The Separation and Complexation Behavior of Trivalent Actinides and Lanthanides

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ABSTRACT

'f' block metal ions show very rich coordination chemistry with large coordination number. The actinides, moreover, show a range of oxidation states resulting in complex behavior in the solution phase. Radiotoxic nature of most of the actinides makes their experimental studies much more challenging and therefore computational chemistry can be a great help for more directed experimental trials. In this present article attempt will be made to cover our contribution to the computational studies of 'f' element complexes in relevance to the mutual separation of trivalent actinides and lanthanides.

Keywords: Actinide, Lanthanide, DFT, Extraction, Separation.

Introduction

Strong electron electron correlation, relativistic effects and spin orbit coupling in the 'f' element complexes, especially for the actinides, throw challenges to the computational chemists who want to deal with the complexes of these metal ions. With enormous development in the computational capability, significant amount of effort is being directed in understanding the complexation of actinides and lanthanides using computational studies. Their chemistry is mainly governed by their oxidation states. Lanthanides show simple chemistry due to their most stable 3+ oxidation state in general. Chemistry of the actinides is, however, much more complex due to the presence of variable oxidation states, especially for the early actinides upto plutonium due to the participation of their '*5f*' electrons in bonding.[1] Bonding of the actinides at higher oxidation states (penta and hexavalent) involving the 'f' orbitals are therefore quite unique in case of early actinides.[2] Heavier actinides, however, show 3+ as the most stable oxidation state similar to the lanthanides due to stabilization of the '*5f*' orbitals similar to the '*4f*' orbitals of the lanthanides. This similar chemistry of the heavier actinides and the lanthanides leads to difficulty in their separation which is quite relevant for the safe management of nuclear waste.[3] In this article, attempt is made to compile our research on the bonding and complexation of trivalent actinides and lanthanides in relevance to their mutual separation.

Computational Methodology

Geometries of all the complexes shown in this article were optimized using def-SV(P) basis sets. In the cases of americium and lanthanides, 60 and 28 electron effective core potential (ECP) along with the corresponding def-SV(P) basis sets for the valence electrons are used. All the geometry optimizations were carried out employing the GGA functional BP86 which is composed of the Becke 1988 exchange functional along with the Perdew 86 correlation functional. The single point energies and electronic structures of the ligands and their complexes were calculated using the hybrid functional B3LYP and the def-TZVP basis set.

Bonding in trivalent actinide and lanthanide complexes

Ligands for Co-extraction of actinides and lanthanides

As we progress along the actinide series, the higher valent oxidation states become less stable and after plutonium, the trivalent is the most stable oxidation state similar to the lanthanide ions. Significant effort of computational chemistry is directed to understand the comparative bonding and complexation of trivalent actinides and lanthanides in relevance to their mutual separation.[4] Since long back, phosphine oxide and diamide based ligands are proposed for the co-extraction of trivalent actinides.[5] Diglycolamide based extractants are reported to be most promising till date for the coextraction of trivalent actinides and lanthanides.[6] There are some literature on the complexation of trivalent actinides and lanthanides with diglycolamide (DGA) based ligands.

Wang *et al.* found that the tetra-octyl diglycolamide (TODGA) is selective for Am^{3+} over Eu^{3+},[7] the experimental observation, however, shows opposite trends. With proper choice of model and incorporation of dispersion correction using DFT-D3 technique, the experimental trends of the extraction of trivalent actinides and lanthanides could nicely be explained.[8]

