to the strong complexing nature of water, which is present in large excess as compared to the HRNTA derivatives, inhibiting the formation of higher stoichiometric complexes.

Luminescence lifetimes of the Eu³⁺ complexes were measured during the course of the titration and the decay profile of the Eu³⁺ complexes at varying ligand to metal ratios and the results are shown in Figure S6. The lifetime values obtained by fitting these decay profiles along with the percentage contribution of different species are listed in Table S1. Figure 2 shows the excitation spectra of 1:2 complexes of different HRNTA derivatives with the Eu³⁺ ion. Interestingly, upon increasing the alkyl chain length the ligand to metal charge transfer (LMCT) band becomes more intense as compared to the *f*-*f* transition peaks of the Eu³⁺ and this suggests that the metal-ligand interactions become stronger as one increases the alkyl chain length. The LMCT band in the excitation spectra of the Eu³⁺ complex of H2EHNTA is, however, weaker than that with HHNTA, indicating weaker interactions in the case of a branched ligand, *i.e.*, H2EHNTA.

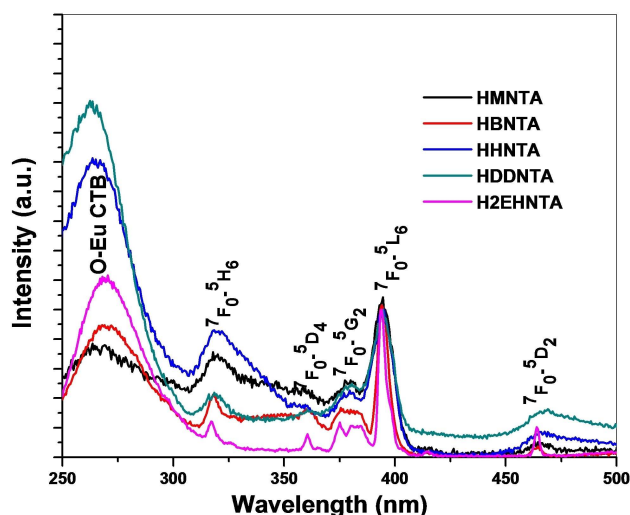


Figure 2. Comparison of excitation spectra of different Eu^{3+} complexes with different HRNTA derivatives in methanol medium ($[\text{Eu}^{3+}]$: 0.1 mM, [L]: 0.8 mM and λ_{em} : 615 nm).

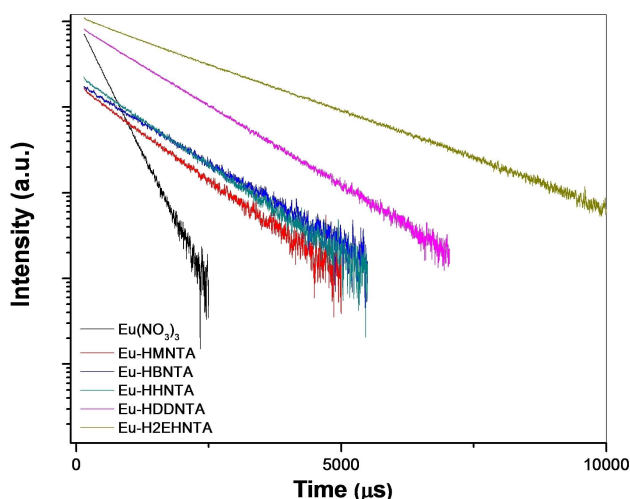


Figure 3. Luminescence decay profiles of europium nitrate and its complexes with different HRNTA derivatives in methanol ($[\text{Eu}^{3+}]$: 0.1 mM, [L]: 0.8 mM and λ_{em} : 615 nm).

Table 1. Comparison of conditional stability constant values of Eu^{3+} complexes of different HRNTA derivatives in methanol medium.					
Ligand	$\log \beta_1$	τ_1 (μs)	$\log \beta_2$	τ_2 (μs)	A.F. ^b
HMNTA	4.53 ± 0.12	520	8.07 ± 0.05	1030	2.07
HBNTA	4.5 ± 0.5 (4.11 ± 0.04) ^a	545	7.8 ± 0.3	1258	2.50
HHNTA	4.9 ± 0.1	550	8.54 ± 0.06	1181	2.32
HDDNTA	4.6 ± 0.1 (4.37 ± 0.07) ^a	500	8.56 ± 0.05	1148	2.28
H2EHNTA	4.96 ± 0.08 (2.10 ± 0.03) ^a	574	7.09 ± 0.07	2072	4.72

^a Data presented inside parentheses are taken from ref. [16]; Medium: MeOH/water (1:1). ^b A.F. = Asymmetry factor

Luminescence decay profiles for the 1:2 complexes of the HRNTA derivatives are shown in Figure 3 and the lifetime values of both the 1:1 (τ_1) and 1:2 (τ_2) complexes observed are listed in Table 1. Both the τ_1 and the τ_2 values are higher in the case of H2EHNTA as compared to all the other HRNTA derivatives studied. The longer luminescence lifetime in the case of H2EHNTA is probably due to the non-approachability of the solvent molecules to the central Eu^{3+} ion in its H2EHNTA complex on account of the presence of branched alkyl groups and weak metal-ligand interactions which result into hindrance in the ligand facilitating quenching.

The emission spectra of the different Eu^{3+} complexes are shown in Figures S7-S11. The H2EHNTA complex exhibits a significantly different emission spectrum as compared to those of the *n*-alkyl derivatives of HRNTA. The asymmetric factor (A.F.), which is determined as the intensity ratio of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ to the $^5\text{D}_0 \rightarrow ^7\text{F}_1$ transition peak, is 4.72 in the H2EHNTA complex, whereas in case of the *n*-alkyl HRNTA derivatives this value is in the range of only 2.0-2.5 (Table 1).

