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A novel highly selective ligand for separation of actinides and lanthanides in the nuclear fuel cycle. Experimental verification of the theoretical prediction†

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We have predicted earlier by DFT simulation that tridentate O,N,O-donor cyclic dilactams (**B**) belonging to the family of pyridine-2,6-dicarboxamides are much more selective and efficient extractants for the separation of lanthanides and actinides than open-structure pyridine-2,6-dicarboxamides due to the higher degree of "ligand preorganization". In the present work, three new ligands of type (**B**) were synthesized. Extraction experiments showed that, in line with the data from DFT simulation, these ligands have 5–6-fold higher selectivity for the separation of an Am^{3+}/Eu^{3+} pair and provide distribution coefficients D which are by three orders of magnitude higher than those for the related parent ligands with an open structure. Determination of the solvate numbers (SNs) for Eu^{3+} and Am^{3+} cations by slope analysis has shown that the stoichiometry of complexes, in the form of which these ions pass from the aqueous into the organic phase, depends to a considerable extent on the polarity of the organic solvent. Strongly polar solvents ($\varepsilon > 20$) extract these cations mainly in the form of 1 : 1 complexes $LM(NO_3)_3$ having according to the DFT simulation the largest dipole moments ($\mu = 18.6$–19.7 D). The solvents of low polarity ($\varepsilon \leq 10$) extract these cations mainly in the form of less polar 2 : 1 complexes $L_2M(NO_3)_3$ ($\mu \approx 1.6$ D). For solvents of intermediate polarity fractional values of solvate numbers were obtained which indicates the coexistence of complexes $LM(NO_3)_3$ and $L_2M(NO_3)_3$ in the organic phase.

Introduction

The separation of minor actinides (Am, Cm, Np) and lanthanides by liquid–liquid extraction is one of the most difficult problems that arise upon spent nuclear fuel reprocessing.[2–5] Significant progress in this field has been achieved using heterocyclic N-donor ligands as extractants.[2,6–14] Polydentate ligands containing soft nitrogen and hard oxygen donor centers such as pyridine-2,6-dicarboxamides,[15–20] 2,2′-bi-pyridyl-6,6′-dicarboxamides,[21–24] 1,10-phenanthroline-2,9-dicarboxamides,[24–30] and (2,2′:6′2″-terpyridine)-6,6″-dicarboxamides[31–33] are very promising for actinide and lanthanide separation. The most important characteristics of extractants are the distribution ratios (D) of Ln^{3+} and An^{3+} ions between organic and aqueous phases and the separation factors ($SF_{An/Ln} = D_{An}/D_{Ln}$). The selectivity of ligands for the separation of An and Ln is usually estimated by the $SF_{Am/Eu}$ value. The search for extractants with a higher selectivity is a challenging task.

Pyridine-2,6-dicarboxamides (**A**, Scheme 1) form complexes of different stoichiometries with lanthanides and actinides. A large number of 1 : 2 complexes[31–35] and 1 : 3 complexes[36–39] of lanthanides with pyridine-2,6-dicarboxamides have been obtained and characterized by X-ray diffraction. Several uranyl complexes of a 1 : 1 metal-to-ligand stoichiometry have been synthesized and studied by X-ray analysis[40–42] as well, but to the best of our knowledge no single 1 : 1 complex of lanthanides with pyridine-2,6-dicarboxamides has been isolated so far.

The composition of the complexes in the form of which the cations of lanthanides and actinides pass from an acidic

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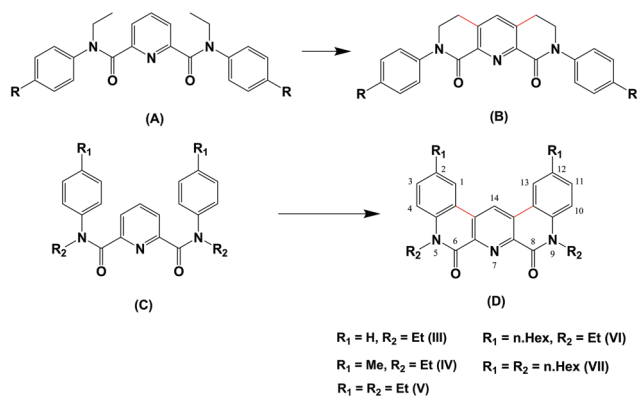
Scheme 1 Cyclic dilactams (**B**) and (**D**) are conformationally rigid analogues of pyridine-2,6-dicarboxamides (**A**) and (**C**).