We also carried out the complexation of Ln^{3+} ions with DGA derivatives with systematically varying the alkyl chain length and branching and the experimentally observed complexation bahaviour of the DGA derivatives was explained successfully employing DFT calculations.[9] Optimized structures of Nd^{3+} complex of TMDGA and the frontier molecular orbitals of the complex are shown in Fig.1 where significant contribution of the metal based '*f*' orbitals is noticed.
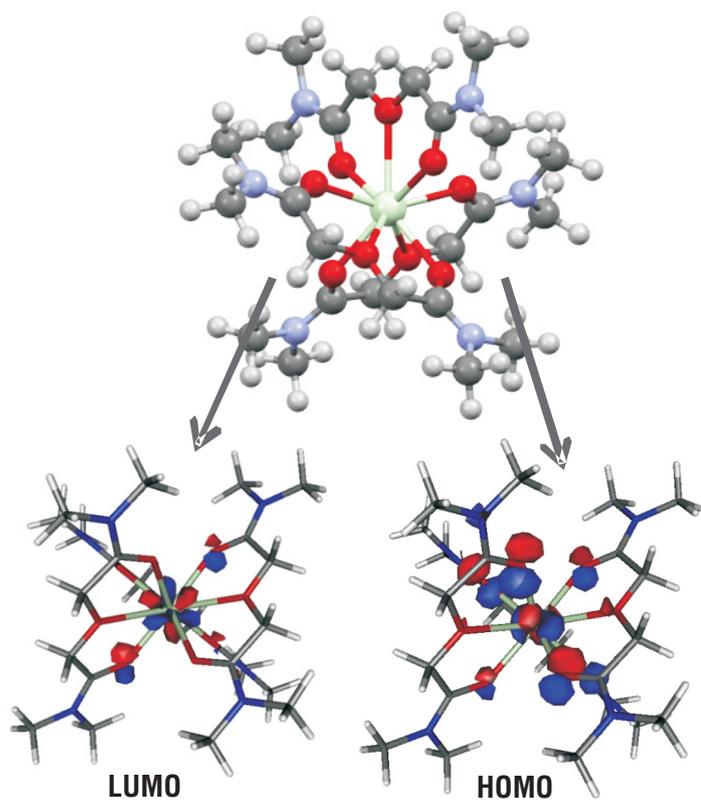
Fig.1: Optimized structure of Nd³⁺ complex of TMDGA and Frontier molecular orbitals of the complex (Nd: Light Green; O: Red; N: Light Purple; C: Grey; H: Light Grey).

## Complexes with ligands for separation of actinides and lanthanides

Similar chemistry of the trivalent actinides and lanthanides leads to their separation an extremely challenging task to the chemists and only some soft donor ligands show selectivity towards the trivalent actinides over the lanthanides. A sulphur donor ligand, dithiophosphinic acid (Cyanex 301, Fig. 2) showed very high selectivity towards Am³⁺ over Eu³⁺.[10] It was, therefore, be of interest to understand the difference in bonding in its Am³⁺ and Eu³⁺ complexes. Cao. *et al.* found that the presence of solvent is the major factor contributing to the selectivity of Cyanex-301.[11] We, however, observed experimentally the formation of different extractable species for Am³⁺ and various lanthanides (viz. La³⁺, Eu³⁺ and Lu³⁺) which could be explained on the basis of their relative stabilities of their complexes as compared to their corresponding trinitrato species calculated using DFT based technique. Further, the metal-ligand complexation energy was segregated into electrostatic, Pauli repulsion, and orbital interaction components. Higher covalence in the M-S bond in the dithiophosphinate complexes as compared to the M-O bond in the nitrate complexes was reflected in the higher orbital and lower electrostatic interactions for the complexes with increasing number of dithiophosphinate ligands. Higher affinity of the dithiophosphinate ligands for Am³⁺ over Eu³⁺ was corroborated with higher covalence in

the Am-S bond as compared to the Eu-S bond, which was reflected in shorter bond length in the case of the former and higher ligand to metal charge transfer in Am³⁺-dithiophosphinate complexes. The results were found to be consistent in gas phase density functional theory (DFT) calculations using different GGA functional.[12] Thus, computational studies were able to explain the experimentally observed trends of the dithiophosphinate complexation of the trivalent actinides and lanthanides.

