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Evaluation of two aza-crown ether-based multiple diglycolamide-containing ligands for complexation with the tetravalent actinide ions Np^{4+} and Pu^{4+}: extraction and DFT studies†

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Two multiple diglycolamide (DGA)-containing extractants where the DGA arms are tethered to the nitrogen atoms of two aza-crown ether scaffolds, a 9-membered aza-crown ether containing three 'N' atoms (L_I) and a 12-membered aza-crown ether containing four 'N' atoms (L_{II}), were evaluated for the extraction of the tetravalent actinide ions Np^{4+} and Pu^{4+}. The tripodal ligand with three DGA arms (L_I) was relatively inferior in its metal ion extraction properties as compared to the tetrapodal ligand with four DGA arms (L_{II}) and Pu^{4+} ion was better extracted than Np^{4+} ion with both the ligands. A solvation extraction mechanism, where species of the type $ML(NO_3)_4$ are extracted, was found to be operative for both the ligands involving both the tetravalent actinide ions. While the extraction of the metal ions increased with the feed nitric acid concentration up to 4 M, a sharp decline in the extraction was seen after that. Quantitative extraction (>99%) of the actinide ions was observed with L_{II} from 4 M HNO_3, suggesting the possible application of the ligands for actinide partitioning of high-level waste. The structure and the composition of the complexes were optimized by DFT computations.

Introduction

Spent fuel reprocessing using TBP (tri-*n*-butyl phosphate) selectively separates U and Pu from the dissolver solution which contains actinides *viz.* U, Np, Pu, Am, Cm, *etc*, a host of fission product nuclides and also structural materials *viz.* Zr, Fe, Cr, Ni, *etc.*, in 3–4 M nitric acid.[1] In view of the difficulties faced in the separation of trivalent minor actinides which contributes to the major part of the alpha dose emanating from the raffinate stream after the spent fuel reprocessing, several specific extractants such as CMPO (carbamoylmethylphosphine oxide), TRPO (trialkylphosphine oxide), DIDPA (diisodecyl phosphoric acid) were developed by American, Chinese and Japanese researchers, respectively, for this purpose.[2–4] However, all these extractants are phosphorus based which result in large volumes of secondary waste and hence, needed to be replaced with suitable 'green' alternatives.[5] Further research on eco-friendly extractants led to the discovery of the tetraalkyl malonamides

by research groups at the European Union by the end of last century.[6] Subsequently, diglycolamide (DGA) extractants were reported to be highly efficient in view of the significantly lower extractant inventory and high extraction efficiency.[7] Typically, a 0.1 M solution of TODGA (*N,N,N',N'*-tetra-*n*-octyl diglycolamide) in *n*-dodecane gives a D_{Am} (distribution ratio) value of 30 with 1 M HNO_3 as the aqueous feed and increases sharply with the feed acid concentration.[8] Under identical conditions, the D_{Eu} value was reported to be *ca.* nine times larger suggesting the possibility of the separation of the lanthanides, which act as neutron poison and also create problems during vitrification of the radioactive wastes, from the trivalent actinides[9,10] under suitable conditions. This has been quite promising as compared to other extractants reported before and hence, has been employed for counter-current extraction runs.[11–13] Though most reported studies involving TODGA were found to deal with trivalent actinides *viz.* Am^{3+} and Cm^{3+}, there is scant data on the extraction of Np, a very important minor actinide.[14] The separation of Np, major constituent being ^{237}Np ($t_{1/2}$: 2.1 × 10^6 years), from the acidic radioactive wastes including the high level waste (a concentrate of the raffinate emanating from the spent fuel reprocessing) can ultimately lead to the production of ^{238}Pu for use as a power source.

The selectivity observed in the case of TODGA is quite different from that seen with other extractants, *i.e.*, trivalent actinides are better extracted than the tetravalent actinide ions,

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while the hexavalent actinides are extracted to a much lower extent. Different research groups have made attempts to understand the unusual extraction behaviour. A size selective extraction of metal ions of 100 pm ionic radii has been proposed by Zhu *et al.*,[15] which was supported subsequently by a theory of aggregate formation as confirmed from SANS (small angle neutron scattering) as well as dynamic light scattering studies.[16] These studies indicated that 3–4 TODGA molecules form a reverse micellar aggregate, which facilitates the extraction of the metal ions.[17] Though this explains the size selective extraction of the metal ions, the formation of aggregates is limited to non-polar diluents such as *n*-dodecane. It was thought appropriate to synthesize multiple DGA ligands where several DGA groups are appended to a scaffold to enhance the efficiency of extraction. These ligands were expected to give the same or better extraction efficiency without any diluent property limitation. In this connection, multiple DGA extractants such as DGA-functionalized calix[4]arenes[18] and pillar[5]arenes[19] containing four and five DGA arms, respectively, were synthesized and evaluated for their extraction efficiency. Other multiple DGA ligands, containing three DGA arms, have also been studied over the years, which include those with a central carbon or nitrogen atom or a set of benzene-centered tripodal DGA ligands.[20–22]