aqueous solution into the organic phase, depends on many factors. Hudson et al.[43] were the first to establish that pyridine-2,6-dicarboxamides containing only alkyl radicals at the amide nitrogen atoms (ethyl, n-butyl, isobutyl) do not extract actinides and lanthanides. Shimada et al.,[15] after studying the extraction of lanthanides with chloroform from nitric acid solutions with N,N'-dimethyl-N,N'-diphenyl-pyridine-2,6-dicarboxamides (**I**), showed that they have a high extraction capacity for lanthanides. The study of the cation distribution ratios (D) as a function of the concentrations of nitric acid and organic ligands ("slope analysis") showed that metals are extracted into chloroform mainly as the $L_3M(NO_3)_3$ complexes. The calculated solvate numbers which are 2.8 for La and 2.9 for Gd suggest $L_2M(NO_3)_3$ complexes to coexist along with the 1 : 3 complexes in the organic phase for these metals. Babain et al.[16] as well as Alyapyshev et al.[18] have studied the extraction of Am and Eu by pyridine dicarboxamides with various substituents at the amide nitrogen atoms using 1,2-dichloroethane, m-nitrobenzotrifluoride (F-3), chloroform, phenyltrifluoromethylsulfone (FS-13) and bis-tetrafluoropropyl ether of diethyleneglycol (F-8) as organic diluents, varying the concentration of nitric acid from 1 M to 6 M. The composition of the extracted complexes was found to vary significantly depending on the structure of the extractant, the type of diluent, and the HNO_3 concentration. Thus, the solvate numbers were found to be 1.07 ± 0.01 for Am^{3+} and 1.23 ± 0.01 for Eu^{3+} cations when N,N'-diethyl-N,N'-di(p-ethylphenyl)-pyridine-2,6-dicarboxamide (**II**) was used as the extractant from 3 M HNO_3. This suggests the preferential formation of $LM(NO_3)_3$ complexes. When using 1,2-dichloroethane and chloroform as the organic phases, the solvate numbers for both metals under these conditions turned out to be close to 2.0. With an increase in the HNO_3 concentration from 1 M to 6 M, there was a marked increase in the solvate numbers to 1.8 for Am^{3+} and to 2.1 for Eu^{3+} in F-3. These results were confirmed by Bubeníková et al.[20] The solvate numbers for Eu^{3+} under extraction from acidic solutions by (**II**) increased from 1.2 to 2.0 in FS-13, from 1.3 to 2.1 in F-3, and from 2.0 to 2.6 in chloroform with an increase in the nitric acid concentration from 1 M to 6 M. A high increase in

the distribution ratios for lanthanides and americium was observed upon an increase in the HNO_3 concentration in all these studies.[15–20] All N,N'-dialkyl-N,N'-diaryl-pyridine-2,6-dicarboxamides show moderate selectivity in the separation of actinides and lanthanides ($SF_{Am/Eu} \approx 6$).

A rapid development in quantum chemistry techniques coupled with a rapid improvement in computer technology offered new opportunities to perform calculations of the structure and properties of complex molecular systems containing 4f- and 5f-elements with high-level theoretical methods to give reliable results, allowing direct comparison of the calculated parameters with experimental data. In the last three decades more than a hundred studies devoted to theoretical modelling of the processes of extraction and separation of lanthanides and actinides have been performed. DFT was used most frequently in calculations, since it adequately describes the structures and energies of formation of lanthanide and actinide complexes with donor organic ligands. DFT simulation makes it possible to reproduce correctly the effects of substituents in the polydentate ligand on the binding constants and selectivity. The state of the art in this rapidly developing field is reflected in reviews[44,45] and in several recent studies.[46–49]

We have performed earlier[1] DFT simulation of pyridine-2,6-dicarboxamides and their complexes $(A)M(NO_3)_3$ (M = Am, Eu). The calculations showed that the increase in the conformational rigidity of the ligand skeleton by closing lactam rings (transformation of the open structure **A** into structure **B**, Scheme 1) should lead to the increase in the selectivity factor $SF_{Am/Eu}$ by about one order of magnitude due to a higher degree of "ligand preorganization". Similar effects have been observed and discussed in the literature more than once.[46,50–57]

The main goal of the present work was to verify experimentally our theoretical prediction. For this purpose, we decided to synthesize cyclic dilactams belonging to the family of pyridine-2,6-dicarboxamides and to study their extraction properties.

The synthesis of dilactams **B** has not been described in the literature but a quite simple preparation protocol has been developed by Majumadar et al.[58] for dilactam (**III**) (type **D**, Scheme 1).

In this paper we performed the DFT simulation of dilactam (**IV**) and its complexes with Am^{3+} and Eu^{3+} to estimate $SF_{Am/Eu}$ for the ligands of this type. Afterwards, we synthesized dilactams (**V**), (**VI**), and (**VII**). The n-Hexyl substituents were attached to the 2 and 12 positions of dilactam (**VI**) and to the 2, 5, 9 and 12 positions of dilactam (**VII**) in order to increase the solubility of these ligands in organic solvents.

Experimental

Commercially available reagent-grade $Eu(NO_3)_3·6H_2O$, pyridine-2,6-dicarboxylic acid, 4-ethylacetanilide, N-ethylaniline, N-ethyl(4-hexyl)aniline, caproic acid and m-nitro(trifluoromethyl)benzene (Lancaster) (F-3) were used as received. All

experiments were performed in dry solvents. THF was dried by successive distillation over calcium hydride and lithium aluminum hydride. DMF was distilled over calcium hydride. Column chromatography was performed on Macherey-Nagel Silica 60 (0.063–0.2 mm). ^{152}Eu and ^{241}Am radionuclides were purchased from Isotope Company (Russia).

