



Cite this: *Dalton Trans.*, 2015, **44**, 12771

Design, synthesis and extraction studies of a new class of conformationally constrained (*N,N,N',N'*-tetraalkyl)7-oxabicyclo[2.2.1]heptane-2,3-dicarboxamides†

Shikha Sharma,^a Surajit Panja,^b Arunasis Bhattachariya,^c Prem S. Dhami,^b Preetam M. Gandhi^b and Sunil K. Ghosh^{*a}

A new class of conformationally constrained 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxamides (OBDA) of three secondary amines was synthesized, and their extraction behavior for trivalent and tetravalent actinides in HNO_3 medium was studied. Amongst the diamides, *N,N*-bis-2-ethylhexyl substituted diamide showed the best results for actinide extraction. This diamide also exhibited a very low level of extraction for $\text{Sr}^{(II)}$ and $\text{Ru}^{(III)}$ which is desirable, thus providing higher selectivity for actinides. The stripping of extracted metal ions was achieved using 0.1 M oxalic acid for $\text{Pu}^{(IV)}$ or $\text{pH} \sim 2$ solution for $\text{Am}^{(III)}$. Third phase formation was not observed for the OBDA ligand even for a higher concentration of Eu up to 5 g L⁻¹ with retention of good D_{Eu} . The tridentate nature of the OBDA ligand was ascertained by studying the IR and NMR spectra of the Eu^(III) complex with the ligand. The OBDA showed the formation of a mixture of mono- and di-solvated species of Eu^(III) as indicated by the slope analysis method and ESI-MS. Density functional theoretical (DFT) study was carried out to determine the energy optimized structure of the free ligand and its Am^{3+} complex.

Received 5th May 2015,
Accepted 29th May 2015

DOI: 10.1039/c5dt01691f

www.rsc.org/dalton

Introduction

Spent nuclear fuel reprocessing is becoming a necessity in the generation of nuclear energy. The spent fuel is dissolved in nitric acid and the combined recovery of U^(VI) and Pu^(IV) is carried out by solvent extraction (PUREX process) by a solution of 1.1 M tri-*n*-butylphosphate (TBP) in *n*-dodecane.¹ The acidic raffinate thus produced is known as high-level liquid waste (HLLW), which contains significant amounts of trivalent lanthanides and minor actinides (Am, Cm and Np). In addition, it also contains a small amount of Pu and fission products (¹³⁷Cs, ⁹⁰Sr, ¹⁰⁶Ru etc.). Although the concentration levels are small, these actinides are α -emitting radioisotopes and need to be separated from HLLW for its management and safe disposal. Thus, partitioning and transmutation (P&T) strategy is becoming vital for the management of HLLW.²

A plethora of complexing reagents (solvents) have been developed over the last three decades for actinide partitioning purposes. The malonamide family of extractants was developed during the 1980s for the extraction of actinides from PUREX raffinate (DIAMEX process). The most promising member of this family was the DIAMEX reference compound *N,N'*-dimethyl-*N,N'*-dibutyl malonamide (DMDBTDMA) **I** (Fig. 1).³

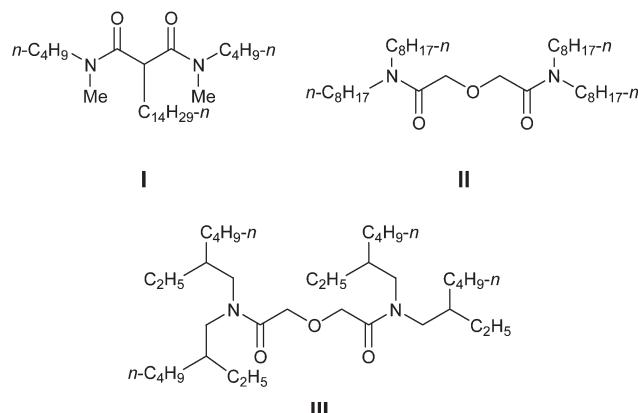


Fig. 1 Structures of important diamides.

^aBio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India. E-mail: ghsunil@barc.gov.in; Fax: +91-22-25505151; Tel: +91-22-25595012

^bFuel Reprocessing Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

^cRadiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5dt01691f



Several phosphorus based compounds *viz.* trialkylphosphine oxides (TRPO process),^{4a} diisodecylphosphoric acid (DIDPA),^{4b} carbamoyl organophosphorous compounds (TRUEX process),^{4c-e} etc. have also been developed for the same purpose. But they are non-incinerable and do not comply with the requirements of the CHON principle of extractant design.

The multidentate diglycolamide (DGA) family of extractants were introduced in the early 1990s for the extraction of different metal ions.⁵ The DGA substance class has close resemblance to the malonamides but possesses an additional arm, an ether group positioned between two acetamide functionalities. Amongst the diglycolamides (DGAs) synthesized, *N,N,N',N'-tetraoctyldiglycolamide* (TODGA) **II**,^{5b-d} and *N,N,N',N'-tetra-2-ethylhexyldiglycolamide* (TEHDGA)^{5e,f} **III** (Fig. 1) have been found to be the most important extractants for the separation of trivalent actinides and lanthanides from HLLW. The change from malonamide (bidentate ligand) to DGA (tridentate ligand) significantly increased the affinity for both trivalent actinides and lanthanides. The main disadvantage of these DGA based extractants is the extraction of Sr(II) ions from the HLLW solution along with Ln(III) and Ac(III) ions.^{5b,g-i,6a} This leads to the requirement of a greater number of stages for scrubbing. The higher extraction of strontium and other elements^{5j} by TODGA was attributed to the higher basicity (K_H) of the TODGA/n-dodecane ($K_H = 4.1$)^{5b} as compared to TEHDGA ($K_H = 1.72$).^{5k} Therefore, the extraction behavior is strongly dependent on the nature of the alkyl groups attached. To optimize the selectivity of extraction/stripping in terms of diluent, phase modifier and reagent concentration, unsymmetrical DGAs have also been developed.^{6a} They have also been pre-organized on various tripodal platforms^{6b} and as bis(DGA).^{6c}

It is known that a small structural change in the substituent at the central carbon in malonamides causes a noticeable change in their extraction abilities.^{3c} Similarly, DGA ligands with structural modifications in their skeleton were also attempted.^{7a} The thioether analogs of DGAs,^{7b} thiadiglycolamide (TGDA) have been made and employed in the extraction. The other modifications include (1) the increase in chain length from one carbon to two carbons between the central ether oxygen (oxydipropionamide or ODPA)/sulfur atom (thiadipropionamide or TDPA) and the amide moieties,^{7b} (2) the addition of substituents on the carbons between the central oxygen atom and the amide moieties on either one or both sides of the central oxygen,^{7a} (3) the replacement of the central oxygen by a (substituted) nitrogen atom,^{7c} (4) synthesis of pillar[5]arene and calix[4]arene based DGA molecules^{7d,e} and (5) synthesis of rigidified diglycolamides on a tetrahydrofuran platform.^{7a} The extraction study experiments showed that these modifications changed some properties of extraction or back-extraction but did not change them in a meaningful way to be superior than TODGA **II** or TEHDGA **III**.