Recently, we reported the first time study on the extraction of actinides using a tripodal DGA ligand where the DGA arms are tethered to a triazamacrocyclic scaffold (**L_I**; Fig. 1).[23] The promising results prompted us to explore the possibility of synthesizing a tetrapodal DGA ligand with a 'cyclen' (1,4,7,10-tetrazacyclododecane) scaffold (**L_II**; Fig. 1). The ligand was synthesized and studied for the separation of the trivalent *f*-cations *viz.* Am^{3+} and Eu^{3+}.[24] The major advantage of such multiple DGA ligands with a macrocyclic scaffold was to add some degree of flexibility to the otherwise pre-organized structures, which could result in a better binding. Results of our recent studies[24] using the tetrapodal DGA ligand **L_II** with trivalent actinide ions were indeed quite spectacular, where a nearly 20 times lower ligand concentration was used to achieve a reasonably high extraction efficiency. In view of the lack of detailed research on the extraction of tetravalent actinides with these multiple DGA extractants, the present attempt was made for a detailed investigation.

The present work deals with the extraction of Np^{4+} and Pu^{4+} from nitric acid feed solutions using millimolar concentrations of **L_I** and **L_II** in a diluent mixture containing 95% *n*-dodecane + 5% isodecanol. The diluent mixture was chosen in view of the poor solubility of such multiple DGA ligands as reported earlier[25] and to make a proper comparison with other analogous extractants. Apart from the solvent extraction studies, DFT computational studies were carried out to get structural information.

Experimental

Materials

The multiple DGA-containing ligand **L_I** was prepared as reported.[23] **L_II** was prepared following an analogous method, details of which are given in the ESI.† The purity of the ligands was checked by elemental analysis, NMR and HR-MS techniques. The diluents, *n*-dodecane and isodecanol (>99% purity), were procured from Lancaster, UK and SRL, Mumbai, respectively, and were used as obtained. HTTA (2-thenoyltrifluoroacetone) was obtained from Sigma-Aldrich (USA) and was used after recrystallization. Suprapur nitric acid (Merck, Germany) was used for the preparation of dilute nitric acid solutions applied in this study, which were standardized using volumetric methods using AR grade NaOH (BDH) with phenolphthalein (Fluka, Switzerland) as the indicator.

Radiotracers. Pu (mainly ^{239}Pu) was used from the laboratory stock after fresh purification from ^{241}Am using a HTTA extraction method reported in the literature.[26] ^{239}Np was prepared by the neutron activation of natural uranium in the Dhruva reactor at BARC, Mumbai, at a neutron flux of 5.0×10^{13} n per cm^2 per s for 5 days. The radiotracer (^{239}Np) was subsequently separated from the bulk of uranium and the fission products as per a reported method which used HTTA extraction.[27]

Methods

Oxidation state adjustment of actinides. The oxidation state of Pu was adjusted to the +4 state by first adding a few drops of 5.0×10^{-3} M NaNO$_2$ solution to the Pu tracer solution in 1 M HNO$_3$ followed by extraction using 0.5 M HTTA in xylene. The
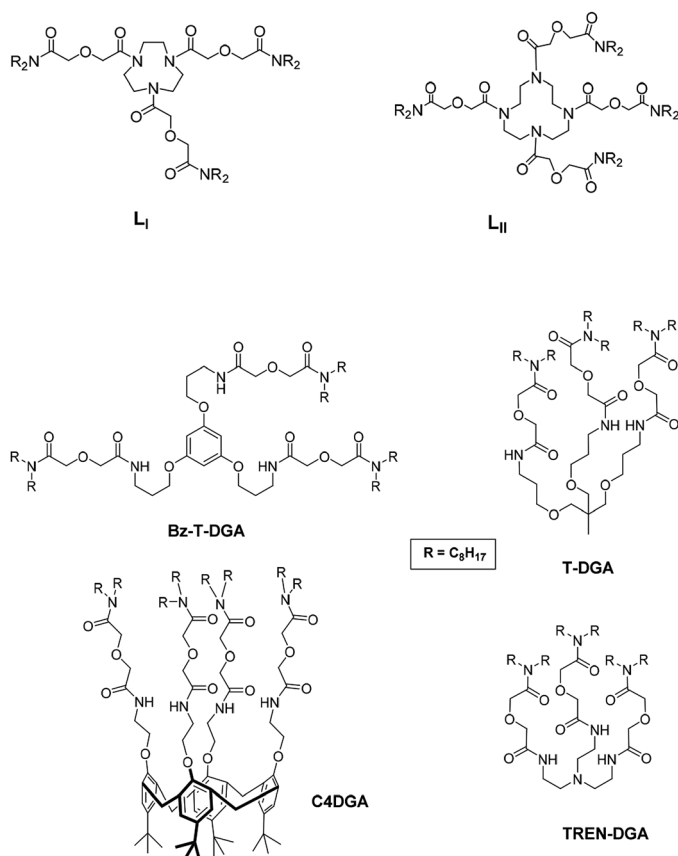