NMR spectra were recorded on a Bruker Avance 600 spectrometer. FT-IR spectra were recorded on a ThermoNicolet IR-200 spectrometer in KBr pellets. ES-HRMS were recorded on an Orbitrap Elite spectrometer (Thermo Fischer Scientific, Bremen). MALDI-TOF mass spectra were recorded on a Bruker Autospec II spectrometer.

Calculation details

As in our previous studies[1,29] we used first-principles DFT (GGA PBE), scalar-relativistic theory,[59] and large relativistic full-electron basis set consisting of: {2,1}/{6,2} for H; {3,2,1}/{10,7,3} for C, N, and O; {4,3,1}/{15,11,3} for Cl; {9,8,6,3,1}/{30,29,20,14,6} for Eu, and {10,9,7,4,1}/{34,33,24,18,6} for Am.[60] The geometries of ligand (**IV**) and complexes $LM(NO_3)_3$, $[L_2M(NO_3)_2]^+$, and $L_2M(NO_3)_3$ (M = Eu, Am, L = (**IV**)) were completely optimized for the gas phase conditions. The stationary points were identified by the analysis of Hessians. The statistical formulae for a rigid rotator and harmonic oscillator were used to calculate thermodynamic functions (Gibbs energy, G) at 298.15 K. The atomic charges were calculated according to Hirshfeld.[61] All calculations were performed at the MBC-100K Cluster of the Joint Supercomputer Center (JSCC, Moscow) using the PRIRODA program developed by D. N. Laikov.[62]

Synthesis of ligands

Ligands (**V**)–(**VII**) were prepared from pyridine-2,6-dicarboxylic acid dichloride as the starting compound using the modified protocol proposed by Majumar *et al.*[58] for the synthesis of compound (**III**) (Scheme 2).

Given here as a typical example is the procedure for the preparation of dilactam (**VII**). The protocols for the synthesis

Scheme 2 Synthesis of cyclic dilactams (**V**)–(**VII**).

of dilactams (**V**) and (**VI**) and for the preparation of the starting di(bromophenyl)-pyridine-2,6-dicarboxamides and the complex of (**VII**)$_2$La(NO$_3$)$_3$ (**VIII**) are presented in the ESI.†

2,5,9,12-Tetra(*n*-hexyl)benzo[*f*]quinolino[3,4-*b*][1,7]naphthyridine-6,8(5*H*,9*H*)-dione monohydrate (VII). A mixture of pyridine-2,6-dicarboxylic acid N,N'-di(*n*-hexyl)-N,N'-di(2-bromo-4-hexylphenyl)diamide (9.66 g, 0.012 mol), potassium acetate (2.33 g, 0.024 mol), tetrabutylammonium bromide (7.66 g, 0.024 mol), and palladium acetate (0.321 g, 12 mol% of the starting diamide) in dry DMF (480 mL) was stirred under an argon atmosphere for 16 h at 110 °C. The mixture was diluted with water (700 mL) and extracted three times with dichloromethane. The organic extracts were washed with water, dried with potassium carbonate, and evaporated. The dry residue was suspended in hexane (50 mL) and filtered. The filtered residue was washed with hexane (2 × 30 mL). The filtrate was left to stand for a day in a freezer and the powdered precipitate that formed was filtered off. The filtrate was washed with hexane (10 mL), and the filtered portions of the target substance were combined and dried in an oil-pump vacuum for 6 h at 90–100 °C to yield 3.50 g (45%) of compound (**VII**) as a light-yellow powder, m.p. 145 °C (in an Ar sealed capillary).

^{1}H NMR (CDCl$_3$), 600 MHz: 8.91 (s, 2H), 7.52 (d, 2H), 7.31 (d, 2H), 4.21 (s, 4H), 2.90 (t, 4H), 1.76 (dt, 8H), 1.47 (s, 8H), 1.31 (m, 16H), 0.92 (m, 12H).

^{13}C NMR (CDCl$_3$), 150 MHz: 158.21, 139.73, 137.57, 134.81, 132.74, 132.13, 129.41, 126.41, 116.63, 115.33, 43.66, 35.14, 31.86, 31.82, 31.51, 29.17, 27.27, 26.66, 22.68, 22.58, 14.15, 14.03.

MS (MALDI-TOF+): m/z 651 (calcd for $[C_{43}H_{59}N_3O_2 + H]^+$ −651).

HRMS (ESI): m/z 650.4696 (calcd for $[C_{43}H_{59}N_3O_2 + H]^+$ is 650.4685), m/z 672.4522 (calcd for $[C_{43}H_{59}N_3O_2 + Na]^+$ is 672.4505).

$C_{43}H_{59}N_3O_2$ calculated: C 77.32%; H 9.20%; N 6.29%.
Found: C 77.48%; H 9.12%; N 6.33%.