So far, the successful tridentate ligands designed and developed mostly consist of linear diglycolamides. The increase in chain length from one carbon to two carbons between the central ether oxygen atom and the amide moieties in ODPA has been attempted but with poor extraction abilities.^{7b} As

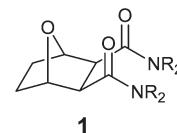


Fig. 2 Conformationally constrained diamides.

mentioned above, the only reported diglycolamides on a rigidified tetrahydrofuran platform (as a mixture of *cis* and *trans*-isomers) have been reported by Iqbal *et al.*^{7a} We were curious to develop tridentate diamide based ligands **1** based on conformationally constrained 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxylic acid, where the ether-oxygen is positioned at the bridgehead and a chain of two carbon atoms lies between the ether oxygen and the amide moieties (Fig. 2). The rigid coordination sphere created by the three donor groups (ether-oxygen and two amide groups) is expected to enhance binding kinetics as the coordination atoms are appropriately oriented for binding to a metal. The co-extraction of some fission product like Ru and Sr is a major issue with the currently used DGA classes of ligands. We were therefore curious to investigate the concept of the rigidity effect of donor groups on an oxabicyclo[2.2.1]heptane skeleton for the selective extraction of lanthanides and actinides. To the best of our knowledge, the syntheses of such simple oxy-diamides have not been attempted to study the effect of such structural modifications on extraction behavior. Herein, we describe the synthesis of three conformationally constrained bridged 7-oxabicyclo[2.2.1]heptane-2,3-dicarboxamides **1a-c** (OBDA **1a-c**) and their extraction properties for $^{241}\text{Am}(\text{m})$, $^{(152+154)}\text{Eu}(\text{m})$, $^{239}\text{Pu}(\text{iv})$, $^{233}\text{U}(\text{vi})$ from the nitric acid medium using 15% isodecyl alcohol (IDA)/n-dodecane as a diluent mixture.

Results and discussion

For the current study, three OBDA **1a-c** having different amine components have been synthesized from commercially available starting materials as shown in Scheme 1. The Diels-Alder reaction of furan and maleic anhydride gave the known *exo* adduct **2** in excellent yield, which was then hydrogenated using Pd/C as catalyst to give the known bridged tricyclic anhydride **3** in quantitative yield. Anhydride **3** was opened up with bis 2-ethylhexylamine to give the hemiamide **4** as an intermediate which was reacted *in situ* with another equiv. of bis 2-ethylhexylamine in the presence of diisopropylcarbodiimide (DIPC) and a catalytic amount of 4-dimethylaminopyridine (DMAP) to give the bridged OBDA **1a** in excellent yield as a waxy solid. The other two dicarboxamides, OBDA **1b** and OBDA **1c** were similarly made in high yields from the anhydride **3** using diocylamine and diisobutylamine, respectively (Scheme 1).

For extraction studies, IDA was used as a phase modifier to suppress the formation of the third phase by OBDA **1a** in contact with 4 M HNO₃ solution, and 15% was found to be



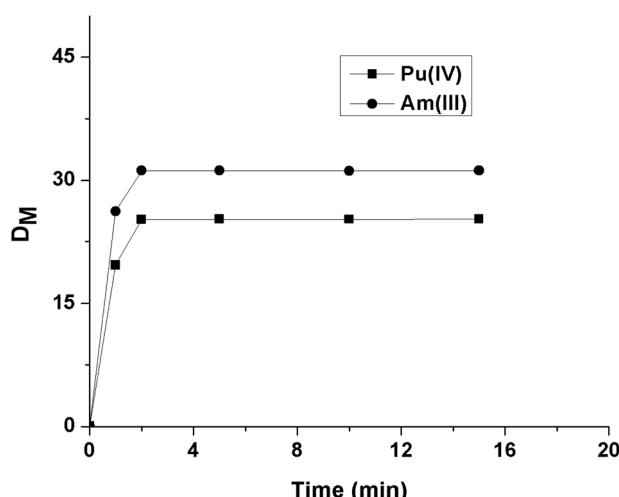
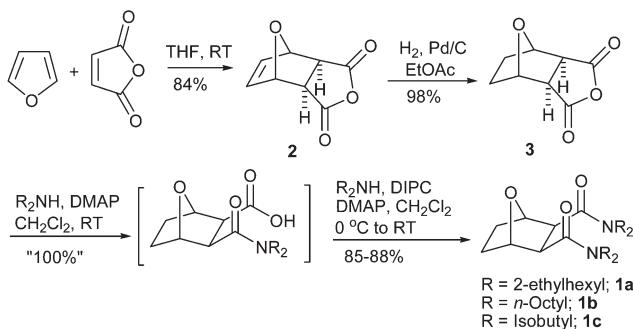


Fig. 3 Kinetics of extraction of Pu(IV) and Am(III) using 0.1 M OBDA **1a** in 15% IDA/n-dodecane from 1 M HNO₃.

enough to prevent that. The time of equilibration required for Am(III) and Pu(IV) by OBDA was studied using 0.1 M OBDA **1a** in 15% IDA/n-dodecane in the presence of 1 M HNO₃. It was found that OBDA **1a** showed very fast kinetics of equilibration (2 min) for both Am(III) and Pu(IV) (Fig. 3). The kinetics of extraction was found to be comparable to TEHDGA **III** under the same conditions. Therefore, in subsequent studies, 5 min equilibration time was maintained.

The D_{Am} value for OBDA **1a** (Fig. 4) at 3 M HNO₃ was found to be 52.3. For comparison purposes, the extraction of Am(III) was also studied with OBDA **1b** and OBDA **1c** at 3 M HNO₃. The D_{Am} value was slightly less for OBDA **1b** (42 at 3 M HNO₃). The solubility of OBDA **1c** was poor in 15% IDA/n-dodecane. Hence, a solution of OBDA **1c** in 30% IDA/n-dodecane was studied which also showed a D_{Am} value of 40 at 3 M HNO₃. Further studies were therefore performed with OBDA **1a** only.

The effect of feed nitric acid concentration on the distribution ratio of Pu(IV), Am(III) and Eu(III) for 0.1 M OBDA **1a** in 15% IDA/n-dodecane was investigated to explore the feasibility of using this ligand for the separation of actinides and lantha-

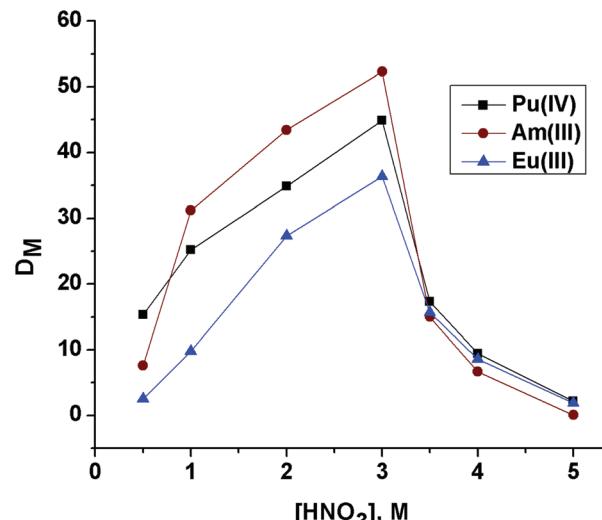


Fig. 4 Effect of feed nitric acid concentration on the extraction of Pu(IV), Am(III) and Eu(III) using 0.1 M OBDA **1a** in 15% IDA/n-dodecane.