Nitrilo-triacetamide (NTA) derivatives are mixed 'N,O' donor ligands reported to be selective for the trivalent actinides over the lanthanides from the liquid-liquid extraction studies.[13] We, therefore, investigated the complexation behavior of the NTA derivatives with the help of spectroscopic studies and DFT based calculations.[14] Two phase liquid-liquid extraction studies indicated that both the Am³⁺ and Eu³⁺ ions are extracted as the 1:2 complex and in this complex, the only possibility considered was ML_2^{3+} as the two NTA ligands can occupy eight coordination sites of the metal ions and the approach of other ligands is expected to be difficult due to the bulkiness of the two NTA ligands. Moreover, solution phase extended X-ray absorption fine structure spectroscopy (EXAFS) and time resolved fluorescence spectroscopy (TRFS) studies of the Eu³⁺ complex indicated that the central Eu³⁺ ion is eight-coordinated and devoid of any water molecules in the inner coordination sphere. DFT calculations were, therefore, carried out on the ML_2^{3+} type of complexes of both Am³⁺ and Eu³⁺. Selectivity of NTA derivative, as observed from the solvent extraction studies, is nicely reflected in the shorter 'Am–N' bond lengths (2.848 and 2.853 Å) as compared to the 'Eu–N' bond lengths (2.886 and 2.892 Å) in their respective complexes (Fig. 3). This is further supported by the higher Wiberg and Mayer's bond orders of the 'Am–N' bonds as compared to that of the 'Eu–N' bonds. A systematic study was, therefore, carried out on the metal-ligand bond lengths varying ionic sizes of the Ln³⁺ ions along with Am³⁺ and the results are presented in Fig. 4. Ionic radii of the Am³⁺ and Ln³⁺ ions, except Pm³⁺, were taken from the literature for the eight-coordinated metal ions.[15] Nice correlation of 'M–O' bond lengths with the ionic size of Ln³⁺ ions was observed, which
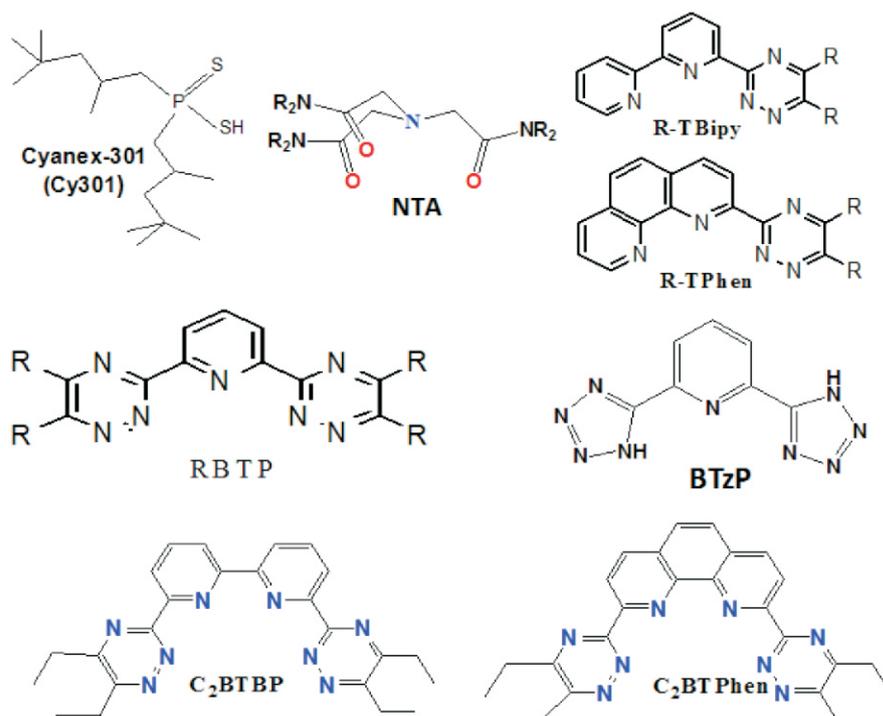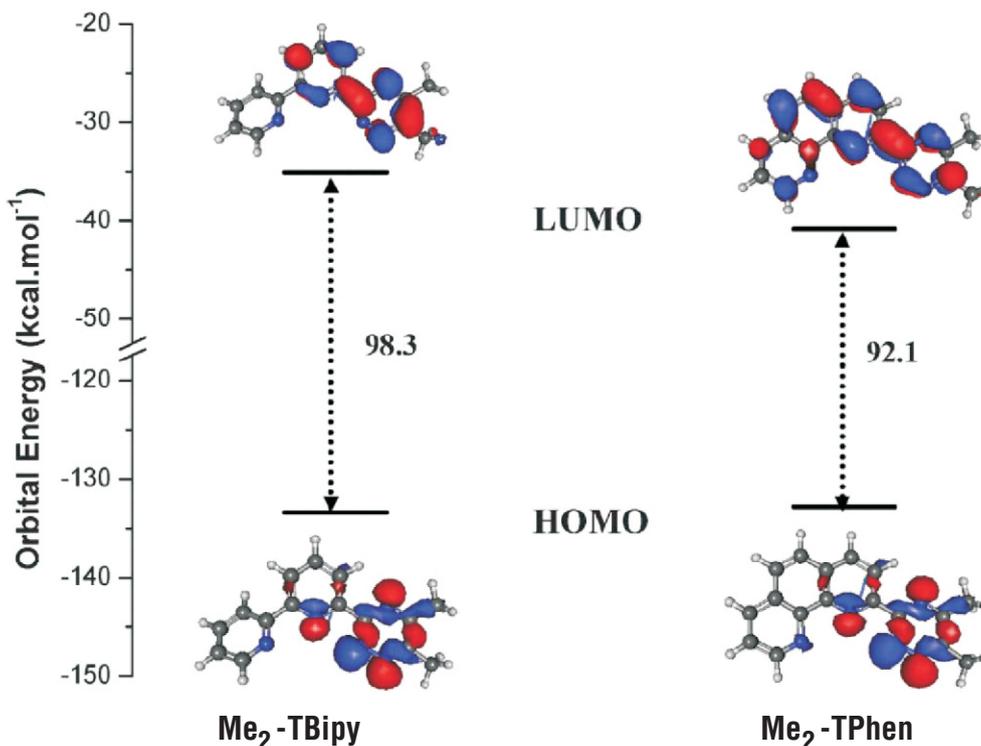