Extraction experiments

The extraction experiments were carried out at the (**VI**) and (**VII**) concentrations of 10^{-3} M with indicated quantities ($\approx 10^{-9}$ M) of ^{152}Eu and ^{241}Am at 25 °C. *m*-Nitro(trifluoromethyl)benzene (F-3), chloroform, and 1,2-dichloroethane were used as organic diluents.

The organic and aqueous phases (1 mL each) were placed in 5 mL polypropylene vials. Before extraction, the organic phase was preequilibrated with a solution of nitric acid of a desired concentration. The aqueous phase contained nitric acid of a desired concentration, 1×10^{-5} M europium nitrate and was spiked with ^{241}Am or ^{152}Eu. The samples were vigorously agitated for 3 min. The phases separated after a short centrifugation for 5–10 min and aliquots (0.4 ml) were taken for the analysis. The distribution ratios were determined radiometrically. The activities of americium and europium were determined using a DeskTop InSpector-1270 scintillation γ-spectrometer designed on the basis of a well-type NaI-detector 51 × 51 mm "Canberra" Co. All of the experiments were
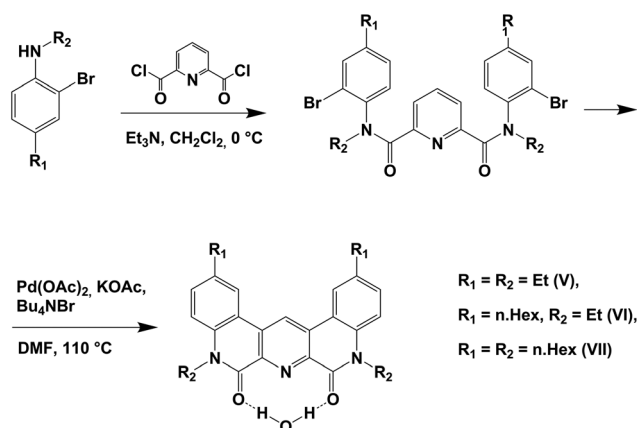
carried out in triplicate; the measurement error was less than 10% in all of the measurements. The solvate numbers upon extraction of Eu^{3+} and Am^{3+} from 3 M HNO_3 by dilactams (**VI**) and (**VII**) were determined in a standard manner using toluene, chloroform, cyclohexanol, chlorobenzene, 1,2-dichloroethane, F-3, and nitrobenzene as organic phases. The concentrations of metal ions were 10^{-5} M, and the concentrations of ligand (**VII**) in these experiments varied in the range from 10^{-3} to 10^{-2} M.

Results and discussion

Quantum chemical simulation

According to the data from X-ray diffraction studies[36,63–65] and DFT calculations,[1] pyridine-2,6-dicarboxamides (structures **A** and **C**, Scheme 1) exist in twisted nonplanar *syn–anti* conformations, while the type **D** ligands have a planar skeleton. The structure of dilactam (**IV**) and its calculated geometrical parameters are shown in the ESI.† The X-ray structure of (**V**) will be described elsewhere.

The calculated structures of the 1 : 1 complexes (**IV**)M(NO$_3$)$_3$ [M = Eu(**IX**), Am(**X**)] are shown in Fig. 1 together with the structures of the corresponding complexes of *N*,*N*′-diethyl-*N*,*N*′-diphenylpyridine-2,6-dicarboxamides (**XI**, M = Eu) and (**XII**, M = Am) from ref. 1. Dilactam (**IV**) in complexes (**IX**) and (**X**) acts as the O,N,O-tridentate ligand. The nitrate anions as bidentate ligands complement the metal coordination numbers to 9. The Cartesian atomic coordinates of complexes (**IV**)M(NO$_3$)$_3$ [M = Eu(**IX**), Am(**X**)] are given in the ESI.†

There is a good correlation between the geometrical parameters of coordination units in complexes (**IX**) and (**X**) and the parameters of the corresponding complexes of *N*,*N*′-diethyl-*N*,*N*′-diphenylpyridine-2,6-dicarboxamides (**XI**) and (**XII**) with an open structure (Table 1).

Note some special features. The interatomic M–O distances are shorter than the M–N ones. The interatomic Am–O and Am–N distances are significantly shorter than the interatomic Eu–O and Eu–N ones. Taking into account the difference in

Table 1 Geometrical parameters of coordination units, dipole moments and formation energy of 1 : 1 complexes (**IX**)–(**XII**)