Solvent Extraction Studies

A single-phase complexation study in methanol medium showed the formation of both 1:1 and 1:2 complexes in case of all the HRNTA derivatives. It was pertinent, therefore, to understand the nature of the extracted species during the solvent extraction studies of trivalent actinides and lanthanides using H2EHNTA. For this, the extraction of Am^{3+} and Eu^{3+} was carried out using varying concentrations of H2EHNTA in *n*-dodecane medium and the results showed that the extraction of Am^{3+} increased with a slope value of 2.03 in the logarithmic plot, which clearly indicates that a 1:2 complex is extracted (Figure 4).

In the case of Eu^{3+} , however, a slope value of 1.71 was observed in the log-log plot of the distribution ratio vs the H2EHNTA concentration, indicating some contribution of a 1:1

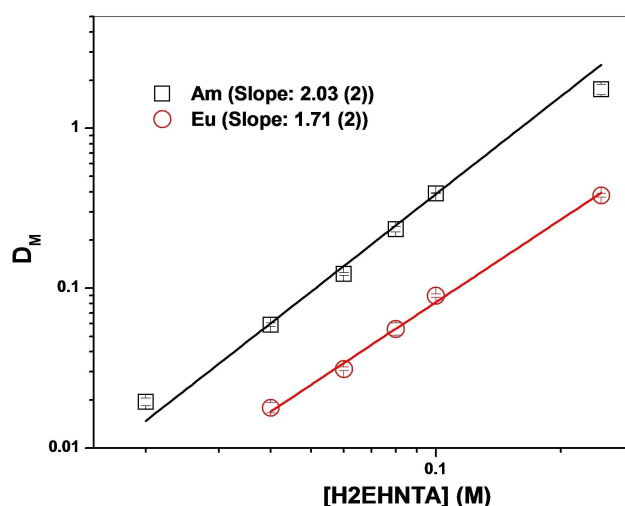


Figure 4. Effect of H2EHNTA concentration on the D_{Am} and D_{Eu} ; Org. phase: varying concentrations (0.02-0.25 M and 0.04-0.25 M for Am^{3+} and Eu^{3+} , respectively) of H2EHNTA in *n*-dodecane; Aq. phase: 0.1 M HNO_3

complex along with the 1:2 complex in the extract. In our previous studies using the *n*-octyl derivative (HONTA), we observed that both Am^{3+} and Eu^{3+} were extracted as 1:2 complexes from 0.1 M HNO_3 .^[17] Sasaki et al., however, reported that Am^{3+} was extracted as 1:2 complex, whereas Eu^{3+} was extracted as a 1:1 complex from 0.2 M HNO_3 and upon increasing the aqueous phase nitric acid concentration to 1 M, both the metal ions were extracted as 1:1 complex^[14] which could be due to the stronger competition from the nitrate ion at higher nitrate concentration. The presence of a 1:1 complex during the extraction of Eu^{3+} by H2EHNTA is in line with the observation from the luminescence studies in methanol medium where it is clear that the tendency to form a 1:2 complex is lower in this branched alkyl chain HRNTA derivative. The extraction studies of Am^{3+} and Eu^{3+} were also carried out at varying concentrations of H2EHNTA in a mixture of 5% isodecanol in *n*-dodecane. The results are shown in Figure 5, where the slope value for Eu^{3+} further decreased to 1.52, indicating more dominance of the 1:1 complex in the extract. This suggests that the composition of the extracted species can be altered by changing the diluent medium. Wang et al. investigated the extraction of Am^{3+} and Eu^{3+} using HRNTA derivatives varying the alkyl chain length and branching.^[16] They observed that both the Am^{3+} and Eu^{3+} ions were extracted as their 1:1 complexes in the case of all the ligands even at 0.1 M HNO_3 . This can probably be attributed to the diluent (MIBK) they used for their studies as we have already mentioned that diluents have a significant role in controlling the composition of the extracted species.

Based on the results obtained from the ligand concentration variation study, the following extraction equilibrium can be proposed.

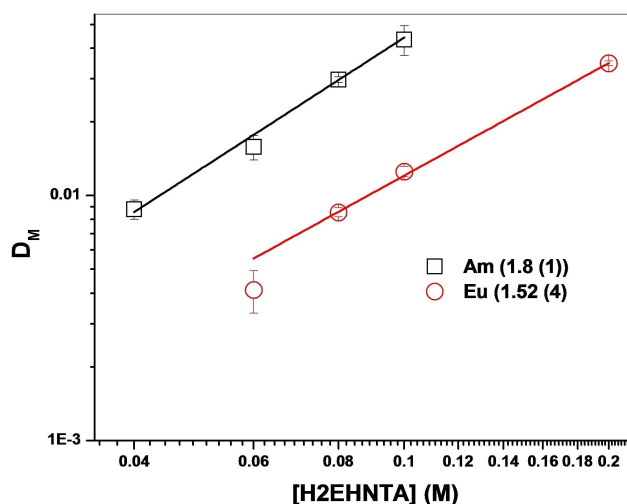
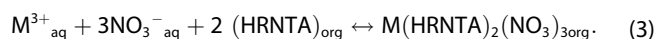


Figure 5. Effect of H2EHNTA concentration on the D_{Am} and D_{Eu} . Org. phase: varying concentrations (0.04–0.1 M and 0.06–0.2 M for Am^{3+} and Eu^{3+} , respectively) of H2EHNTA in *n*-dodecane-isodecanol (95:5) mixture; Aq. phase: 0.1 M HNO_3

Where $\text{M}^{3+} = \text{Am}^{3+}$ or Eu^{3+}

In general, diluents have influence on the extraction behavior of the metal ions, which is also expected in the extraction of trivalent actinides and lanthanides by HRNTA derivatives. We, therefore, compared the extraction and separation behavior of Am^{3+} and Eu^{3+} using H2EHNTA in different diluent media and the results are presented in Figure 6. The highest extraction of both Am^{3+} and Eu^{3+} was observed in the nitrobenzene medium. This can be explained based on the formation of a complex of the type ML_2^{3+} , which can only be extracted by ion pair formation and a polar solvent like nitrobenzene favors the extraction of such species. The effect of the carrier concentration (Eu was used as the carrier while Am was at tracer scale. As in the actual nuclear waste, Ln^{3+} ions are present in much excess as compared to the An^{3+} concentration) on the extraction behavior of Am^{3+} and Eu^{3+} was also studied using H2EHNTA in *n*-dodecane and the results indicated that both the extraction and separation factor increased in the presence of Eu^{3+} carrier (100 ppm), however with further increasing the Eu^{3+} concentration to 200 ppm the change in the extraction behaviour was found to be insignificant (Figure 7). More detailed and systematic studies are required to explain this observation.