Fig. 1 Structural formulae of the ligands used in the present study (L_I and L_II) and other relevant ligands.

organic phase contained the converted Pu^{4+}, which was subsequently stripped using 8 M HNO_3. Np^{4+} conversion was done as mentioned above and the aqueous stock solution was found to be stable for over one month. The stability of the oxidation state for both Pu and Np was tested by a HTTA concentration variation experiment (distribution ratio (D) was measured at varying HTTA concentrations) where the linear log D vs. log[HTTA] plot yielded a positive slope of ca. 4.

Solvent extraction. The solvent extraction experiments were carried out by equilibrating equal volumes (usually 1 mL) of the organic phase containing 1.0×10^{-3} M of the multiple DGA-containing ligands L_I and L_{II} (or as specified) and the aqueous phase containing the required radiotracer in the acidity of interest. The equilibrations were done in leak tight Pyrex glass tubes (10 mL capacity), in a thermostated water bath at 25 ± 0.1 °C. The time of equilibration was maintained at about 1 h after confirming the extraction kinetics was over much before that (vide infra). Subsequently, the tubes were rested, centrifuged and 100 μL aliquots were taken out from both phases for subsequent radiometric assay. While the radiometric assay of ^{239}Np was done using a well type NaI(Tl) scintillation counter (Para Electronics) coupled with a multi-channel analyzer (ECIL, India), Pu was assayed using a liquid scintillation counting system (Hidex, Finland) where an Ultima Gold (PerkinElmer, USA) scintillation cocktail was used. The distribution ratio of the 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 distribution experiment was carried out in triplicate and the accepted data were within the relative standard deviation of 5%.

DFT methodology. We considered the corresponding methyl derivatives of the DGA-containing ligands L_I and L_{II}, respectively, to avoid difficulties in convergence due to the C–C single bond rotation of the long hydrocarbon chains. All the DFT based studies were performed using the TURBOMOLE 7.2 program package.[28–30] The geometries of L_I and its Am^{3+} and Eu^{3+} complexes were optimized by using Becke's exchange functional[31] in conjunction with Perdew's correlation functional[32] (BP86) with generalized gradient approximation (GGA). The geometries obtained by energy minimization were used for the calculation of the vibrational frequencies. 60 Electron core pseudo-potentials (ECPs) along with the corresponding def-SV(P) basis set as implemented in the TURBOMOLE suit of program were selected for the Am^{3+} ion, whereas 28 electron core potentials (ECPs) along with the corresponding def-SV(P) basis set were chosen for Eu^{3+}. All the other lighter atoms were treated at the all electron (AE) level. Natural population analysis (NPA)[33] has improved numerical stability as compared to the conventional "Mulliken Population Analysis (MPA)". The electron distribution in compounds of high ionic character, such as metal complexes, is also described in a much superior way by the NPA. NPA analysis was, therefore, performed in the present work to calculate the natural charges on different atoms in the Am^{3+} and Eu^{3+} complexes. Natural population analysis (NPA)[33] was performed on the complexes of Am^{3+} and Eu^{3+} using the hybrid B3LYP density functional[31,34,35] employing the triple zeta valence plus polarization (TZVP) basis set[36,37] using

equilibrated structures obtained at the BP86/SVP level of theory as implemented in the TURBOMOLE suit of program. In case of Am^{3+} and Eu^{3+}, the high spin septet was found to be the ground state configuration. In the present chemical system, the close matching of the $\langle S^2 \rangle$ values with the $S(S + 1)$ ideal values indicated negligible spin contamination. In order to have a quantitative idea about the comparative 'M–O' bond strength for the Np^{4+} and Pu^{4+} complexes the molecular orbitals were analyzed to calculate the two-center Wiberg's bond order using the AOMix program.[38,39]