Fig.2: Different soft donor ligands considered for the comparative complexation of trivalent actinides and lanthanides.
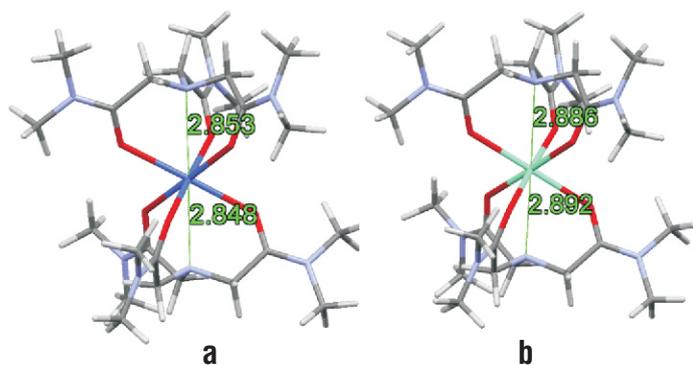
Fig.3: Optimized structures of Am^{3+} and Eu^{3+} with NTA (Am: Purple; Eu: Light Green; O: Red; N: Light Purple; C: Grey; H: Light Grey).
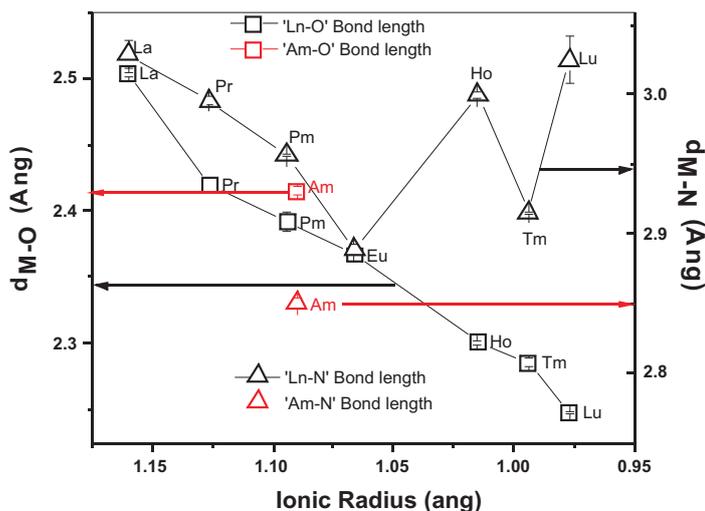
Fig.4: Variation of 'M-O' and 'M-N' bond length along the lanthanide series (Ln^{3+}) and their comparison with Am^{3+}.