DFT Studies

Effect of the alkyl chain length

We observed from the solvent extraction and luminescence studies that in the presence of excess of the ligand, 1:2 complexes were formed in the case of all the HRNTA derivatives. DFT calculations were, therefore, performed on the ML_2 type of complexes of Am^{3+} and Eu^{3+} with HRNTA derivatives with varying alkyl chain lengths from methyl to butyl. In the case of all the complexes, each of the two ligands

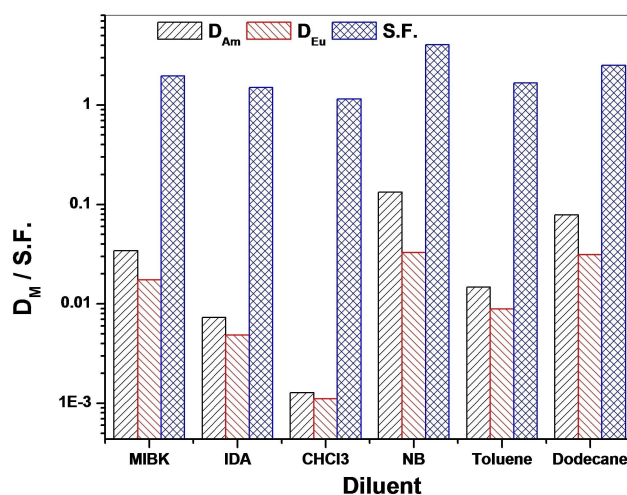


Figure 6. Effect of diluent on the extraction behavior of Am^{3+} and Eu^{3+} using H2EHNTA; Org. phase: 0.1 M H2EHNTA in different diluents; Aq. phase: 0.1 M HNO_3 containing ^{241}Am or $^{152,154}\text{Eu}$ tracer. (IDA = isodecanol; NB = nitrobenzene)

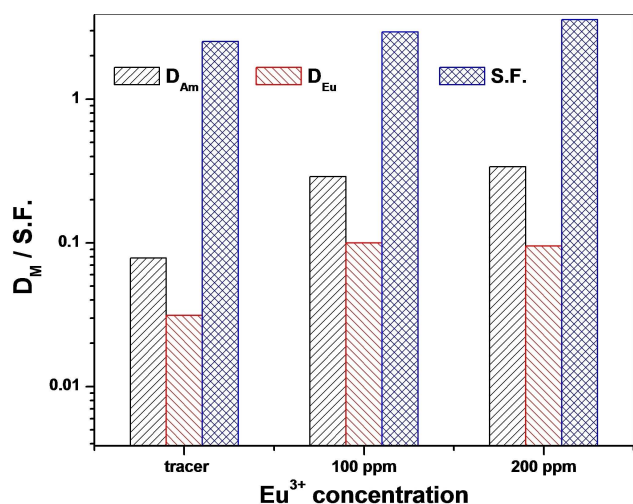


Figure 7. Effect of Eu^{3+} concentration on the extraction behavior of Am^{3+} and Eu^{3+} using H2EHNTA; Org. phase: 0.1 M H2EHNTA in *n*-dodecane; Aq. phase: 0.1 M HNO_3 containing different concentrations of Eu^{3+} and ^{241}Am or $^{152,154}\text{Eu}$ tracer.

bonded in tetradentate fashion having three-coordination from the carbonyl oxygen atoms of the amide groups and one from the central 'N' atom. In all HRNTA derivatives, the 'Am–N' bond distances were found to be shorter than the 'Eu–N' bond distances (Figure 8), which was reported earlier in case of the methyl derivative.^[17] The selectivity of this class of ligands can be explained on the basis of higher covalence in the 'Am–N' bonds as compared to that in the 'Eu–N' bonds as reflected in the shorter 'Am–N' bond distances. Variations in 'M–N' and 'M–O' bond distances are shown in Figures 9a and 9b, where it is clearly observed that the 'M–N' bond distances decreased, whereas the 'M–O' bond lengths increased monotonously upon increasing the alkyl chain length from methyl to *n*-butyl. As the alkyl chain length increases, it becomes more difficult for the carbonyl oxygen atoms to approach closer to the central metal ion. It is interesting to note here that the trend in the 'M–N' bond distances upon varying the alkyl groups, exactly matches with the trend observed in the torsional angle between the three carbonyl 'C' atoms and the central 'N' atom of the HRNTA derivatives (Figure 9c). This suggests that the closer approach of the central 'N' atom of the HRNTA derivatives with increasing alkyl chains length is due to more opening of the umbrella like shape of the HRNTA derivatives as indicated by a smaller torsional angle and this is represented pictorially in Figure 10. Irrespective of the alkyl groups attached to the HRNTA ligand, the torsional angle was found to be lower in the Am^{3+} complexes as compared to that in the Eu^{3+} complexes, which is probably due to the stronger 'Am–N' than the 'Eu–N' interactions.