	(**IV**)M(NO$_3$)$_3$		(**A**, R = H) M(NO$_3$)$_3$	
	IX (M = Eu)	**X** (M = Am)	**XI** (M = Eu)	**XII** (M = Am)
R(M–N) (Å)	2.624	2.586	2.760	2.629
R(M–O) (Å)	2.564	2.539	2.584	2.487
	2.576	2.542	2.760	2.540
φ (°)	5.5	2.4	23.3	23.9
$-\Delta E^b$ (kcal mol^{-1})	51.9	54.3	40	40.9
$-\Delta G_{298}^b$ (kcal mol^{-1})	34.7	36.9	20.7	22.1
Dipole moment, μ (D)	19.72	18.56	15.24	14.97

the ionic radii (R_{Am} = 1.09 Å; R_{Eu} = 1.066 Å),[66] one can assert that the Am–N and Am–O coordination bonds are significantly stronger than the Eu–N and Eu–O ones. The higher dipole moments of the europium complexes indicate that the metal-to-ligand bonds in these complexes are more ionic than those in the corresponding americium complexes. The M–O and M–N metal-to-ligand distances are somewhat shortened in (**IX**) and (**X**) compared to those in (**XI**) and (**XII**), which suggests strengthening of the coordination M–N and M–O bonds. An interesting feature of lanthanide and actinide complexes with the conformationally labile pyridine-2,6-dicarboxamides (**A**) and 1,10-phenanthroline-2,9-dicarboxamides[29] is that the metal atoms do not lie in the planes of aromatic rings.[1,29] The shifts in the angles of the metal ions from the ligand planes φ (Table 1) in complexes (**IX**) and (**X**) of the structurally rigid planar ligand (**IV**) are much smaller. The total electronic formation energies and the Gibbs formation energies of complexes (**IX**) and (**X**) were calculated as the differences between the corresponding values for ligand (**IV**) and nitrates M(NO$_3$)$_3$ as described previously for (**XI**) and (**XII**)[1] (eqn (1)):

$$L + M(NO_3)_3 \rightarrow LM(NO_3)_3 \tag{1}$$
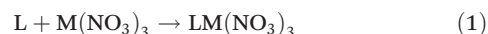
Several minima were localized on the potential energy surfaces for complexes (**IV**)$_2$M(NO$_3$)$_3$ (M = Eu, Am). The global minimum corresponds to the neutral complexes (**XIII**) and (**XIV**) (Fig. 2) where the coordination spheres of americium and europium ions besides two O,N,O-tridentate ligands include three bidentate nitrates complementing the coordination number of each ion to 12. Their formation energies (according to eqn (2)) and the geometrical parameters of coordination sites are given in Table 2. It should be specially
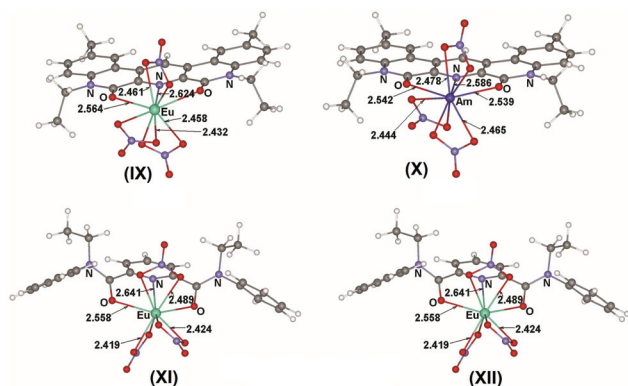

Fig. 1 Calculated structures of (**IV**)Eu(NO$_3$)$_3$ (**IX**), (**IV**)Am(NO$_3$)$_3$ (**X**), and complexes of *N*,*N*′-diethyl-*N*,*N*′-diphenylpyridine-2,6-dicarboxamides (**XI**) and (**XII**) from ref. 1.
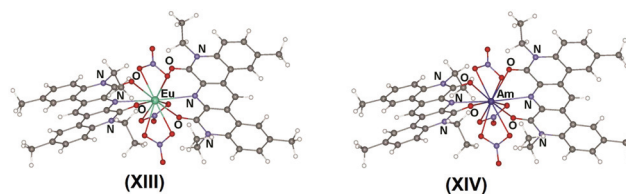

Fig. 2 Calculated structures of (**IV**)$_2$Eu(NO$_3$)$_3$ (**XIII**) and (**IV**)$_2$Am(NO$_3$)$_3$ (**XIV**).

Table 2 Geometrical parameters of coordination units, dipole moments and formation energies of the 2 : 1 complexes (XIII) and (XIV)
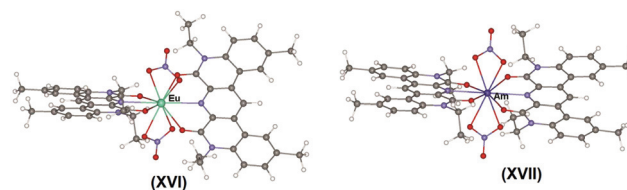
	XIII (M = Eu)	**XIV** (M = Am)
R(M–N) (Å)	2.729; 2.723	2.739; 2.687
R(M–O) (Å)	2.823; 2.833;	2.725; 2.811;
	2.798; 2.711	2.804; 2.643
φ (°)	12.7; 13.0	12.5; 13.1
$-\Delta E^{\mathrm{b}}$ (kcal mol^{-1})	60.9	63.5
$-\Delta G_{298}^{\mathrm{b}}$ (kcal mol^{-1})	27.4	29.2
Dipole moment, μ (D)	1.566	1.565

Fig. 3 Structures of cations [(IV)$_2$Eu(NO$_3$)$_2$]$^+$ (XVI) and [(IV)$_2$Am(NO$_3$)$_2$]$^+$ (XVII).

noted that the dipole moments of complexes (XIII) and (XIV) dramatically decrease for complexes (IX) and (X).