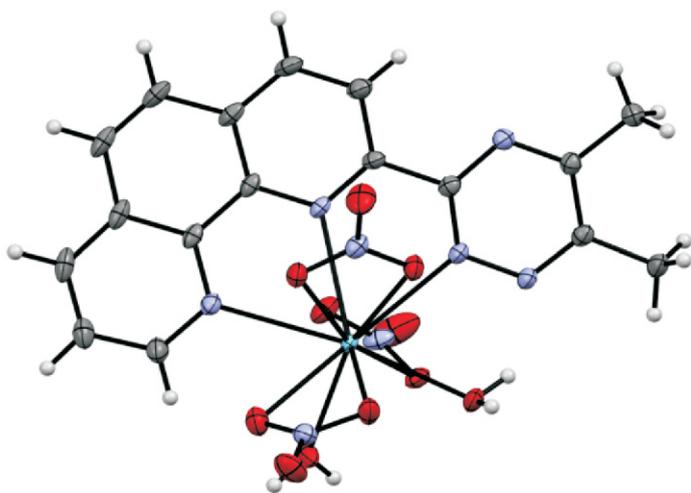suggests that the 'M–O' bonds are predominantly governed by purely ionic interactions in all the Ln^{3+} complexes. The 'Am–O' bond distance is somewhat higher than that expected from the observed trends of the Ln^{3+} complexes. However, when the 'M–N' bonds were considered, no such correlation was noticed and unlike the 'Am-O' bonds, 'Am–N' bond length was found to be significantly shorter than any of the 'Ln–N' bonds in the series, which is a clear indication of a higher degree of covalence in the 'Am–N' bond which made this ligand selective for Am^{3+} over the Ln^{3+} ions. DFT study, therefore, nicely corroborates with the experimental results. Besides the 'S' donor and mixed 'N,O' donor ligands, 'N'-donor heteropolycyclic ligands found to be promising for the separation of trivalent actinides and lanthanides.

Triazinyl bipyridine (TBipy) derivatives, a class of 'N' donor hetero polycyclic ligand, was reported to show some degree of selectivity for the trivalent actinides.[16] We designed a new ligand, Triazinyl phenanthroline (TPhen) derivative (Fig. 2), having more structural rigidity and evaluated for the separation of trivalent actinides and lanthanides. Improved extraction and separation of Am^{3+} over Eu^{3+} was experimentally observed using TPhen derivative as compared to TBipy derivative. Higher extraction of Am^{3+} with Me$_2$-TPhen was explained on the basis of its lower conformational energy requirement for complexation as compared to Me$_2$-TBipy. The higher selectivity of Me$_2$-TPhen for Am^{3+} over Eu^{3+} as compared to Me$_2$-TBipy, on the other hand, was attributed to the higher softness of Me$_2$-TPhen as compared to Me$_2$-TBipy as a result of the lower HOMO-LUMO gap (Fig. 5). Crystals of La^{3+}-Me$_2$-TPhen complex was prepared and its structure as determined from the single crystal XRD technique is shown in Fig. 6.[17-18]

Bis(1,2,4-triazinyl) pyridine (BTP) derivatives, where two triazinyl rings are present along with the central pyridine ring (Fig. 2), are found to be very promising for the separation of trivalent actinides and lanthanides.[19] We reported remarkable enhancement of selectivity of the methyl derivative of BTP (MeBTP) in room

Fig.5: A Walsh diagram showing the HOMO and LUMO and their energies (kcal.mol^{-1}) for Me$_2$(TBipy) and Me$_2$(TPhen).

Fig.6: Crystal structure of La^{3+} complex of Me$_2$-TPhen (La: Light Green; O: Red; N: Light Purple; C: Grey; H: Light Grey).

temperature ionic liquid medium as compared to that in the molecular solvent which was attributed to the formation of different complexes of Am^{3+} and Eu^{3+} in RTIL medium as shown in Fig. 7. Computational studies showed higher overlap between metal and ligand based orbitals for Am^{3+} complex extracted in the RTIL medium as compared to that in the molecular solvent (Figs. 7d and 7e) resulting in increased selectivity of MeBTP for Am^{3+} in RTIL medium.[20]