nides (Fig. 4). OBDA **1a** showed an interesting trend in the distribution ratio of Pu(IV), Am(III) and Eu(III). In the case of OBDA **1a**, an initial increasing trend of the distribution ratios for Pu(IV), Am(III) and Eu(III) was observed on increasing the feed nitric acid concentration. Beyond 3 M HNO₃, the distribution ratios rapidly decreased. The results obtained for Am(III) were compared with the results obtained from TEHDGA **III** to understand the effect of conformational restrictions of the ligand structure on the extraction performance (Fig. 5). In the case of TEHDGA **III**, the distribution ratio continuously increased with increasing HNO₃ concentration up to 6 M concentration. Between 3–4 M HNO₃ (the commonly used acidity

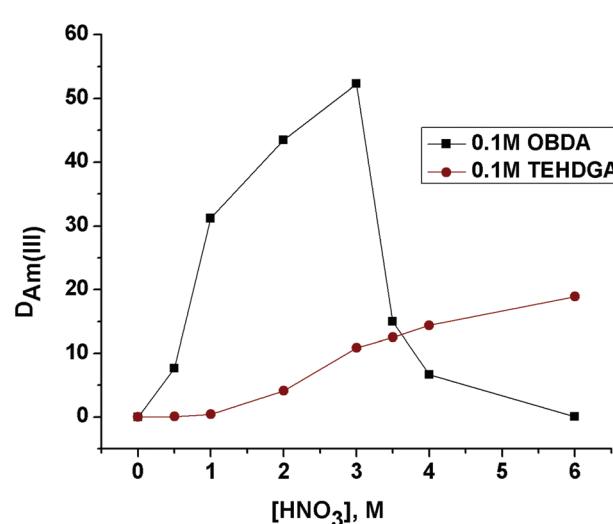
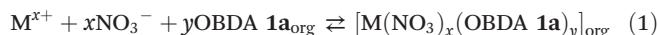


Fig. 5 Comparative extraction of Am(III) using 0.1 M OBDA **1a** and 0.1 M TEHDGA **III** in 15% IDA/n-dodecane at different feed nitric acid concentrations.

of nuclear waste), the D_M values for OBDA **1a** are comparable with TEHDGA **III**. Like TEHDGA **III**, OBDA **1a** is a neutral extractant. Hence, the extraction mechanism takes place *via* nitrate ion assisted complex formation (eqn (1)). The subscript 'org' refers to species in the organic phase and the absence of subscript refers to those present in the aqueous phase:



So, increasing nitric acid concentration leads to increased formation of the neutral metal–nitrate complex leading to a higher D_M value. This explains the trend observed for TEHDGA **III** and the increasing trend of D_M for OBDA **1a** on the increasing nitric acid concentration. But the decreasing trend in the distribution ratio beyond 3 M HNO₃ for OBDA **1a** needed more investigation. One possible reason for this abnormal behavior of OBDA **1a** could be its stability at higher nitric acid concentration. This provoked us to study the stability behavior of OBDA **1a** at different nitric acid concentrations. OBDA was found to be sensitive to hydrolytic degradation. In lower acid

concentration, the degradation rate was found to be slow. In 1 M HNO₃, the OBDA **1a** was observed to be stable up to about 15 min after which degradation started and complete hydrolysis was observed in 2.5 h. In 3 M HNO₃, the OBDA **1a** solution in *n*-dodecane–IDA mixture is stable for a very short period of time. The hydrolysis pattern of OBDA **1a** showed that after 5 min of contact with 3 M HNO₃, its degradation was initiated followed by rapid degradation thereafter (Table 1, ESI†).⁸ The complete degradation of OBDA **1a** took about 30 min resulting in the formation of bis-2-ethylhexylamine and the corresponding dicarboxylic acid, a product further independently confirmed by hydrolyzing the anhydride **3**. It was therefore necessary to find out the ligand species responsible for the extraction of Pu(IV) and Am(III). Independent studies using either bis-2-ethylhexylamine or di-carboxylic acid of anhydride **3** or a mixture of both did not show any extraction of Pu(IV) and Am(III). This clearly proved that OBDA **1a** is responsible for the extraction of Pu(IV) and Am(III). The OBDA molecules that are complexed to Pu(IV) or Am(III) did not undergo hydrolysis. This has been augmented by stripping studies of the OBDA **1a** complexed to Pu(IV) or Am(III) with a