Results & discussion

## Solvent extraction studies

Extractions of Np^{4+} and Pu^{4+} were carried out using the valency adjusted stock solutions as mentioned above. The extraction studies were carried out with a holding oxidant (ammonium metavanadate[27]) for Pu^{4+} and a holding reductant (hydroxylamine hydrochloride and ferrous sulphamate[40]) for Np^{4+}. In the absence of any extractant in the diluent mixture, the extraction of the metal ions was negligible ($D < 0.001$). On the other hand, the presence of 1×10^{-3} M ligands resulted in very high extraction of the metal ions (Table 1). Table 1 also includes the reported D values with other analogous extractants with Pu^{4+} and Am^{3+} at 3 M HNO_3 as Np^{4+} ion extraction data is not available. The relative extraction of M^{4+} and M^{3+} ions does not show any clear trend in the previously reported multiple DGA-containing extractants: while Am^{3+} ion extraction is more than that of Pu^{4+} ion for **TREN-DGA** and **Bz-T-DGA**, an opposite trend was reported for **T-DGA** and **C4DGA**. On the other hand, the extraction of the metal ions was nearly comparable (within experimental error limits) when L_I and L_{II} were used (Table 1). The extraction of Np^{4+} was found to be significantly inferior as compared to that of Pu^{4+}, which may be attributed to the smaller ionic size and hence, higher complexation of the latter. This suggests that the extraction of Np^{4+} ensures that of Pu^{4+} as well. Knowing very well about the poor extraction of UO_2^{2+} ion with multiple DGA-containing ligands,[18,21–23] decontamination of the actinides can be easily achieved from U. The following sections include results of the other extraction studies.

Extraction kinetics. Extraction kinetics is one of the important parameters needed to be assured in solvent extraction to obtain equilibrium D values, particularly with bulky ligands where the mass transfer of the bulky metal/ligand complex is slow. This could be due to slow binding of the multiple ligating groups with the metal ion. On the other hand, if the metal ion is coordinated to only a few donor atoms present in the ligand, the extraction can be fast. Scheme 1 gives a pictorial representation of the complexation of the metal ion with the multiple DGA-containing ligand (L_I) for (a) one (b) two and (c) three DGA arm binding. A tetravalent metal ion, as in the present case, is always associated with four nitrate counter anions to result in a charge neutralized complex. However, association with a ligand is mandatory for a better partitioning into the organic phase. As the ligand is assumed to be pre-organized, we started with interaction of the metal ion with one of the DGA groups. Subsequently, another DGA may interact due to its proximity to

Table 1 Actinide ion extraction data with multiple DGA ligands from aqueous phase containing 3 M HNO₃ using 1×10^{-3} M ligand solution in 95% n-dodecane + 5% isodecanol

Ligand	$D_{Np(IV)}$	$D_{Pu(IV)}$	$D_{Am(III)}$	Reference
T-DGA	—	19.0 ± 1.1^a	11.1 ± 0.06^a	21
TREN-DGA	—	0.25 ± 0.01^a	0.36 ± 0.02^a	21
Bz-T-DGA	—	103 ± 10.6	235 ± 19.4	22
C4DGA	—	67.9 ± 1.40^b	26.5 ± 1.40^b	18
L$_I$	42.7 ± 4.1	51.4 ± 3.7	71.1 ± 6.1^c	This work
L$_{II}$	163 ± 11	183 ± 8.5 $(12.4 \pm 0.52)^d$	4.83 ± 0.26^d	This work

^{a} Diluent: 90% n-dodecane + 10% isodecanol. ^{b} 3×10^{-3} M ligand solution in n-dodecane. ^{c} Data taken from ref. 23. ^{d} Between brackets: 5×10^{-5} M ligand solution in 95% n-dodecane + 5% isodecanol.
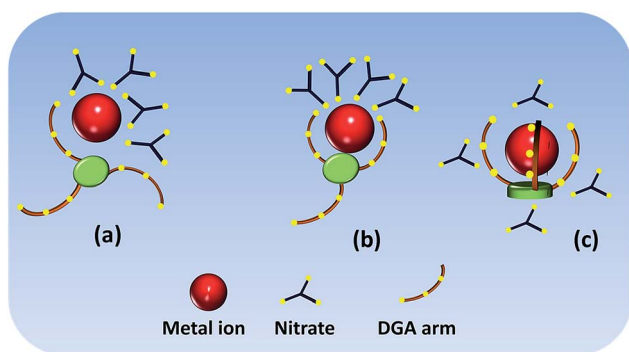

Scheme 1 Representative binding of the M⁴⁺ ion with multiple DGA-containing ligands and nitrate ions in case of L$_I$: (a) one DGA arm binding, (b) two DGA arm binding; (c) all three DGA arm binding.

the metal ion. In view of the coordination of four nitrate ions to the metal ion in a 'solvation' type extraction mechanism (*vide infra*), the number of coordination sites available for binding to the DGA groups is limited (considered in the range of 9 to 10) and hence, not more than two DGA arms should be binding to the metal ion at one time if one considers inner-sphere nitrate ion binding. If one considers three DGA arm binding, all four nitrate ions should be present in the outer sphere (Scheme 1(c)). For the sake of simplicity, we discount outer-sphere coordination in the present study and hence consider binding by either one or two DGA arms. It may be considered that binding to two DGA arms can result in sluggishness due to more steric crowding, while binding to a single DGA arm may result in relatively faster extraction. Similar model can be presented for **L$_{II}$** which has four DGA arms. However, binding to all four DGA arms does not appear logical if one needs to restrict the coordination number in the range of 9.