We observed that with increasing number of 'N' atoms in the lateral rings selectivity for trivalent actinides over lanthanides improved significantly. We, therefore, designed a new ligand, bis-tetrazolyl pyridine (BTzP, Fig. 2), having four 'N' atoms in the lateral tetrazole rings. Two phase liquid-liquid extraction studies using BTzP showed a separation factor value >50. Complexation behavior of BTzP was studied using both experimental and computational studies. Absorption spectroscopic studies of the Am^{3+} complex indicated the presence of two chemically non equivalent Am^{3+} ions
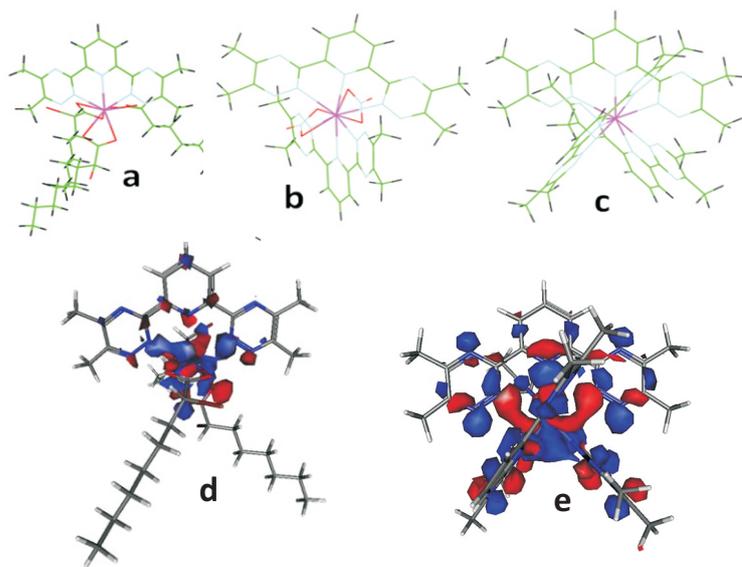
**Fig.7:** Optimized structures of (a) Am^{3+} and Eu^{3+} complexes of MeBTP observed in molecular diluents in presence of 2-Br-decanoic acid; (b) Eu^{3+} and (c) Am^{3+} complex of MeBTP in C4mim.NTf2 (Am/Eu: Magenta; O: Red; N; Light Blue; C: Green; H: Black); (d) HOMO of the Am^{3+} complex 'a' and (e) HOMO of the Am^{3+} complex 'c'.

in the complex, which was also supported from the time resolved fluorescence study of the Eu^{3+} complex of BTzP with two different Eu^{3+} ions having lifetime values of 479 and 1841 µs. In order to further understand this interesting complexation behavior, solid Nd^{3+} complex of BTzP was prepared and single crystal XRD study indicated formation of ion pair type of complex (Fig. 8a), where in the cationic part, Nd^{3+} ion is surrounded by one binegative BTzP and six water molecules and in the anionic part the Nd^{3+} ion is surrounded by two binegative BTzP units. DFT calculations revealed that in the cationic part, the distances between the metal ion and the coordinating 'N' atoms of the lateral tetrazole rings (M- Nt) are shorter in the case of Am^{3+} complex as compared to that in the Nd^{3+} complex in spite of comparable ionic radii of Am^{3+} and Nd^{3+} for a fixed coordination number. This indicates stronger metal- nitrogen interaction in the cationic part of the Am^{3+} complex, and this is also supported by higher Mayer's bond order in the Am- N$_t$ bonds as compared to the Nd- N$_t$ or Eu- N$_t$ bonds. Similar observation was also noticed in case of the bond between the metal ion and the coordinating 'N' atom of the central pyridine ring (M- Np) in the cationic part. In the anionic part, however, no such increase in the M- N bond strength in the Am^{3+} complex was noticed. The metal- nitrogen bond orders were found to be higher anonymously in the cationic part as compared to that in the anionic part. This could be due to the sharing of the metal-based orbitals with two doubly negative BTzP molecules in the anionic part, whereas in the cationic part the metal orbitals are shared with only one BTzP molecule other than the neutral water molecules. Frontier molecular orbitals (FMOs) were analysed to understand the bonding between the metal ion and the coordinating 'N' atoms of the BTzP units in their complexes. Orbitals that have contributions from both the metal and the ligand (BTzP) have influence in the metal- ligand bonding. The lowest unoccupied molecular orbitals (LUMO) of the complexes of both the metal ions (Am^{3+} and Eu^{3+}) have contributions from the metal ion and the ligand molecules (BTzP) in the cationic as well as anionic parts. In the LUMO of both the cationic and anionic parts of the BTzP complexes of Am^{3+} and Eu^{3+}, σ-bonding interaction is noticed between the metal f-orbitals and sp^2 hybridized orbitals of the tetrazolyl N atoms. This σ-bonding interaction is stronger in the Am^{3+} complex as compared to that in the Eu^{3+} complex as observed from the higher overlap between the metal and ligand orbitals in case of the former (Figs. 8a and 8b). The occupied molecular orbitals (MOs) are mainly dominated by the ligand based orbitals in the cationic part. In the Am^{3+} complex, π-interaction between the f-orbitals of Am^{3+} and p-orbitals of the tetrazolyl N atoms was noticed (singly occupied molecular orbital (SOMO-13), which further strengthened the metal- ligand interactions in the Am^{3+}-BTzP complex. In the cationic part of the Eu^{3+} complex, however, the occupied MOs that have the metal f-orbitals deeply burried (SOMO-30) do not show any bonding interactions between the metal and the ligand.[21]