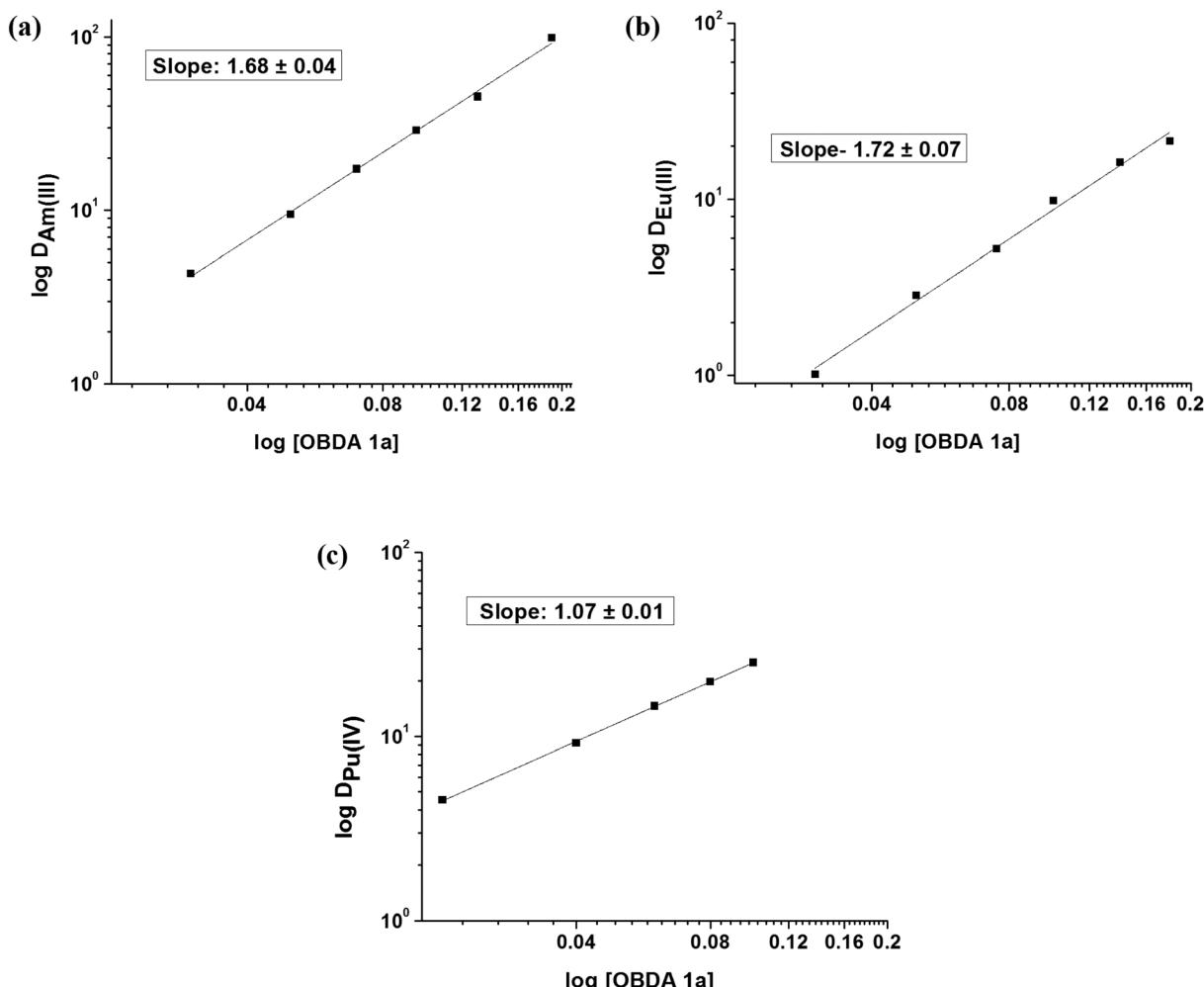


Fig. 6 Plot of $\log D_M$ vs. $\log [OBDA\ 1a]$ for (a) Am (b) Eu and (c) Pu.



higher concentration of nitric acid (6 M HNO_3) where extracted metal ions are not stripped into the aqueous phase. So the combination of fast kinetics for complexation and good D_M values for Pu(IV) and Am(III) at 3–4 M acidity (normally used in HLLW) prompted us to carry out further extraction studies using OBDA **1a**.

To determine the stoichiometry of the extracted metal-ligand species for Pu(IV), Am(III) and Eu(III), the concentration of OBDA **1a** was varied at a fixed aqueous acidity (1 M HNO_3). The plot of $\log D_M$ vs. $\log[\text{OBDA } \mathbf{1a}]$ for Pu(IV), Am(III) and Eu(III) gave straight lines with varying slopes (Fig. 6). Pu(IV) was found to form a mono-solvated species with OBDA **1a** whereas Am(III) and Eu(III) formed a mixture of mono-solvated and di-solvated species. The D_M values for Pu, Am and Eu were studied at different nitrate ion concentrations at a fixed aqueous acidity (1 M HNO_3). The plot of $\log D_M$ vs. $\log[\text{NO}_3^-]$ showed a straight line with a slope of ~4 for Pu(IV) and ~3 for Am(III) or Eu(III) (Fig. 7) indicating that four nitrate ions are involved in the extraction of Pu(IV) while three nitrate ions are involved for Am(III) and Eu(III).

To determine the nature of the bonding between metal and ligand, the complex of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with OBDA **1c**⁹ was studied by IR and ¹H NMR spectroscopy. IR spectra of the obtained complex¹⁰ (Fig. 8) indicates a strong binding of metal at the amide carbonyl group of the ligand. The $\nu \text{ C}=\text{O}$ for OBDA **1c** appeared at 1655 and 1632 cm^{-1} whereas for the metal-ligand complex it appeared at a lower wave number (1593 cm^{-1}). This lowering in $\nu \text{ C}=\text{O}$ was attributed to the coordination of the metal at the carbonyl group of the ligand. The participation of the ether-oxygen of OBDA in binding with the metal in the metal ligand complex has been corroborated from the ¹H NMR spectra (Fig. 9). A significant downfield shift of $\text{CH}-\text{O}-\text{CH}$ resonance was observed after complexation with Eu [δ 4.86 (2 H, s, CHOCH) for free OBDA **1c** vs. 5.96 (2 H, s, broad, CHOCH) for the complexed Eu]. NMR and IR studies confirmed the participation of amide carbonyls and ether-oxygen in metal ligand complex formation. The OBDA ligands thus function as tridentate ligands like DGA ligands. It will, therefore, be of interest to understand the structure and coordination modes in its complex using a density functional

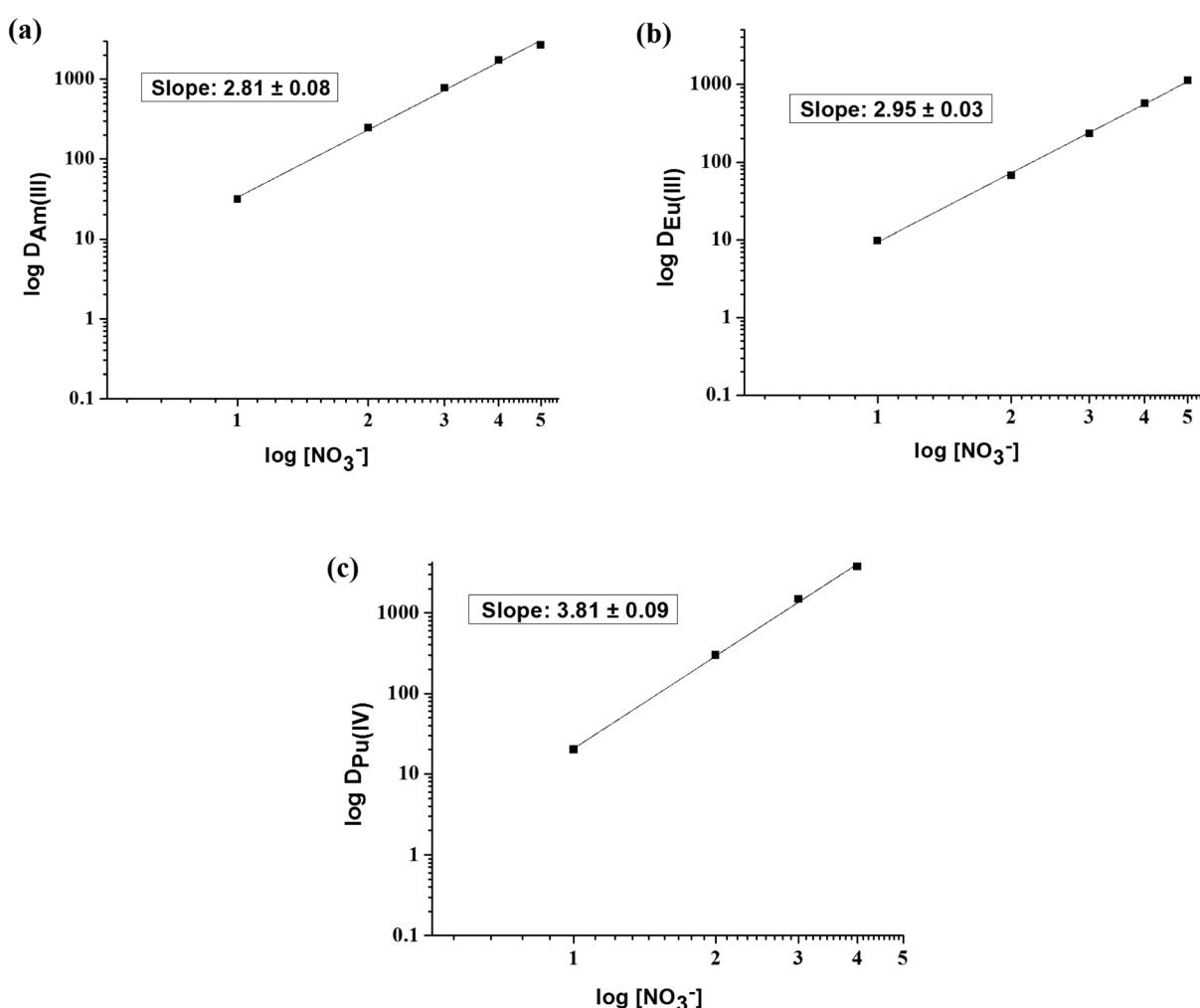


Fig. 7 Plot of $\log D_M$ vs. $\log \text{NO}_3^-$ for (a) Am (b) Eu and (c) Pu.