In the present case, the extraction equilibrium could be reached within 5 minutes of equilibration for both the ligands (Fig. 2). This suggests that the binding of the metal ions to the ligands may be quite simple in the sense that only one DGA arm might be binding out of the three available arms of **L$_I$** and four available arms of **L$_{II}$**. However, for all the subsequent experiments, 30 minutes of equilibration time were kept for the sake of convenience.

Effect of HNO₃ concentration. The equilibrium reaction for the extraction of tetravalent actinides from nitric acid medium with the above two neutral ligands **L$_I$** and **L$_{II}$** can be written as:

$$M_{(aq)}^{4+} + 4NO_{3(aq)}^{-} + xL_{(org)} \overset{K_{ex}}{\rightleftharpoons} \left[M(NO_3)_4 xL \right]_{(org)} \quad (1)$$
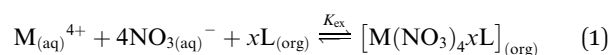
where M⁴⁺ represents either Np⁴⁺ or Pu⁴⁺, and x represents the number of ligand (L is either **L$_I$** or **L$_{II}$**) molecules associated in the extracted complex. The subscripts (aq) and (org) represent the species present in the aqueous and the organic phases, respectively. The two-phase extraction equilibrium constant (K_{ex}) for the above reaction can be written as:

$$K_{ex} = \frac{\left[M(NO_3)_4 xL \right]_{(org)}}{\left[M^{4+} \right]_{(aq)} \left[NO_3^- \right]_{(aq)}^4 \left[L \right]_{(org)}^x} \quad (2)$$

Since the distribution ratio (D) is experimentally obtained as the ratio of the total metal ion concentration in the organic phase to that in the aqueous phase, the above equation can be simplified to:
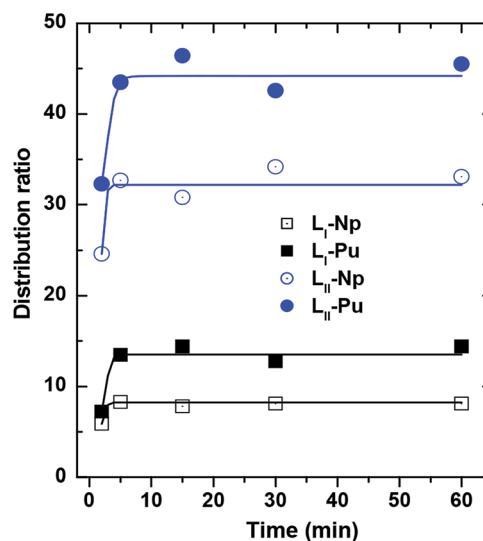

Fig. 2 Distribution ratio of actinides by DGA ligands L$_I$ and L$_{II}$ showing the extraction kinetics for reaching the equilibrium condition. Organic phase: 1.0 mmol L⁻¹ ligands in 95% n-dodecane + 5% isodecanol; aqueous phase: 1 M HNO₃.

$$D = K_{ex}[NO_3^-]_{(aq)}{}^4[L]_{(org)}{}^x \qquad (3)$$

As per the above equation, the distribution ratio must increase with the nitric acid concentration due to increased nitrate ion concentration. This is also reflected in Fig. 3, for both the ligands, up to 4 M HNO₃. However, beyond 4 M HNO₃, a decrease in the distribution ratio indicates that the following equilibrium reaction, which facilitates the adduct formation of the ligand with one or more molecules of nitric acid, is also operational parallell to eqn (1):

$$L_{(org)} + yHNO_{3(aq)} \overset{K_H}{\rightleftharpoons} [LyHNO_3]_{(org)} \qquad (4)$$
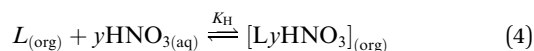
where K_H is the equilibrium constant referred to as acid uptake constant for the ligand or basicity of the ligand. From Fig. 3, it is very obvious that at higher nitric acid concentration, eqn (4) is dominating and that most of the ligand molecules are complexed with nitric acid, and therefore, result in a decrease of the distribution ratio of the metal ions. Such features are common for neutral ligands where a 'solvation' type of extraction mechanism is operating. While studying the extraction profiles of trivalent actinide/lanthanide ions with **TREN-DGA** or **Bz-T-DGA** a monotonous increase in the D values was seen up to 6 M HNO₃.[21,22] On the other hand, extraction with **T-DGA**[20] showed a profile similar to the one shown here.