Till now we discussed the bonding and complexation behavior of tridentate 'N' donor ligands. There are few tetradentate 'N' donor ligands which showed promising selectivity for the trivalent actinides over the lanthanides. Bis-triazinyl bipyridine (BTBP) and phenanthroline (BTPhen) derivatives are the most prominent in this class of ligands. We investigated the complexation of Am^{3+} and different Ln^{3+} ions with BTBP derivatives. Stronger complexation with Am^{3+} ion was noticed from the experimental studies which was supported by the higher bond strength/order in Am–N bonds as compared to the Eu–N bonds in their BTBP complexes from the DFT based calculations. The energetics of the complexation process in the solution phase also supports the observation of favourable Am^{3+}
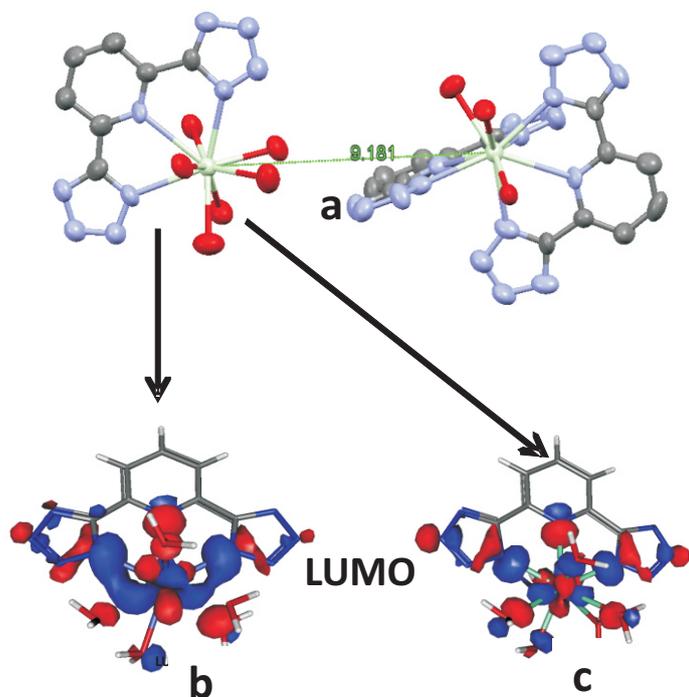
Fig.8: (a) Experimentally observed structure of Nd^{3+} complex of BTzP (Nd: Light Green; O: Red; N: Light Purple; C: Grey); Lowest unoccupied molecular orbital of the (b) Am^{3+} and © Eu^{3+} complexes of BTzP (cationic part).
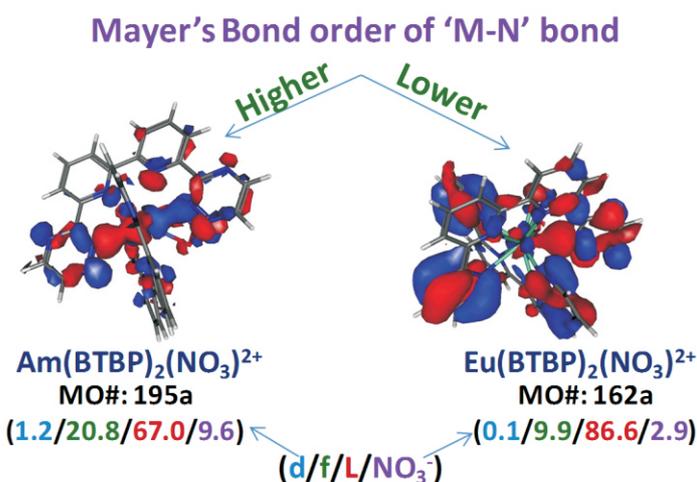

Fig.9: Frontier molecular orbitals (FMOs) of Am^{3+} complexes of BTBP and low lying molecular orbitals of Eu^{3+} complex of BTBP having significant metal ion 'f' orbital contribution and indicating the overlap between metal and ligand orbitals and percentage of Am^{3+} ('f' or 'd') / ligand / nitrate orbitals in those FMOs (Used cutoff: 0.013 e/Bohr^3).