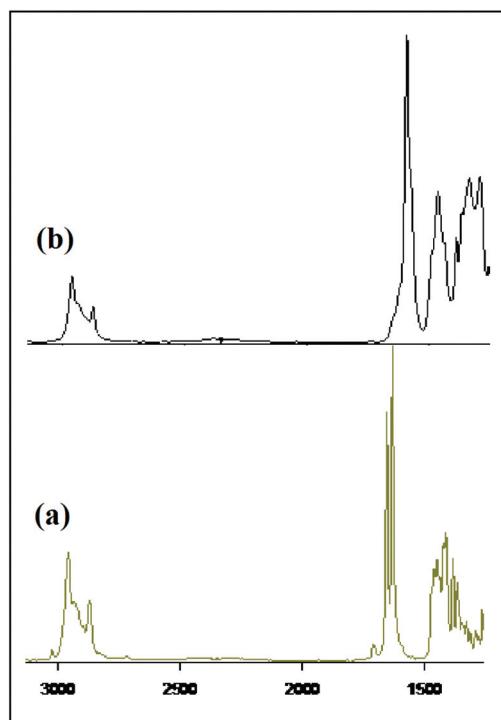


Fig. 8 IR spectra of (a) OBDA 1c and (b) OBDA 1c complexed with $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

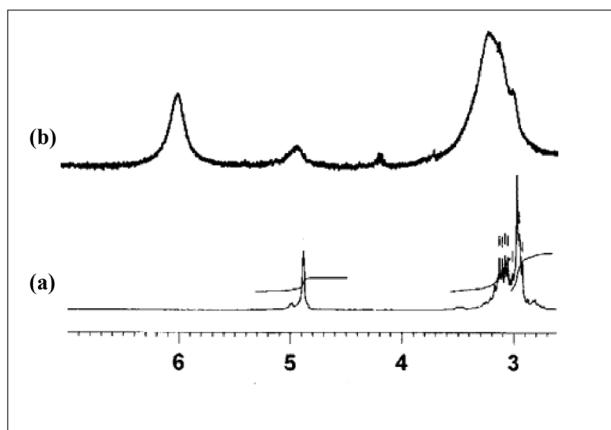


Fig. 9 ^1H NMR spectra of the relevant portion (a) OBDA 1c and (b) OBDA 1c complexed with $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$.

theoretical (DFT) study. ESI-MS spectra provided further insight on the metal ligand complex formation. The complex obtained was a mixture of two species mono- and di-solvated.

The peaks at m/z 720.7 and 841.7 correspond to $[(\text{OBDA } 1\text{c})\text{Eu}(\text{NO}_3)_2(\text{H}_2\text{O})_2]^+$ and $[(\text{OBDA } 1\text{c})\text{Eu}(\text{NO}_3)_3(\text{H}_2\text{O})_4\text{Na}]^+$, respectively, while peaks at m/z 517.5 and 1096.7 correspond to $[(\text{OBDA } 1\text{c})_2\text{Eu}(\text{NO}_3)]^{2+}$ and $[(\text{OBDA } 1\text{c})_2\text{Eu}(\text{NO}_3)_2]^+$, respectively (Fig. 1, ESI†).

The presence of macro concentrations of trivalent lanthanides in HLLW often leads to the formation of a third phase during 'actinide partitioning'. To simulate the situation, the D_M value of Eu(III) was studied with OBDA 1a at 3 M HNO_3 with varying concentrations of Eu. No third phase formation was observed even up to 5 g L^{-1} of Eu. Also, significant D_{Eu} was found at higher concentrations (Table 2, ESI†).

Stripping of loaded metal ions from the organic phase is an important factor for the extractant to be considered for separation of actinides and lanthanides. It was possible for OBDA 1a loaded with Pu(IV) to be stripped by 0.1 M Oxalic acid (~85% stripping in a single contact) whereas Am(III) was found to be stripped by pH 2 solution (~90% stripping in a single contact).

The selectivity of OBDA 1a in reference to other elements present in HLLW was investigated in 3 M HNO_3 and was found to be higher compared to TEHDGA III (Table 1). It was interesting to observe that D_{Sr} and D_{U} values were low compared to those observed for TEHDGA III ($D_{\text{Sr}} \sim 0.65$ and $D_{\text{U}} \sim 2.1$ for 0.1 M TEHDGA III/15% IDA)^{5e,k} thus offer better purification of the trivalent actinides and lanthanides over the other constituents present in HLLW.

DFT calculations were performed on the free OBDA with the di-methyl substituent on the amidic 'N' atoms in order to reduce the computational cost. The result shows that the ligand is most stable in the conformation, where two carbonyl oxygens of amide groups are in *trans* position (Fig. 10a). However, prior to the complexation with the metal ions, both the amidic oxygens should be in *cis* position. Two possible conformers with the amidic oxygens in the *cis* position were considered (Fig. 10b and 10c) and their relative energies were compared with respect to the most stable *trans* conformer. The results showed that the conformer 'c' (relative energy: 5.39 kcal mol^{-1}) is more stable than the conformer 'b' (relative energy: 11.18 kcal mol^{-1}). FTIR studies also showed the participation of the ethereal oxygen atom in the bonding with the metal ion, which is possible if the ligand forms complexes in the conformer 'c'. The DFT study, therefore, substantiates the results of the FTIR studies. The slope analysis study indicated the presence of two OBDA molecules and three nitrate ions in the extracted species of Am^{3+} . The guessed structure of the Am^{3+} complex was, therefore, prepared with two OBDA and three nitrate ions coordinated to the central Am^{3+} ion. The opti-

Table 1 Extraction behavior of different elements present in HLLW solution using 0.1 M OBDA 1a in 15% IDA/n-dodecane

Elements	Cs	Sr	Ru	Nb	Ce	U	Pu	Eu	Sb	Am
$D_M(\text{OBDA})$	<0.01	0.05	0.04	<0.01	14.86	0.5	44.29	35.46	<0.01	52.21
$D_M(\text{TEHDGA})$	<0.01	0.65	0.05	<0.01	13.17	2.1	34.16	9.15	<0.01	11.15