Nature of the extracted complex. The stoichiometry of the extracted complex in solvent extraction is generally obtained by 'slope analysis' as detailed below. Eqn (3) can be rearranged after taking logarithms as follows:

$$\log D = \log K_{ex} + 4 \log [NO_3]_{(aq)}{}^- + x \log[L]_{(org)} \qquad (5)$$

Dependence of the extraction of Np⁴⁺ and Pu⁴⁺ was studied as a function of the concentration of the extractant (**L_I** or **L_II**) at a fixed nitrate ion concentration and *vice versa*. The slopes of the

straight-line log D *vs.* log ligand concentration plots (Fig. 4) are used to determine the number of ligand molecules present in the extracted species. As shown in Fig. 4, linear plots of slope values of 1 (approx.) were obtained for the tetravalent actinides with both the ligands. Considering the fact that **L_I** and **L_II** have 9 and 12 coordinating atoms, respectively, and four nitrate ions are required to coordinate with the metal ions (for charge neutralization purpose), the possibility of participation of more than one extractant molecule in the extracted species appears to be improbable. As per eqn (4), four nitrate ions are required to be present in the complex to maintain the charge neutrality on the metal ion. The log D *vs.* log[NO₃⁻] plots (the experiments were carried out using varying concentrations of NaNO₃ along with a fixed amount of HNO₃, required to prevent hydrolysis of the metal ions) yielded slope values of *ca.* 3, which after corrections due to nitrate ion complexation in a manner similar to that reported by Horwitz *et al.*[41] resulted in slope values close to 4 (Fig. 5). The slope values of the log D *vs.* log[NO₃⁻] straight-line plots from the nitrate ion concentration variation experiments are listed in Table S1.† The slope analysis suggested that the extracted species conform to ML(NO₃)₄, where M = Np and Pu, while L = **L_I** and **L_II**. The extraction constants were obtained from the intercept values and are listed in Table 2. The extraction constant value for the extraction of Pu⁴⁺ with TODGA (using *n*-dodecane as the diluent) is also included in the table for comparison purpose. The values obtained with the present ligands are higher than that reported for TODGA. TODGA operates as a reverse micelle-based extraction system[16,17] where the metal ion sits inside the aggregate based on its size. Pu⁴⁺, its ionic size being very close to 100 pm,[42] gets extracted favourably by TODGA.[15] However, the ligands used in the present study apparently form a stronger complex with the metal ion and in view of the pre-organized structure favour the extraction in a more effective way. The higher extraction constant with **L_II** can
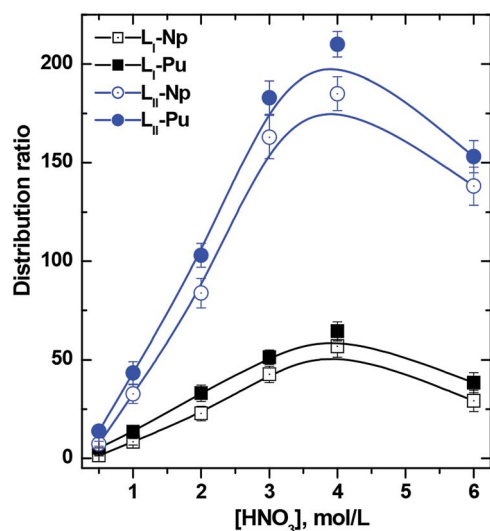

Fig. 3 Effect of nitric acid concentration on the distribution ratio of actinides with DGA ligands **L_I** and **L_II**. Organic phase: 1 mmol L⁻¹ ligands in 95% *n*-dodecane + 5% isodecanol.

Fig. 4 Effect of ligand concentration on the distribution ratio of actinides with DGA ligands **L_I** and **L_II**. Aqueous phase: 1 M HNO₃; diluent: 95% *n*-dodecane + 5% isodecanol.