Effect of alkyl chain branching

In order to understand the role of branching in the alkyl groups, we compared the complexes of the butyl and isobutyl

derivatives of HRNTA (HBNTA and HiBNTA). Luminescence titration studies indicated the formation of 1:1 and 1:2 complexes for all the HRNTA derivatives and the tendency to form a 1:2 complex is lower in case of the branched HRNTA derivative H2EHNTA (*vide supra*). Both 1:1 and 1:2 complexes of HBNTA and HiBNTA were, therefore, considered for the DFT calculations. Kaneko *et al.* studied the complexation of Am^{3+} and Eu^{3+} with HMNTA using DFT-based calculations where they considered only the 1:1 complex, where, beside the four-coordination from the ligand molecule, five water molecules were present in the inner coordination sphere.^[18] We, however, observed lifetime values for the 1:1 complexes in the range of 520–574 μs which cannot account for five water molecules in the inner sphere.^[19] However, the lifetime value of less than 1000 μs , suggests that there may be few solvent (methanol) molecules are present in the inner coordination sphere of the Eu^{3+} ion along with the HRNTA molecule and nitrate ions. Kimura *et al.* have systematically studied the quenching by different solvent molecules and reported that the lifetime of europium perchlorate decreased from 4100 to 230 μs when the solvent was changed from methanol- d_4 to methanol.^[20] The methanol molecules acted as the quencher in the present work and reduced the lifetime values to 520–570 μs . In case of a 1:2 complex, on the other hand, an $\text{M}(\text{HRNTA})_2^{3+}$ type of species was considered. Different structural parameters in the Am^{3+} and Eu^{3+} complexes of HBNTA and HiBNTA are listed in Table 2. Metal-nitrogen bond distances were significantly higher in the 1:1 complexes as compared to that in the 1:2 complexes. The optimized structures of the 1:2 and 1:1 complexes of Am^{3+}

Table 2. Structural parameters in the Am^{3+} and Eu^{3+} complexes with HBNTA and HMNTA ($\text{M}^{3+} = \text{Am}^{3+}$ and Eu^{3+} , L = HBNTA and HiBNTA) calculated at the BP86/SVP level of theory.

TComplex	M	HBNTA			Torsional angle (c-c-c-o)
		$d_{\text{M-N}}$	$d_{\text{M-O(carb)}}$	$d_{\text{M-O(nit)}}$	
ML_2^{3+}	Am	2.735	2.415 2.421	–	19.64 20.46
		2.747	2.421 2.413		
	Eu	2.794	2.399 2.408	–	21.34 21.09
		2.799	2.413 2.395		
$\text{ML}(\text{NO}_3)_3$	Am	2.962	2.421 2.486	2.380 2.449	28.81
			2.601	2.461 2.495	
	Eu	2.986	2.418 2.477	2.542	30.58
			2.609	2.408 2.464	
ML_2^{3+}	Am	2.726	2.415 2.423	–	19.04 19.92
		2.735	2.431 2.423		
	Eu	2.779	2.428 2.434	–	20.57 21.47
		2.783			
$\text{ML}(\text{NO}_3)_3$	Am	2.996	2.420 2.483	2.380 2.450	29.39
			2.567	2.467 2.500	
	Eu	3.591	2.421 2.494	2.532	39.16
			2.455	2.354 2.464	
			2.499 2.478		
			2.488		