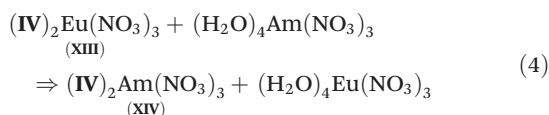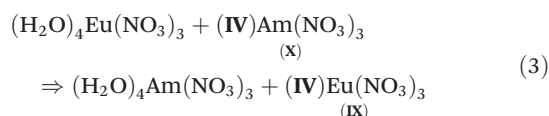$$2L + M(NO_3)_3 \rightarrow L_2M(NO_3)_3 \qquad (2)$$
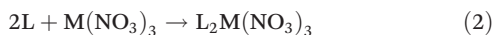
The type of structure obtained in the calculations for complexes (XIII) and (XIV) is exactly the same as in the stable complex of N,N'-dimethyl-N,N'-diphenylpyridine-2,6-dicarboxamide (I) with lanthanum trinitrate (I)$_2$La(NO$_3$)$_3$ (XV) which was synthesized and studied by X-ray diffraction by Fujiwara et al.[36] In this complex, the inner coordination sphere of the La^{3+} ion contains two O,N,O-tridentate diamides and three bidentate NO$_3$-anions which complement the coordination number of the metal up to 12. In other diamide complexes of lanthanides and actinides, the coordination numbers usually do not exceed 10, which is due to the spatial requirements of bulky ligands. But the coordination number 12 is quite typical of lanthanide and actinide complexes with macrocyclic polydentate ligands (crown ethers, cryptands and cyclic Schiff bases).[67] Since the coordination spheres of Eu^{3+} and Am^{3+} cations in the 12-coordinated complexes (XIII) and (XIV) are more crowded than that in the 9-coordinated complexes (IX) and (X), the bond lengths would vary to reduce the steric hindrance. Indeed, the M–N coordination bonds in complexes (XIII) and (XIV) are 0.2 Å longer and the M–O bonds are 0.24 Å longer than those in (IX) and (X) complexes, which suggest weakening in metal-to-ligand bonding. The same effect was observed by Fujiwara et al.[36] in complex (XV). In NMR experiments, they recorded a rapid ligand exchange between complex (XII) and the free ligand (I) in an acetonitrile solution at room temperature. The most other complexes of lanthanides with pyridine-2,6-dicarboxamides are ionic. According to the X-ray diffraction data, the coordination numbers of metals in them are 9, and as a rule, in complexes of the composition L$_2$MX$_3$ one or two anionic ligands X, and in complexes of the composition L$_3$MX$_3$ all three anionic ligands X are in the outer coordination sphere of the metal. In aqueous solutions such complexes dissociate into ions. The calculated structures of cations [(IV)$_2$M(NO$_3$)$_2$]$^+$ (M = Eu (XVI); M = Am (XVII)) are shown in Fig. 3.

The calculated Gibbs formation energies $\Delta G_{298}^{\mathrm{b}}$ of complexes (IV)M(NO$_3$)$_3$ and (IV)$_2$M(NO$_3$)$_3$ (Tables 1 and 2) are more than 10 kcal mol^{-1} higher than those of the pyridine-2,6-dicarboxamide (A) complexes (XI) and (XII). The formation constants of complexes increase exponentially with an increase in $\Delta G_{298}^{\mathrm{b}}$. If we assume that the distribution ratios (D) in extrac-

tion experiments increase linearly with an increase in the formation constants, and if we use a correct approach for simulation, then the metal distribution ratios for the dilactam **D** complexes should be at least two orders of magnitude higher than those demonstrated by the open-structure pyridine-2,6-dicarboxamides (A) under similar conditions.

To estimate the separation factor SF$_{\mathrm{Am/Eu}}$ in the extraction experiments, we considered two equilibria (3) and (4). The structures of Eu and Am aqua complexes with nitrate anions (H$_2$O)$_4$Eu(NO$_3$)$_3$ and (H$_2$O)$_4$Am(NO$_3$)$_3$ have been studied and their formation energies have been calculated by the authors of ref. 68 and by us[1] previously.

$$(H_2O)_4Eu(NO_3)_3 + \underset{(X)}{(IV)Am(NO_3)_3}$$
$$\Rightarrow (H_2O)_4Am(NO_3)_3 + \underset{(IX)}{(IV)Eu(NO_3)_3} \qquad (3)$$

$$\underset{(XIII)}{(IV)_2Eu(NO_3)_3} + (H_2O)_4Am(NO_3)_3$$
$$\Rightarrow \underset{(XIV)}{(IV)_2Am(NO_3)_3} + (H_2O)_4Eu(NO_3)_3 \qquad (4)$$