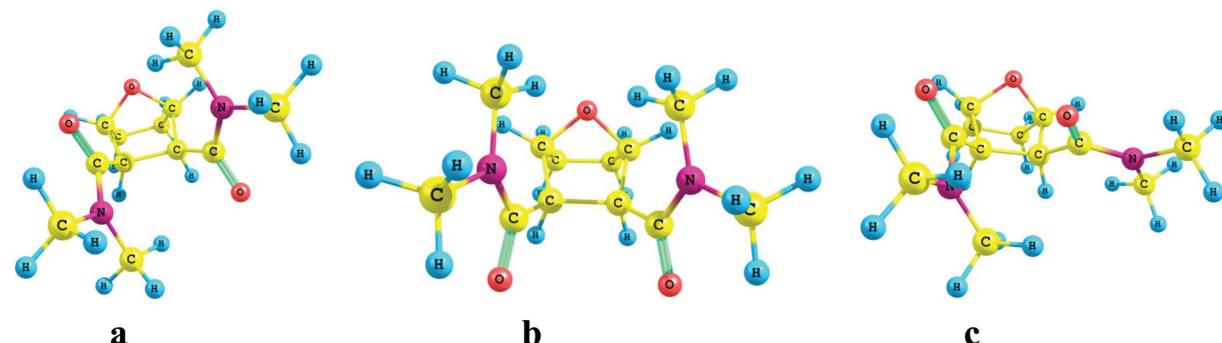


Fig. 10 Three different conformers of free OBDA ligand obtained by geometry optimization.

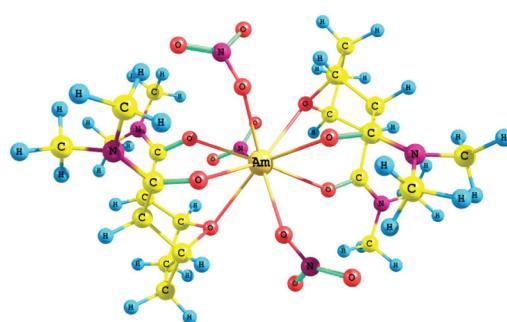


Fig. 11 Energy optimized structure of the Am(III) complex of OBDA.

imized geometry of the Am^{3+} complex is shown in Fig. 11. In this complex the amidic oxygens are closer to the central Am^{3+} ion with an 'Am-O' bond length of 2.51 ± 0.02 Å as compared to the ethereal oxygen atoms (2.70 ± 0.04 Å). The nitrate ions are, however, closer to the Am^{3+} ion as compared to the OBDA with an 'Am-O' distance of 2.403 ± 0.002 Å. In order to further understand the metal-ligand bonding the natural charges on the Am^{3+} ion and coordinating sites of the ligand molecules were calculated and the results are shown in Table 2. The electron density on the amidic oxygen atom increased from -0.60 e to -0.641 after complexation in spite of transfer of electron density to the Am^{3+} ion. This indicates more charge polarization in the ligand molecule after complexation due to the pulling of electron density by the amidic oxygen atoms from the adjacent carbon atom resulting in change in the electronic charge on the amidic carbon atom from -0.412 e to 0.714 e.

Conclusion

A conformationally constrained class of diamides (OBDA) has been found to be an excellent extractant for tri- and tetravalent actinides as well as trivalent lanthanides in nitric acid medium. The synthesis of extractants is achieved from cheap commercially available materials in three steps in high yields and purity. OBDA **1a** showed excellent extraction behavior with fast kinetics, and high loading capacity for lanthanides without third phase formation, very low extraction of fission products and easy stripping of the extracted metal ions. Very poor extraction of Sr(II) and Ru(III) by the ligand is advantageous because no scrubbing was needed before stripping. This class of molecules forms a mixture of mono-solvated and di-solvated species with Am and Eu as obtained by the slope analysis method and ESI-MS. OBDA **1a** was found to be sensitive to hydrolytic degradation. This detrimental effect has been surpassed by fast kinetics of complexation and hydrolytic stability of the complexed OBDA as supported by good D_M values at 3–4 M HNO_3 and stripping studies with 6 M HNO_3 . DFT study indicates the participation of both carbonyl and ethereal oxygens in the bonding with metal ion, which is also supported by FTIR and NMR studies.

Experimental

Synthesis of diamides OBDA **1a–c**

exo-3,6-Epoxy-1,2,3,6-tetrahydrophthalic anhydride **2.** Freshly distilled furan (11 mL, 151.5 mmol) was added to a stirred solution of maleic anhydride (14.7 g, 150 mmol) in dry THF

Table 2 Natural charges on the carbonyl and ethereal oxygen and carbonyl carbon atoms before and after complexation and on the $\text{Am}^{(III)}$ ion in the complex

$Q(\text{Am})$	$Q(\text{O})_{\text{amide}}$		$Q(\text{C})_{\text{amide}}$		$Q(\text{O})_{\text{ether}}$	
In complex	In free ligand	In complex	In free ligand	In complex	In free ligand	In complex
1.582	-0.60 ± 0.01	-0.641 ± 0.007	-0.412	0.714	-0.572	-0.570 ± 0.001



(45 mL) at room temperature. The reaction mixture was left standing for 5 days. The resulting crystals were filtered to obtain anhydride **2** (21 g, 84%). M.P. 116–118 °C. ¹H NMR (200 MHz, CDCl₃): 3.17 (2 H, s, COCHCHCO) 5.46 (2 H, s, CHOCH), 6.58 (2 H, s, CH=CH).

exo-3,6-Epoxy-hexahydrophthalic anhydride 3. Palladium on charcoal (400 mg, 10% Pd) was added to a solution of unsaturated anhydride **2** (4 g, 24.09 mmol) in dry ethyl acetate (72 mL). The mixture was degassed and flushed with hydrogen gas several times followed by stirring under a hydrogen atmosphere for 24 h. The mixture was filtered through celite and the filtrate was evaporated to give the saturated anhydride **3** (3.97 g, 98%). M.P. 112 °C. ¹H NMR (300 MHz, CDCl₃): 1.57–1.62 (2 H, m, CH_AHCH_AH), 1.85–1.95 (2 H, m, CHH_BCHH_B), 3.18 (2 H, s, COCHCHCO), 5.03–5.05 (2 H, m, CHOCH).

General procedure 1

Preparation of OBDA 1a–c from anhydride 3 and *N,N*-dialkylamines. A solution of a *N,N*-dialkylamine (20.1 mmol) in dry CH₂Cl₂ (5 mL) was added slowly to a solution of anhydride **3** (1.68 g, 10 mmol) in dry CH₂Cl₂ (15 mL) at room temperature followed by the addition of DMAP (122 mg, 1 mmol). The reaction mixture was stirred for 0.5 h and cooled on an ice-water bath. Diisopropylcarbodiimide (1.57 mL, 10.1 mmol) was added dropwise to the stirred reaction mixture. The reaction mixture was allowed to attain room temperature and stirred overnight. The reaction mixture was diluted with 1/1 ethyl acetate–petroleum ether and washed with 5% citric acid solution and with water and concentrated under reduced pressure. The residue was purified by column chromatography to give OBDA **1a–c**.