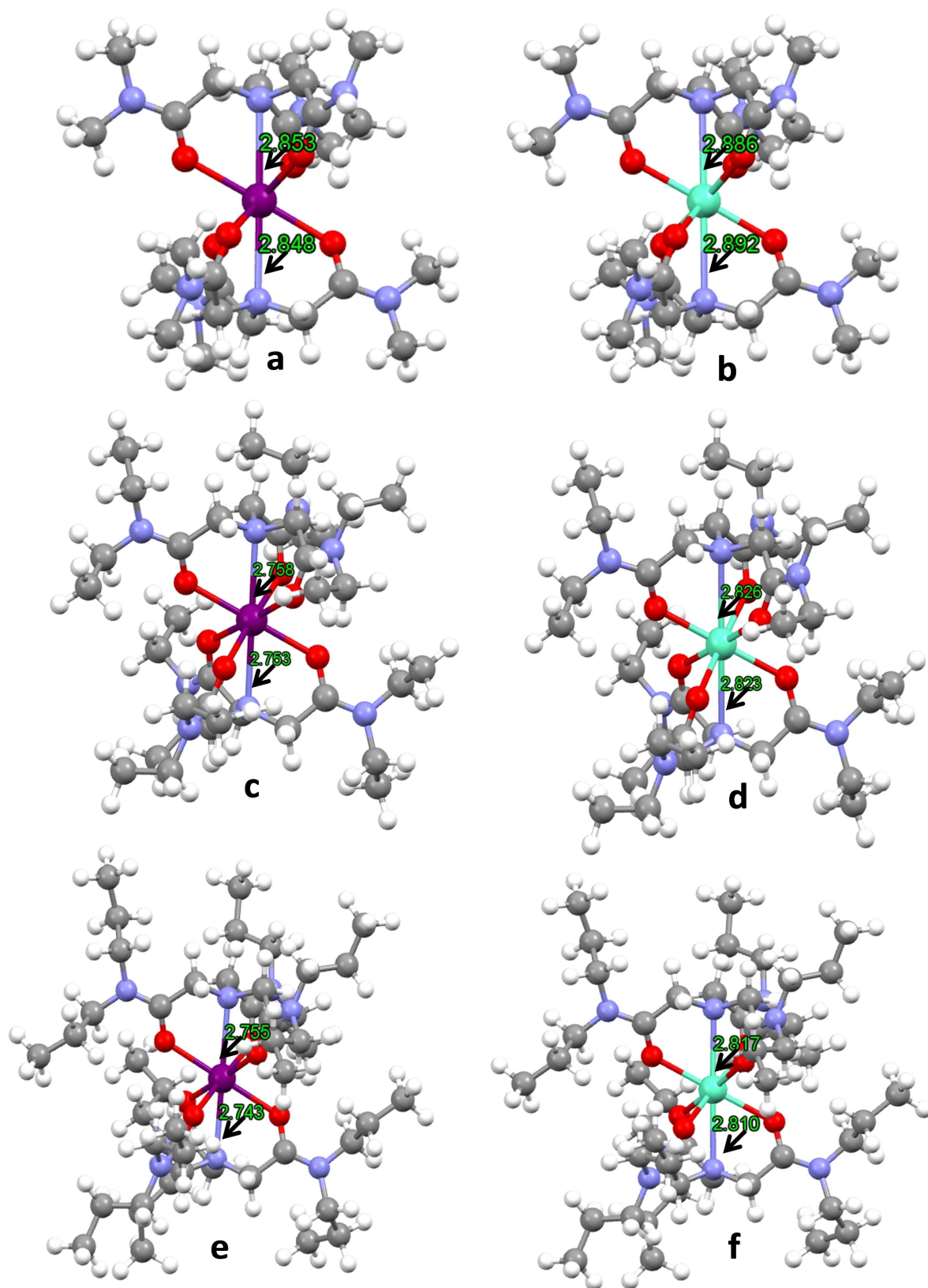


Figure 8. Optimized structures of (a) Am³⁺ complex and (b) Eu³⁺ complex of HMNTA, (c) Am³⁺ complex and (d) Eu³⁺ complex of HENTA, (e) Am³⁺ complex and (f) Eu³⁺ complex of HPNTA at the BP86/SVP level of theory.

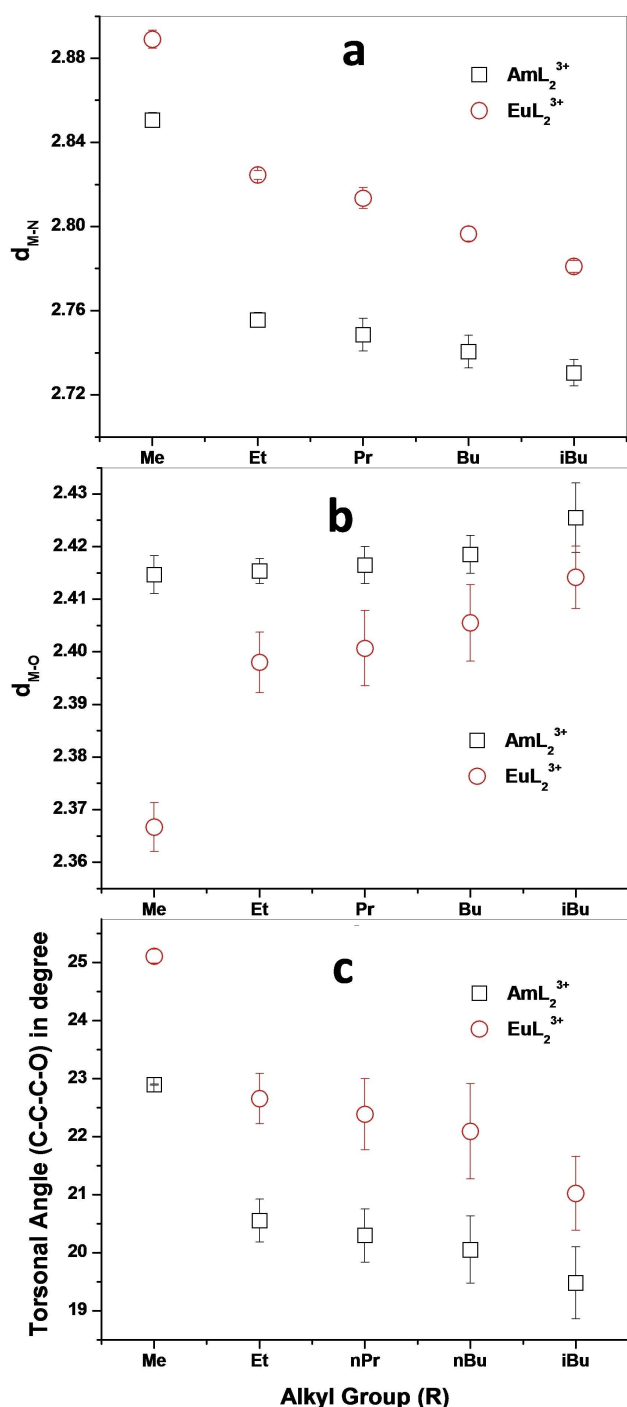
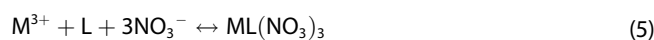


Figure 9. Effect of alkyl groups (R) on (a) metal-nitrogen bond length (Å), (b) metal-oxygen bond length (Å) and (c) torsional angle between three carbonyl 'C' atoms and central 'N' atom of the HRNTA derivatives (errors shown in the data indicate the range of the values observed for multiple 'M–N', 'M–O' bonds and two torsional angles in two coordinated ligand molecules)

and Eu^{3+} with HBNTA and HiBNTA are shown in Figures 11 and 12, respectively. Interestingly, in the 1:2 complexes, for a particular metal ion, the metal-nitrogen bond distances were found to be marginally shorter in case of HiBNTA.

This is a result of more opening of the umbrella-like structure of a HRNTA ligand with branching as indicated from the smaller torsional angle in the complexes of TiBNTA (Figure 9c). The average 'M–O' bond distance was larger in the TiBNTA complexes of both Am^{3+} and Eu^{3+} as compared to those in the TBNTA complexes due to the more bulkiness of the iso-butyl as compared to the *n*-butyl groups. This was reflected in the inferior extraction capability in the solvent extraction studies and also in the formation of a weaker 1:2 complex in the luminescence titration study. In the 1:1 complex of both the ligands, the metal-nitrogen bond distances are much larger than in the 1:2 complexes, indicating a closer structure of the HRNTA backbone reflected in a higher torsional angle (Table 2).