The Gibbs energies $\Delta G_{298}^{\mathrm{eq}}$(Am–Eu) for these equilibria were calculated as the differences between the respective values of the initial and final products. The selectivity factors estimated by using the standard formula (eqn (4)) are given in Table 3.
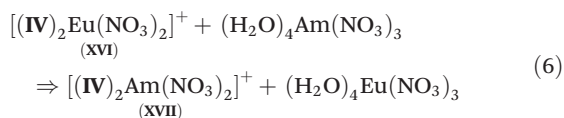
$$-RT \ln \mathrm{SF}_{\mathrm{Am/Eu}} = \Delta G_{298}^{\mathrm{eq}}(\mathrm{Am–Eu}) \qquad (5)$$

The calculations were performed for the gas phase conditions, i.e. taking no account of solvation effects. Therefore, the calculated selectivity factors SF$_{\mathrm{Am/Eu}}$ have to be used only as rough qualitative evaluation. However, both models under consideration clearly show that cyclic dilactams must be much more selective and efficient extractants for the separation of lanthanides and actinides. The complexation between the metal and ligands occurs at the interface between the organic and aqueous phases. If the cationic complexes (XVI) and (XVII)

Table 3 Gibbs energies $\Delta G_{298}^{\mathrm{eq}}$(Am–Eu) and separation factors SF$_{\mathrm{Am/Eu}}$ for the equilibria (3) and (4), and for the hypothetical equilibrium (6)

Equation	$\Delta G_{298}^{\mathrm{eq}}$(Am–Eu) (kcal mol^{-1})	SF$_{\mathrm{Am/Eu}}$
(3)	2.2	40.1
(4)	1.8	20.9
(6)	3.8	606

are produced in the aqueous phase, they pass into the organic phase, likely in the form of tight ion pairs but not as un-solvated ions. Nevertheless, it is of interest to estimate the separation factor for the hypothetical equilibrium (6) as well.

$$[(\textbf{IV})_2\text{Eu}(\text{NO}_3)_2]^+ + (\text{H}_2\text{O})_4\text{Am}(\text{NO}_3)_3$$
$$\underset{(\textbf{XVI})}{}$$
$$\Rightarrow [(\textbf{IV})_2\text{Am}(\text{NO}_3)_2]^+ + (\text{H}_2\text{O})_4\text{Eu}(\text{NO}_3)_3 \qquad (6)$$
$$\underset{(\textbf{XVII})}{}$$

The estimated values (Table 3) are much higher than for two "more realistic" models (eqn (3) and (4)) under consideration. This result suggests that an increase in the polarity of the organic phase into which the extraction takes place should contribute to an increase in the selectivity, since the degree of ionicity of the extracted complexes must increase.

Extraction experiments

Solubility of new dilactams (V)–(VIII) in *m*-nitro(trifluoro-methyl)benzene (F-3). A sufficiently high solubility in organic solvents is a necessary requirement for using a donor ligand as an effective extractant. The solubility of dilactam (**V**) with four ethyl substituents in the 2, 5, 9 and 12 positions in F-3 does not exceed 2×10^{-4} M. The increase in the length of the alkyl chain in these positions leads to a significant increase in the solubility. It is 3×10^{-3} M for **VI**. As concerns the solubility of **VII** in F-3, it exceeds 0.05 M.

Comparison of the extraction capacities of the cyclic dilactam (VII) and open-structure diamide (II). Fig. 4 shows the distribution ratios D of Am^{3+} and Eu^{3+} cations when 0.1 M (**II**) in F-3 was used as the extractant at varying concentrations of nitric acid from 1 to 6 M. When dilactam (**VII**) is used as an extractant, similar D values are reached at concentrations that are more than two orders of magnitude lower than the concentrations of (**II**) (see Fig. 4). To evaluate the

increase in the extraction capacity for ligand (**VII**) compared to (**II**), we estimated the metal distribution ratios D for equal ligand concentrations (0.001 M) in F-3. The values for 0.001 M (**II**) in F-3 ($D_{Am} \sim 0.014$ and $D_{Eu} \sim 0.003$) were obtained by the linear extrapolation of the plot of D *vs.* (**II**) concentration using known solvation numbers.[19] Thus, the transition from the con-formationally labile open-structure pyridine-2,6-dicarbox-amides to the conformationally rigid dilactams results in an increase in the Am^{3+} and Eu^{3+} distribution ratios by more than three orders of magnitude, which agrees completely with the theoretical prediction.

Comparison of the extraction capacities of dilactams (VI) and (VII). The values of the distribution coefficients D and the separation factors SF$_{Am/Eu}$ for Am^{3+} and Eu^{3+} extraction with dilactams (**VI**) and (**VII**) in three organic diluents are shown in Table 4.

The two dilactams (**VI**) and (**VII**) differ in the length of alkyl substituents in the 5 and 9 positions only. As can be seen, the increase in the length of the alkyl radical leads to an increase in the distribution coefficients, but practically does not change the separation factors SF$_{Am/Eu}$. The SF$_{Am/Eu}$ takes values from 20–30 which agrees very well with the theoretically predicted values (see Table 4). The SF$_{Am/Eu}$ values increase somewhat with increasing the nitric acid concentration. In this respect, rigid dilactams are different from the open-structure pyridine-2,6-dicarboxamides. Previously, Alyapyshev *et al.*[18] found that for the latter the selectivity factors SF$_{Am/Eu}$ decrease with an increase in the nitric acid concentration.