***N,N,N',N'*-Tetrakis(2-ethylhexyl)-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxamides 1a.** Yield: 5.56 g (88%); M.P. 100–103 °C. IR (neat): 2955, 2916, 2874, 2857, 1643, 1632, 1416 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 0.75–1.00 (24 H, m, 8 \times CH₃), 1.05–1.41 (32 H, bs, 4 \times CH₂CH₃, 4 \times CH(CH₂)₃CH₃), 1.41–1.68 (4 H, m, CHCH₂CH₂CH), 1.72–1.95 (4 H, m, 4 \times CHCH₂CH₃) 2.93 (2 H, s, COCHCHCO), 3.0 (4 H, d, J = 6.4 Hz, 2 \times NCH₂CH), 3.15 (4 H, d, J = 7.2 Hz, 2 \times NCH₂CH), 4.86 (2 H, s, 2 \times CHOCH); Anal. Calcd for C₄₀H₇₆N₂; C, 75.89; H, 12.1; N, 4.43%; Found C, 75.91; H, 12.18; N, 4.26%.

***N,N,N',N'*-Tetraoctyl-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxamides 1b.** Yield: 5.37 g (85%); IR (neat): 2953, 2916, 2851, 2818, 1643, 1632, 1416, 746, 719 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 0.8–0.98 (12 H, m, 4 \times CH₃), 1.16–1.4 (48 H, m, 24 \times CH₂), 1.4–1.68 (4 H, m, CHCH₂CH₂CH), 2.85–2.95 (2 H, m, COCHCHCO), 2.95–3.2 (4 H, m, 2 \times NCH₂CH), 3.23–3.42 (4 H, m, 2 \times NCH₂CH), 4.86 (2 H, t, J = 2.4 Hz, 2 \times CHOCH); ¹³C NMR (75 MHz, CDCl₃): δ 14 (2 C), 22.6 (2 C), 27 (2 C), 27.2 (2 C), 27.3 (2 C), 29 (2 C), 29.2 (3 C), 29.3 (3 C), 29.33 (3 C), 29.4 (3 C), 29.5 (2 C), 31.7 (2 C), 31.8 (2 C), 46.2 (2 C), 47.7 (2 C), 51.1 (2 C), 79.2 (2 C), 169.2 (2 C); Anal. Calcd for C₄₀H₇₆N₂; C, 75.89; H, 12.10; N, 4.43%; Found C, 76.13; H, 12.24; N, 4.34%.

***N,N,N',N'*-Tetrabutyl-7-oxabicyclo[2.2.1]heptane-2,3-dicarboxamides 1c.** Yield: 3.51 g (86%); M.P. 156 °C; IR (neat): 2956, 2869, 1655, 1632, 1414 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 0.75–1.00 (24 H, m, 8 \times CH₃), 1.45–1.58 (2 H, m, CH_AHCH_AH), 1.76–1.88 (2 H, m, CHH_BCHH_B), 1.88–2.0 (2 H, m, 2 \times CH₂CH(CH₃)₂), 2.0–2.19 (2 H, m, 2 \times CH₂CH(CH₃)₂), 2.8–3.2 (10 H, m, 4 \times NCH₂CH, COCHCHCO), 4.86 (2 H, s, 2 \times CHOCH); ¹³C NMR (75 MHz, CDCl₃): δ 19.9 (2 C), 20.2 (2 C), 20.5 (2 C), 20.6 (2 C), 26.2 (2 C), 27.6 (2 C), 29.5 (2 C), 51.3 (2 C), 53.8 (2 C), 55.5 (2 C), 79.4 (2 C), 170 (2 C); Anal. Calcd for C₂₄H₄₄N₂; C, 70.54; H, 10.85; N, 6.86%; Found C, 70.74; H, 11.08; N, 6.73%.

Extraction studies

Solutions of desired concentration of OBDA **1a–c** were prepared in *n*-dodecane (with 15% iso-decanol as the phase modifier) and agitated with an equal volume of the aqueous phase (containing the requisite quantity of ²³⁹Pu/²⁴¹Am tracer) in a rotary thermostated water bath for 5 minutes at 25.0 ± 0.1 °C. The two phases were then centrifuged and assayed by taking suitable aliquots from both the phases. The distribution ratio (D_M) is defined as the ratio of concentration of metal ion in the organic phase to that in the aqueous phase. The valency of Pu during extraction was maintained as Pu(iv). For the preparation of Pu(iv) stock, NaNO₂ was used as an oxidant in 1 M HNO₃ solution. The oxidized Pu(iv) solution was subsequently extracted by 0.5 M 2-thenoyltrifluoroacetone (TTA) in xylene where Pu(iv) is quantitatively extracted. The loaded Pu was stripped by 7 M HNO₃ and equilibrated 3 times with xylene to remove the dissolved TTA from the aqueous phase. The stripped Pu solution was used as stock for Pu(iv). For extraction studies of various fission products, HLLW solution generated from PUREX process was diluted in 3 M HNO₃ and used as feed. HLLW originating from a research reactor fuel reprocessing plant from a particular batch having the composition of uranium (predominantly ²³⁸U) 7.51 g L⁻¹, plutonium (predominantly ²³⁹Pu) 3.19 mg L⁻¹, ¹³⁷Cs 8.89 Ci L⁻¹, ¹⁰⁶Ru 7.99 Ci L⁻¹, ¹⁴⁴Ce 27.75 Ci L⁻¹, ⁹⁰Sr 4.0 Ci L⁻¹, ¹²⁵Sb 0.2 Ci L⁻¹, ⁹⁵Nb 14.32 mCi L⁻¹ was used. In view of the high activity of HLLW, it was diluted by a factor of 100 to bring down the activity to a measurable level. Consequently, the activity of the radionuclide ¹⁵²⁺¹⁵⁴Eu became too low to determine and hence, had to be spiked. Owing to the pure β activity of ⁹⁰Sr present in the diluted solution, ⁸⁵⁺⁸⁹Sr was spiked where a gamma emitter, namely, ⁸⁵Sr, was used as a tracer. The acidity was finally adjusted to 3 M HNO₃. All distribution studies were carried out in duplicate and the data were reproducible within an error limit of ±5%.

Computational methods

Gas phase geometries of the free ligand (OBDA) and its Am³⁺ complex were optimized at the GGA level of density functional theory (DFT) by using Becke's exchange functional^{11a} in conjunction with Perdew's correlation functional^{11b} (BP86) with



the generalized gradient approximation (GGA) where 60 electron core pseudopotentials (ECPs) along with the corresponding def-SV(P) basis set were selected for the Am^{3+} ion. All other lighter atoms were treated at the all electron (AE) level. All the calculations were performed using the TURBOMOLE program package.^{11c,d}