Kaneko *et al.*, however, reported a shorter metal-nitrogen bond length in the 1:1 complex of HMNTA, which is due to the consideration of five water molecules in the inner coordination sphere in place of three nitrate ions in our case.¹ Unlike the 1:2 complexes, no increase in 'M–O' bond length was observed in the case of the 1:1 complexes of HiBNTA as compared to that of HBNTA. This may explain why the 1:1 Eu^{3+} complex of H2EHNTA is equally or more stable in comparison to the 1:1 Eu^{3+} complexes of other HRNTA derivatives having an *n*-alkyl chain (Table 1). In order to explain this phenomenon, the interaction energies in the 1:1 and 1:2 complexes of TBNTA and TiBNTA were compared. The interaction energies were calculated for the following equilibria



Interaction energies for 1:2 ($\Delta E_{\text{ML}_2^{3+}}$) and 1:1 ($\Delta E_{\text{ML}(\text{NO}_3)_3}$) complexes were calculated from equations (5) and (6), respectively.

$$\Delta E_{\text{ML}_2^{3+}} = E_{\text{ML}_2^{3+}} - (E_{\text{M}^{3+}} + 2E_{\text{L}}) \quad (6)$$

$$\Delta E_{\text{ML}(\text{NO}_3)_3} = E_{\text{ML}(\text{NO}_3)_3} - E_{\text{M}^{3+}} + E_{\text{L}} + 3E_{\text{NO}_3^-} \quad (7)$$

The interaction energies for the Am^{3+} and Eu^{3+} complexes of HBNTA and HiBNTA are provided in Table 3. It shows that the relative interaction energies for HiBNTA (as compared to HBNTA) in the case of the 1:2 complexes are more positive as compared to that in the case of the respective 1:1 complexes. This suggests that the 1:2 complex of HiBNTA is much weaker than that of HBNTA, whereas the 1:1 complex of both HBNTA

Table 3. Interaction energies (ΔE in eV) and relative interaction energies ($\Delta\Delta E = \Delta E(\text{HiBNTA complex}) - \Delta E(\text{HBNTA complex})$) in the 1:2 and 1:1 complexes of Am^{3+} and Eu^{3+} with HBNTA and HiBNTA calculated at the B3LYP/Def-TZVP//BP86/SVP level of theory.

M^{3+}	$\Delta E_{\text{ML}_2^{3+}}$ HBNTA	HiBNTA	$\Delta\Delta E_{\text{ML}_2^{3+}}$	$\Delta E_{\text{ML}(\text{NO}_3)_3}$ HBNTA	HiBNTA	$\Delta\Delta E_{\text{ML}(\text{NO}_3)_3}$
Am^{3+}	-29.07	-28.52	0.55	-44.52	-44.45	0.07
Eu^{3+}	-29.93	-29.19	0.75	-45.37	-45.26	0.11

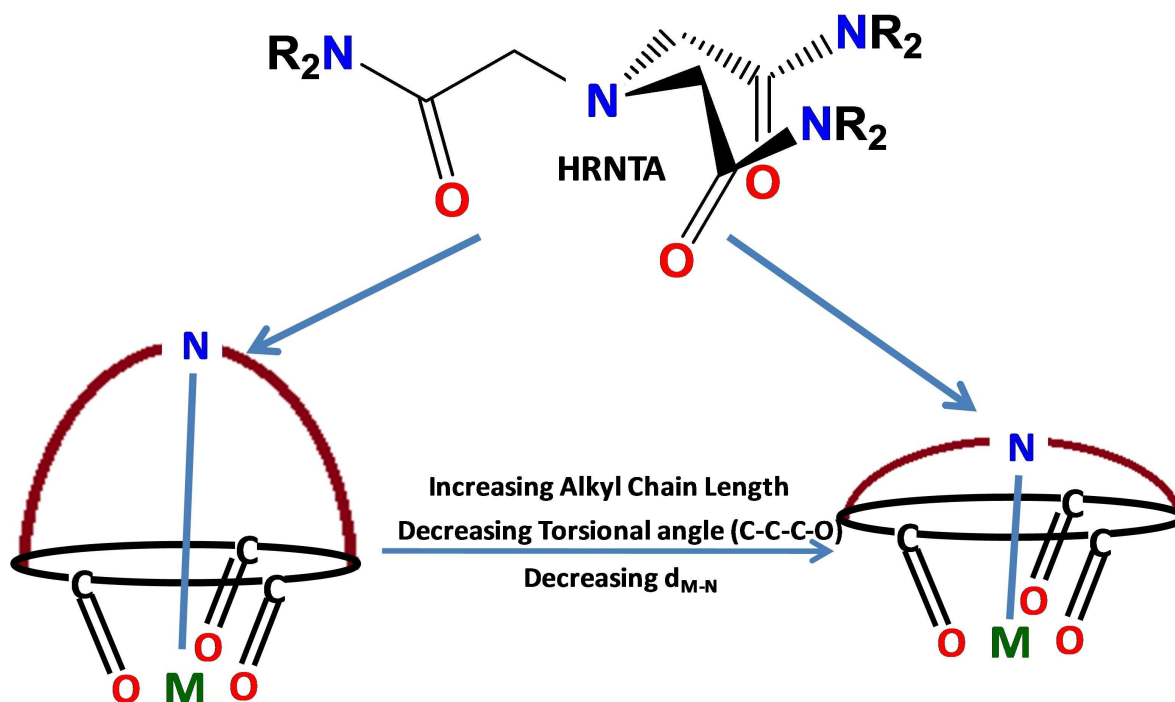


Figure 10. Pictorial representation of the effect of alkyl chain length on the torsional angle between three carbonyl 'C' atoms and central 'N' atom of the HRNTA derivatives on the metal-nitrogen bond distance in their Am^{3+} and Eu^{3+} complexes

and HiBNTA are of comparable stability. This is exactly observed from the luminescence studies where the branched HRNTA derivative (H2EHNTA) formed weaker 1:2 complexes as compared to the complexes of straight chain HRNTA derivatives, whereas the HRNTA derivatives having both branched or straight chain alkyl groups form 1:1 complexes of similar stability (Table 1).

Natural charges on different atoms of the free ligand molecules and their Am^{3+} and Eu^{3+} complexes were calculated by natural population analysis (NPA). The ligand to metal charge transfer (LMCT) calculated from the NPA analysis were found to be increasing with increasing the alkyl chain length. This indicates that the increasing alkyl chain length favours LMCT. On the other hand, with increasing branching (HBNTA vs HiBNTA), the LMCT was found to be decreased from the NPA analysis (Figure 13).