complexation with the BTBP derivatives.[22] Contribution of metal based orbitals is observed by analyzing the frontier molecular orbitals of the Am^{3+} complex whereas that was observed for much deep seated molecular orbitals in case of Eu^{3+} complex. The contribution of both the metal 'd' and 'f' based orbitals are higher in the Am^{3+} complex as compared to that in the Eu^{3+} complex (Fig. 9) which resulted into higher bond order between the metal ion and the ligand molecule in the Am^{3+} complex leading to preference of this class of ligands towards the trivalent actinides over the lanthanides.[22]

Computational study in Am^{3+}/Cm^{3+} Separation

Separation of Am^{3+} and Cm^{3+} is even more challenging than the intergroup separation of trivalent actinides and lanthanides. We have systematically studied the separation of Am^{3+} and Cm^{3+} using hydrophilic BTP, BTBP and BTPhen derivatives using two phase liquid-liquid extraction techniques and the comparative extraction bahaviour of Am^{3+} *vis-à-vis* Cm^{3+} was explained with the help of DFT studies. In order to compare the complexation of Am^{3+} and Cm^{3+}, the complexation energies (ΔE_{COMP}) for the following equilibrium are calculated and listed in Table 1.

$$M(H_2O)_9^{3+} + L \rightleftharpoons ML(H_2O)_x + (9-x)H_2O \quad (1)$$
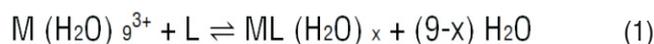
Where M is Am or Cm and L is BTP, BTBP or BTPhen derivatives. As expected the complexation is more favourable in case of the tetradenate ligand BTBP as compared to the tridenate BTP derivative. In case of BTPhen, the complexation is still more favourable as compared to BTBP due to preorganized structure of BTPhen. However, when the complexation of Am^{3+} and Cm^{3+} is compared, all the ligands show preference for Cm^{3+} over Am^{3+} due to the smaller ionic radius of Cm^{3+}. This suggests that the complexation of Am^{3+} and Cm^{3+} with these ligands is mainly governed by the electrostatic interactions.

Experimental trends of the Am^{3+} and Cm^{3+} extraction by TODGA in presence of the hydrophilic BTP, BTBP and BTPhen derivatives in the aqueous phase could be explained after consideration of the complexation of TODGA. For the computational simplicity the methyl derivative (TMDGA) was considered in place of the octyl derivative (TODGA). Considering the complexation energy (ΔE_{TMDGA}) for the following equilibrium, TODGA is selective towards Cm^{3+} over Am^{3+} by 32.0 kJ.mol^{-1} ($\Delta\Delta E_{TMDGA}$). Therefore, even if one considers the competion by TMDGA, BTP remains selective towards Cm^{3+} over Am^{3+} as reflected in the difference between the ($\Delta\Delta E_{Cm-Am}$) and ($\Delta\Delta E_{TMDGA}$) values and, therefore, Am^{3+} is selectively extracted in the organic phase by TODGA. In the case of BTPhen, on the other hand, Cm^{3+} is extracted selectively by TODGA as the selectivity of TMDGA for Cm^{3+} over Am^{3+} is observed to be higher

Table 1 Complexation energies (ΔE_{COMP}) of Am^{3+} / Cm^{3+} complexes (kJ.mol^{-1}).

Ligand	M^{3+}	ΔE_{comp}	$\Delta\Delta E_{Cm-Am}$	$\Delta\Delta E_{Cm-Am} - \Delta\Delta E_{TMDGA}$
BTP	Am^{3+}	-187.4	-52.0	-20.0
	Cm^{3+}	-239.4		
BTBP	Am^{3+}	-256.2	-36.3	-4.3
	Cm^{3+}	-292.5		
BTPhen	Am^{3+}	-275.6	-24.7	7.3
	Cm^{3+}	-300.2		

than that of BTPhen ($\Delta\Delta E_{Cm-Am}$ = 24.7 kJ.mol^{-1}). BTBP, however, shows comparable selectivity as TMDGA from Cm^{3+} over Am^{3+} and therefore, no selectivity is noticed in the solvent extraction study employing the BTBP derivative.[23]

Conclusions

With the advent of advanced codes for the computational studies, understanding the chemistry of the 'f' block elements is improved remarkably. Experimental observations on the complexation of these elements in relevance to their mutual separation could be explained successfully with the help of DFT based calculations. However, more challenges in the computational chemistry still lies in the prior prediction of the complexation and extraction behavior of the ligands thereby reducing the number of experimental trials.

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