Notes and references

- 1 J. L. Swanson, in *Science and Technology of tributyl phosphate*, ed. W. W. Schultz, L. L. Burger, J. D. Navratil and K. P. Bender, CRC Press Inc., Boca Raton, 1984, vol. III.
- 2 (a) Actinide and Fission Product Partitioning and Transmutation: Status and Assessment report, OECD/NEA, Paris, 1999; (b) Potential Benefits and Impacts of Advanced Nuclear Fuel Cycles with Actinide Partitioning and Transmutation, in *Nuclear Science*, OECD/NEA, Paris, 2011; (c) V. Anastasov, M. Betti, F. Boisson, F. Depisch, F. Houlbreque, R. Jeffree, I. Khamis, S. Lattemann, J. C. Miquel, S. Nisan and P. K. Tewari, Status of Minor Actinide Fuel Development, IAEA Nuclear Energy Series No. NF-T-4.6, 2009; (d) J. O. Denschlag, M. C. Duijvestijn, Th. Ethvignot, F. J. Hambisch, J. Katakura, Yu. V. Kibkalo, M. Lammer, T. Liu, V. M. Maslov, R. W. Mills, A. C. Wahl and S. V. Zhdanov, Fission Product Yield Data for the Transmutation of Minor Actinide Nuclear Waste, IAEA-TECDOCSTI/PUB/1286, 2008; (e) V. Smirnov, V. Sobolev, J. Somers, R. Srivenkatesan, A. Stanculescu, V. Subbotin, A. Surenkov, T. Suzuki, M. Szieberth, S. Taczanowski, J. Tommasi, I. Tretiakov, K. Tucek, J. Uhlir, D. Vidovic, H. Wider, S. Wang, Y. Wu, R. Zakirov, Q. Zeng and S. Zheng, Advanced Reactor Technology Options for Utilization and Transmutation of Actinides in Spent Nuclear Fuel, IAEA-TECDOC-1626, 2009.
- 3 (a) L. B. Kumbahre, D. R. Prabhu, G.R. Mahajan, S. Sriram, V. K. Manchanda and L. P. Badheka, *Nucl. Technol.*, 2002, **139**, 253; (b) V. K. Manchanda and P. N. Pathak, *Sep. Purif. Technol.*, 2004, **35**, 85; (c) G. R. Mahajan, D. R. Prabhu, V. K. Manchanda and L. P. Badheka, *Waste Manage.*, 1998, **18**, 125.
- 4 (a) X. Liu, J. Liang and J. Xu, *Solvent Extr. Ion Exch.*, 2004, **22**, 163; (b) S. Tachimori and H. Nakamura, *J. Nucl. Sci. Technol.*, 1982, **19**, 326; (c) E. P. Horwitz, D. G. Kalina, L. Kaplan, G. W. Mason and H. Diamond, *Sep. Sci. Technol.*, 1982, **17**, 1261; (d) E. P. Horwitz and D. G. Kalina, *Solvent Extr. Ion Exch.*, 1984, **2**, 179; (e) J. N. Mathur, M. S. Murli, P. R. Natarajan, L. P. Badheka, A. Banerji, A. Ramanujam, P. S. Dhami, V. Gopalakrishnan, R. K. Dhumwad and M. K. Rao, *Waste Manage.*, 1993, **13**, 317.
- 5 (a) Y. Sasaki, Y. Sugo, S. Suzuki and S. Tachimori, *Solvent Extr. Ion Exch.*, 2001, **19**, 91; (b) S. A. Ansari, P. N. Pathak, V. K. Manchanda, M. Hussain, A. K. Prasad and V. S. Parmar, *Solvent Extr. Ion Exch.*, 2005, **23**, 463; (c) G. Modolo, H. Asp, C. Schreinemachers and H. Vijgen, *Solvent Extr. Ion Exch.*, 2007, **25**, 703; (d) S. J. Ansari, P. Pathak, P. K. Mohapatra and V. K. Manchanda, *Chem. Rev.*, 2012, **112**, 1751; (e) S. Manohar, J. N. Sharma, B. V. Shah and P. K. Wattal, *Nucl. Sci. Eng.*, 2007, **156**, 96; (f) P. Deepika, K. N. Sabharwal, T. G. Srinivasan and P. R. Vasudeva Rao, *Solvent Extr. Ion Exch.*, 2010, **28**, 184; (g) Z. X. Zhu, Y. Sasaki, H. Suzuki, S. Suzuki and T. Kimura, *Anal. Chim. Acta*, 2004, **527**, 163; (h) H. Suzuki, Y. Sasaki, Y. Sugo, A. Apichaibuol and T. Kimura, *Radiochim. Acta*, 2004, **92**, 463; (i) V. Kumar, A. Kumar, S. Mondal, J. N. Sharma, R. C. Hubli, P. K. Wattal and A. K. Suri, *Sep. Purif. Technol.*, 2012, **98**, 118; (j) D. Magnusson, B. Christiansen, J. P. Glatz, R. Malmbeck, G. Modolo, D. Serrano-Purroy and C. Sorel, *Solvent Extr. Ion Exch.*, 2009, **27**, 26; (k) J. N. Sharma, R. Ruhela, K. N. Harindaran, S. L. Mishra, S. K. Tangri and A. K. Suri, *J. Radioanal. Nucl. Chem.*, 2008, **278**, 173.
- 6 (a) J. Ravi, A. S. Suneesh, T. Prathibha, K. A. Venkatesan, M. P. Antony, T. G. Srinivasan and P. R. Vasudeva Rao, *Solvent Extr. Ion Exch.*, 2011, **29**, 86; (b) D. Jańczewski, D. N. Reinhoudt, W. Verboom, C. Hill, C. Allignol and M. T. Duchesne, *New J. Chem.*, 2008, **32**, 490; (c) M. T. Murillo, A. G. Espartero, J. Sánchez-Quesada, J. de Mendoza and P. Prados, *Solvent Extr. Ion Exch.*, 2009, **27**, 107.
- 7 (a) M. Iqbal, J. Huskens, W. Verboom, M. Sypula and G. Modolo, *Supramol. Chem.*, 2010, **22**, 827; (b) Y. Sasaki, Y. Kitatsuji, Y. Sugo, Y. Tsubata, T. Kimura and Y. Morita, *Solvent Extr. Res. Dev.*, 2012, **19**, 51; (c) Y. Sasaki, M. Ozawa, T. Kimura and K. Ohashi, *Solvent Extr. Ion Exch.*, 2009, **27**, 378; (d) L. Wu, Y. Fang, Y. Jia, Y. Yang, J. Liao, N. Liu, X. Yang, W. Feng, J. Ming and L. Yuan, *Dalton Trans.*, 2014, **43**, 3835; (e) P. K. Mohapatra, A. Sengupta, M. Iqbal, J. Huskens, S. V. Godbole and W. Verboom, *Dalton Trans.*, 2013, **42**, 8558.
- 8 To the best of our knowledge, this type of diamide hydrolysis in acid media is not reported. But, the amide hydrolysis by the carboxy-group of substituted maleamic acids is known. See: A. J. Kirby and P. W. Lancaster, *J. Chem. Soc., Perkin Trans. 2*, 1972, 1206.
- 9 For this study OBDA **1c** was chosen because of its relatively simpler ^1H NMR spectra.
- 10 Synthetic procedure for complex of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with OBDA **1c**: A solution of $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (85.6 mg, 0.2 mmol, 1 eq.) in a mixture of $\text{CH}_2\text{Cl}_2/\text{MeOH}$ (90 : 10) was added to a solution of OBDA **1c** (326 mg, 0.8 mmol, 4 eq.) in CH_2Cl_2 . The reaction mixture was stirred at room temperature for 2 d. The resulting solution was evaporated and the residue was triturated with petrol several times to remove excess OBDA **1c**. The residual product is the complex of Eu with OBDA **1c** which was used for all the analyses.
- 11 (a) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098; (b) J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8822; (c) *TURBOMOLE is a program package developed by the Quantum Chemistry Group at the University of Karlsruhe, Germany*, 1988; (d) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165.