In order to compare the calculated LMCT with the experimental observation, the intensity ratio of charge transfer band to the Eu^{3+} centered ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$ peak ($I(\text{LMCT})/I({}^7\text{F}_0 \rightarrow {}^5\text{L}_6)$) were determined from the excitation spectra of the Eu^{3+} complexes of different NTA derivatives varying the alkyl chain length and branching (Figure 2). This intensity ratio values were also found to be increasing with increasing alkyl chain length and decreasing with increasing branching as observed from the NPA analysis (Figure 13).

Conclusions

Solution-phase complexation of Eu^{3+} was studied in methanol medium with HRNTA derivatives of varying alkyl chain length

and branching using steady-state and time-resolved luminescence. The extent of ligand to metal charge transfer was found to be increasing with increasing the alkyl chain length of the HRNTA derivatives. In the case of the HRNTA derivative having a branched alkyl chain (H2EHNTA), the intensity of the LMCT band decreased, indicating weak metal-ligand interactions. Luminescence titration studies showed that in the case of all the HRNTA derivatives, both 1:1 and 1:2 complexes were formed in the methanol medium. The tendency to form a 1:2 complex was, however, found to be lower in the case of branched HRNTA derivative H2EHNTA. This phenomenon was explained using DFT-based calculations by comparing the interaction energies of Am^{3+} and Eu^{3+} complexes of a branched (HiBNTA) and a straight chain (HBNTA) derivatives of HRNTA.

The lifetime values of both the complexes of the branched HRNTA derivative (H2EHNTA) were found to be higher than those of the HRNTA derivatives having straight chain alkyl groups (HMNTA, HBNTA, HHNTA and HDDNTA). Two-phase liquid-liquid extraction studies of Am^{3+} and Eu^{3+} also indicated the presence of 1:1 complexes as the extractable species along with a 1:2 complex in the case of the branched HRNTA derivative H2EHNTA. The proportion of the 1:1 and 1:2 complexes in the solvent extraction process was significantly affected by the diluent medium.

Supporting Information Summary

Synthesis and characterization of all the HRNTA derivatives used in the present work are provided in the Supporting

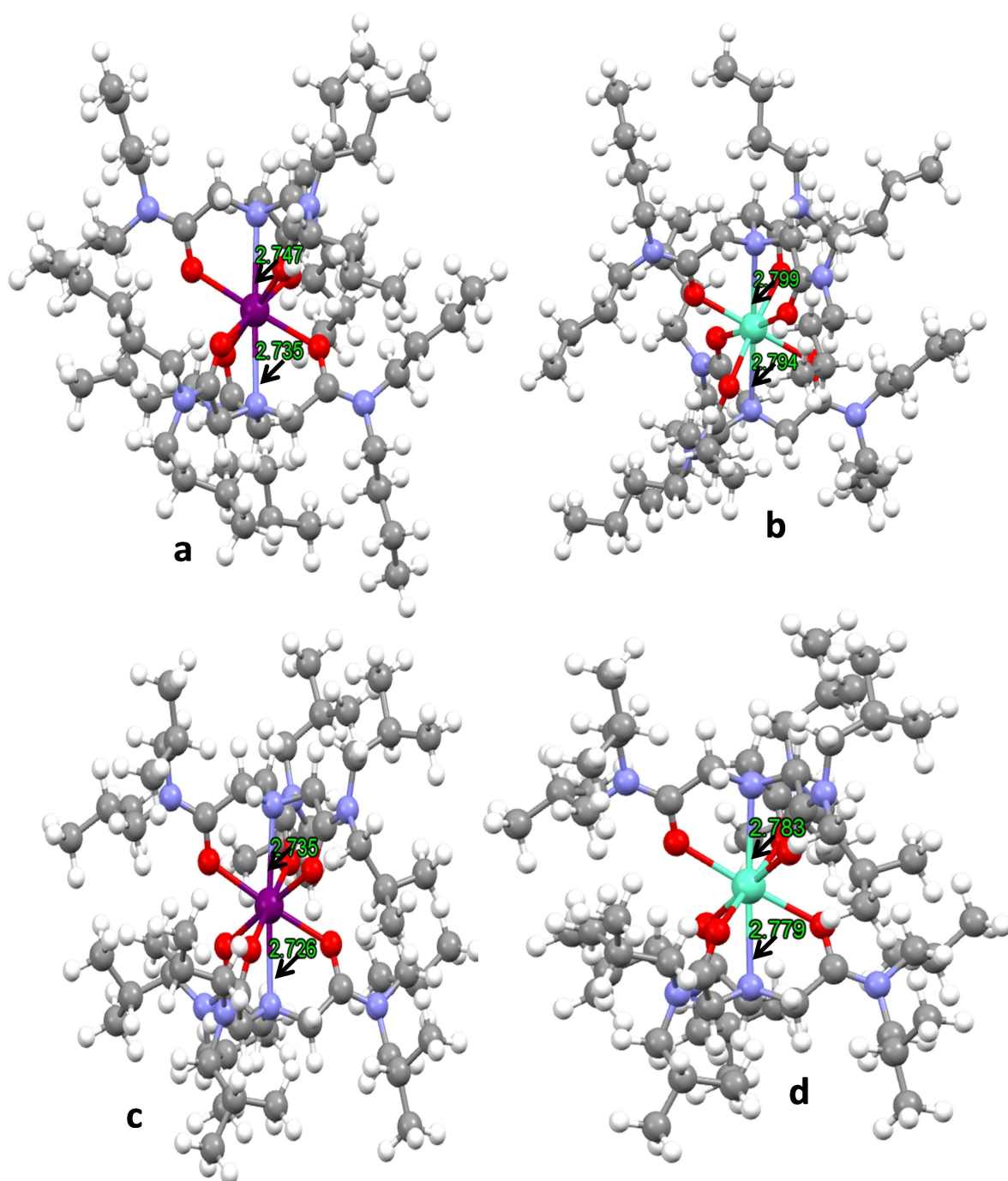


Figure 11. Optimized structures of 1:2 complexes of (a) Am^{3+} and (b) Eu^{3+} with HBNTA, (c) Am^{3+} and (d) Eu^{3+} with HiBNTA at the BP86/SVP level of theory