Fig. 5 Effect of nitrate concentration on the distribution ratio of actinides with DGA ligands L_I and L_{II}. Organic phase: 0.2 mmol L^{-1} ligands in 95% n-dodecane + 5% isodecanol; aqueous phase: 1 M H^+ + varying nitrate ions.
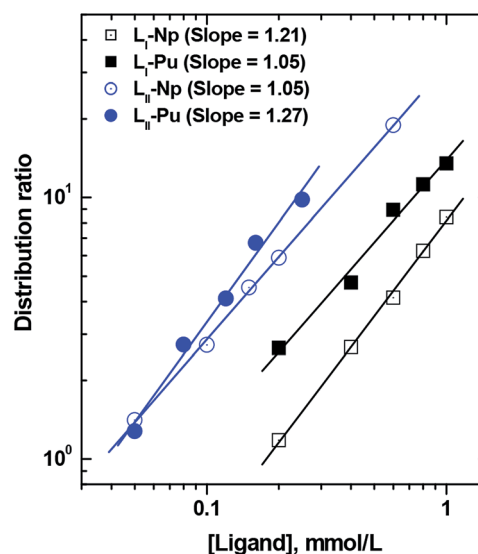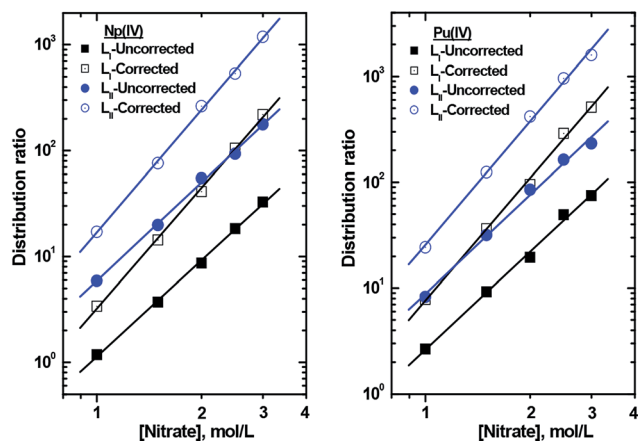
Table 2 Two-phase extraction constant values for the extraction of Np^{4+} and Pu^{4+} ions using ligands L_I and L_{II} and TODGA

Metal ion	Log K_{ex} values		
	L_I	L_{II}	TODGA
Np^{4+}	3.98 ± 0.02	4.58 ± 0.01	—
Pu^{4+}	4.21 ± 0.03	4.86 ± 0.02	4.0 ± 0.4^a

^{a} Data taken from ref. 6.

be attributed to a higher lypophilicity of the complex due to the presence of eight n-octyl groups vis-à-vis six n-octyl groups present in L_I.

However, the position of the nitrates in the complex, outer sphere or inner sphere, will be decided by how many coordination sites of the ligands are directly bonded to the metal ions and the vacant coordination positions on the metal ions. Considering nine ligating sites through 'O' atoms in L_I (three arms) and 12 in L_{II} (four arms), and also the possibility of coordination by the four nitrate ions (either by mono- or bidentate mode), it is logical that only very few DGA arms are coordinating to the metal ion. For an in-depth understanding of the bonding in the metal/ligand complex, DFT calculations were done as described below.

DFT calculations

For both the metal ions, viz. Pu and Np, a ML type of complex was found to be the most stable for both the ligands (L_I and L_{II}). The energy minimized structures of the complexes of Np^{4+} and Pu^{4+} with both ligands are presented in Fig. 6. In case of the complexes with L_I, the metal ions were found to be nine-coordinated, where one DGA arm of the ligand coordinated in tridentate fashion. It should be noted that, out of three DGA arms, only one arm is coordinating via two >C=O groups and one ethereal group. Out of four nitrate ions present in the
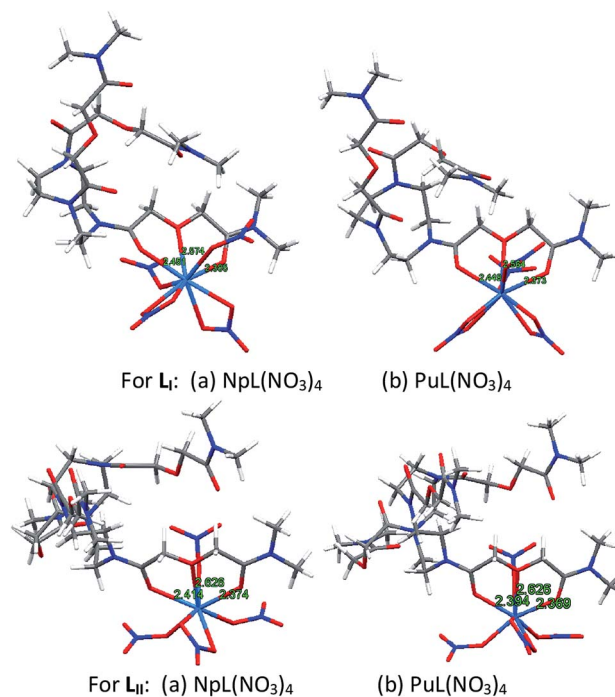

For L_I: (a) NpL(NO$_3$)$_4$ (b) PuL(NO$_3$)$_4$

For L_{II}: (a) NpL(NO$_3$)$_4$ (b) PuL(NO$_3$)$_4$

Fig. 6 DFT optimized structures of the Np^{4+} and Pu^{4+} complexes with L_I and L_{II} (with methyl instead of octyl chains).

complex, two were found to be bidentate and the other two were monodentate.