Information. The experimental procedure followed and the details of the computational methodology are also given in the Supporting Information. The changes in the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$ transition peak of Eu^{3+} upon successive addition of HRNTA during luminescence titration in methanol medium are shown in figures S1-S5 in the Supporting Information. Luminescence decay profile and lifetime values of Eu^{3+} and its complexes with H2EHNTA in methanol at varying ligand to metal ratio are provided in figure S6 and Table S1, respectively. Figures S7-S11

show the excitation and emission spectra of Eu^{3+} complexes of different HRNTA derivatives in methanol medium. Cartesian coordinates of all the geometry optimized structures of the free ligands and their Am^{3+} and Eu^{3+} complexes also listed in the Supporting Information.

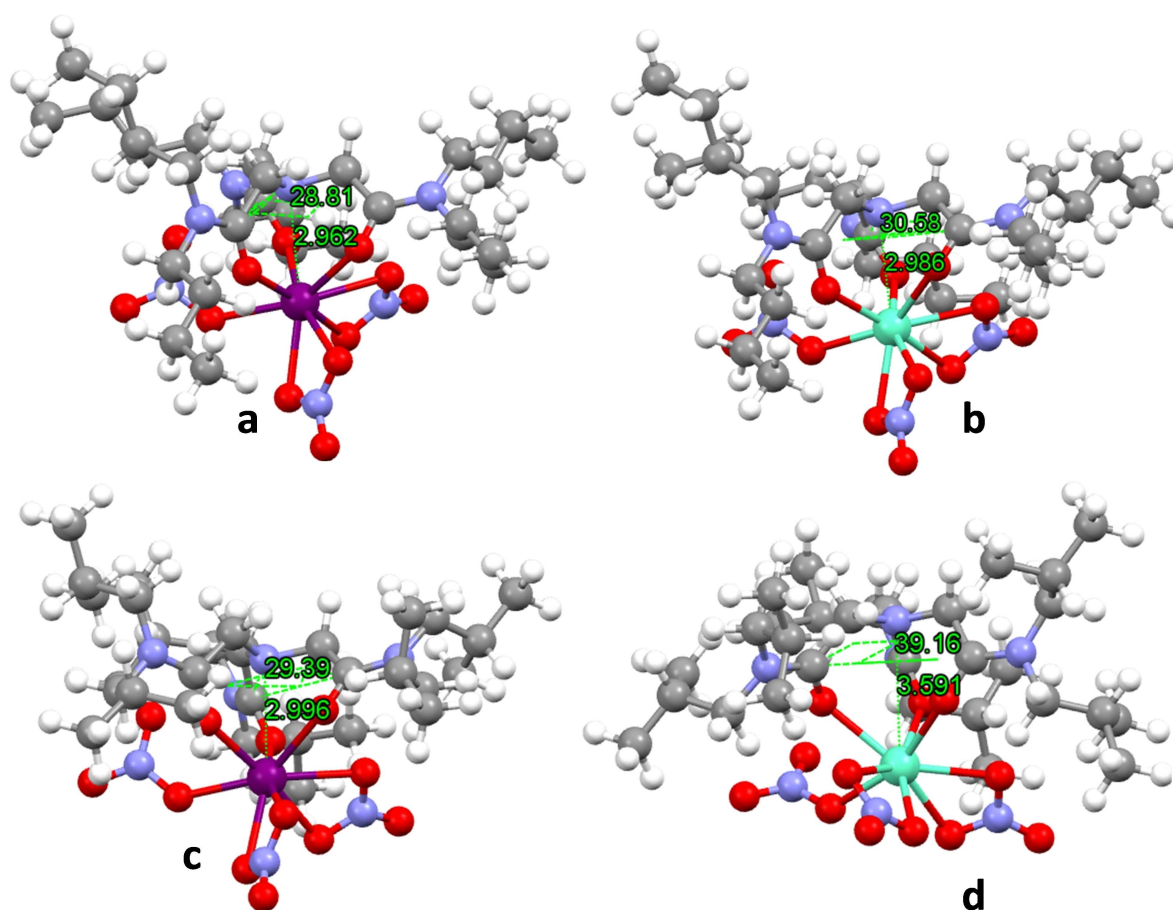


Figure 12. Optimized structures of 1:1 complexes of (a) Am³⁺ and (b) Eu³⁺ with HBNTA, (c) Am³⁺ and (d) Eu³⁺ with HiBNTA at the BP86/SVP level of theory

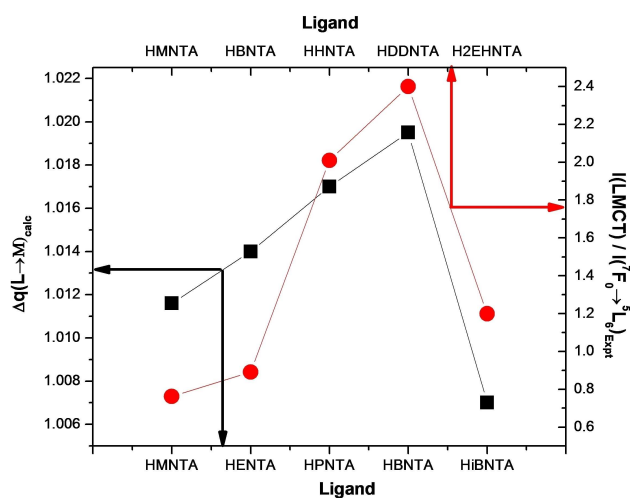


Figure 13. Effect of alkyl chain length and branching in NTA derivatives on LMCT-Experimental and DFT results

Associated content

Supporting Information available on solvent extraction, luminescence and DFT data.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Actinide · DFT · Luminescence · NTA · Solvent extraction

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