In case of L_{II}, on the other hand, the metal ions were eight-coordinated, where one DGA arm of the ligand coordinated in tridentate fashion, and out of four nitrate ions, three coordinated as monodentate and one as bidentate mode. Similar to L_I, out of four DGA arms, only one arm is coordinating via two >C=O groups and one ethereal group. In case of both the ligands, in spite of having multiple DGA arms, only one arm is coordinating to the metal ions which could be due to the fact that bringing multiple DGA arms to coordinate a metal ion is energy intensive. Significant increase in the metal ion extraction employing these ligands as compared to ligands having only one DGA arm is probably due to the increase in lipophilicity of the metal ion complexes of these multiple DGA ligands due to the presence of six and eight n-octyl groups per ligand molecule.

For both the ligands, the carbonyl bond of a DGA site with Pu is shorter than that with Np, implying that the former complex is stronger than the latter (Table 3). Bond order calculations also indicated that the Pu complex is more stable than the Np complex by 0.85 eV and 0.76 eV for L_I and L_{II}, respectively. This feature has also been observed experimentally from the solvent extraction studies. The natural charges on the central metal ions (Q_M) in the respective complexes of plutonium and neptunium are also shown in Table 3, which shows that neptunium contains lesser positive charges as compared to plutonium in the complexes of both the ligands (L_I and L_{II}) indicating lesser ligand to metal charge transfer in case of plutonium complexes as compared to that in case of neptunium complexes. The higher stability of plutonium complexes in spite

Table 3 Different 'M–O' bond distances along with the Wiberg's bond order (numbers in parenthesis) and the natural charges on the metal ion (Q_M) obtained for Pu(IV) and Np(IV) complexes

Bond/Q_M	L_I		L_{II}	
	PuL(NO₃)₄	NpL(NO₃)₄	PuL(NO₃)₄	NpL(NO₃)₄
d(M–O$_{carb}$)	2.451 (0.435)	2.449 (0.422)	2.394 (0.372)	2.414 (0.352)
	2.385 (0.572)	2.373 (0.546)	2.369 (0.421)	2.374 (0.409)
d(M–O$_{ether}$)	2.574 (0.132)	2.564 (0.118)	2.626 (0.105)	2.626 (0.100)
d(M–O$_{NO_3(m)}$)	2.290 (0.580)	2.313 (0.626)	2.169 (0.740)	2.170 (0.782)
	2.213 (0.662)	2.224 (0.674)	2.189 (0.725)	2.189 (0.757)
			2.294 (0.551)	2.286 (0.587)
d(M–O$_{NO_3(b)}$)	2.486 (0.335)	2.504 (0.334)		
	2.407 (0.532)	2.373 (0.530)	2.411 (0.489)	2.419 (0.481)
	2.441 (0.463)	2.437 (0.474)	2.452 (0.459)	2.468 (0.456)
	2.425 (0.512)	2.406 (0.512)		
Q_M	1.678	1.630	1.829	1.761

of the lesser ligand to metal charge transfer, suggests that the metal–ligand interactions here are mainly dominated by ionic interactions.

Conclusions

The extraction of tetravalent actinide ions, *viz.* Np^{4+} and Pu^{4+}, was investigated using the two aza-macrocycle-based multiple DGA-containing ligands L_I and L_{II}. The extraction of Pu^{4+} was significantly larger than that of Np^{4+}, while that using L_{II} was superior to that with L_I. The extracted species contained four nitrate ions for charge neutralization purpose, while one ligand molecule was associated with the complex, possibly by bonding to a single DGA arm. The structures of the complexes were optimized by DFT computations and conformed to two bidentate nitrates, two monodentate nitrates and a multiple DGA-containing ligand coordinating through a single DGA arm. The D values of both Pu^{4+} as well as Np^{4+} were found to be reasonably good for possible application of these ligands for their recovery from acidic wastes such as the HLW. Published data on trivalent actinide ion such as Am^{3+} suggested its co-extraction along with Np^{4+} and Pu^{4+} and a good decontamination from UO$_2^{2+}$ ion.

Conflicts of interest

The authors have no conflicts of interest to declare.

Acknowledgements

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