Solvent effect on the composition of extractable complexes. Slope analysis was used to determine the composition of the complexes in the form of which the cations pass into the organic phase upon extraction with dilactam (**VII**). The solvate numbers (SNs) for several solvents of different polarities are given in Table 5. The distribution factors D for each solvent and the plots in the coordinates lg(D)/lg[L] are given in the ESI.† One can see that, in solvents of both aromatic and ali-phatic nature with a dielectric constant below 10, complexes of the 2 : 1 composition pass predominantly into the organic phase. For highly polar solvents, F-3 and nitrobenzene, the extractable complexes have the 1 : 1 composition. For cyclo-hexanol (CyOH), which has an intermediate permittivity, the solvate number is 1.6, which suggests the coexistence of 1 : 1 and 2 : 1 complexes.

In this particular case, this influence of solvent polarity is most likely due to the dramatic difference in the dipole moments of the 1 : 1 and 2 : 1 complexes (compare data in Tables 1 and 2) which is due to the different mutual arrange-ments of the anionic ligands in their structures (see Fig. 1 and 2). Strongly polar solvents stabilize more polar (**VII**)M(NO$_3$)$_3$ complexes, while less polar complexes of (**VII**)$_2$M(NO$_3$)$_3$ are predominant in solvents of lower polarity.

Thus, the transition from the conformationally flexible pyri-dine-2,6-dicarboxamides with the open structure **A** or **C** to the conformationally rigid structure **D** results not only in an increase in the Am^{3+} and Eu^{3+} distribution ratios by more than three orders of magnitude, but also in 5-fold increase in the
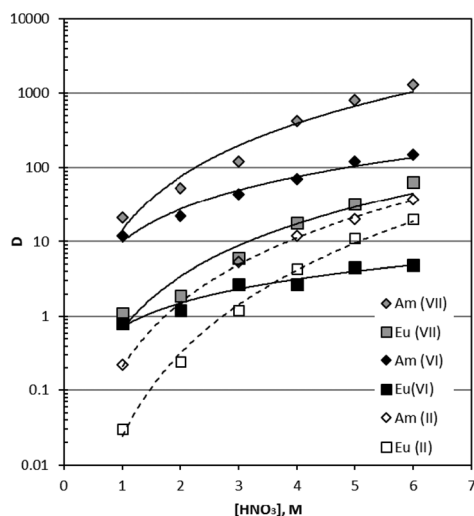

Fig. 4 Am and Eu distribution ratios D as a function of the nitric acid concentration. The extractants are 0.001 M (**VII**) in F-3 and 0.1 M (**II**) in F-3.

Table 4 Distribution ratios of Am^{3+} and Eu^{3+} and separation factors $SF_{Am/Eu}$ for dilactams (**VII**) and (**VI**)/in parentheses/at different concentrations of nitric acid for F-3, $CHCl_3$ and $C_2H_4Cl_2$ used as diluents (concentrations of (**VII**) and (**VI**) are 0.001 M)

[HNO₃], M	F-3			CHCl₃			C₂H₄Cl₂		
	D_{Am}	D_{Eu}	$SF_{Am/Eu}$	D_{Am}	D_{Eu}	$SF_{Am/Eu}$	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
1	21(12)	1.1(0.8)	19(15)	0.3(0.2)	0.04(0.10)	8(20)	2.0(3)	0.18(0.2)	11(15)
2	53(22)	1.9(1.2)	18(18)	0.7(0.5)	0.07(0.04)	10(13)	6(7)	0.5(0.4)	12(18)
3	120(44)	6.0(1.9)	20(23)	4(1)	0.36(0.08)	11(13)	14(14)	1.4(0.8)	10(18)
4	420(70)	18(2.7)	25(26)	20(1.9)	2.3(0.18)	9(11)	60(24)	5(—)	12(—)
5	800(120)	32(4.5)	25(27)	35(3.8)	3.5(0.36)	10(11)	120(49)	9(2)	14(25)
6	1300(150)	64(4.9)	27(31)	50(8.5)	4.2(0.79)	12(11)	150(22)	13(—)	12(—)

Table 5 Solvate numbers for dilactam (**VII**) in different diluents calculated by slope analysis. Aqueous phase – 3 M nitric acid

Solvent	Dipole moment, μ (D)	ε	$SN(Am^{3+})$	$SN(Eu^{3+})$
PhMe	0.36	2.38	1.71 ± 0.02	1.76 ± 0.05
CHCl₃	1.15	4.81	1.96 ± 0.02	1.61 ± 0.03
PhCl	1.54	5.6	1.83 ± 003	1.77 ± 0.04
CyOH	1.46	13.4	1.60 ± 0.04	1.61 ± 0.03
C₂H₄Cl₂	1.90	10.42	2.07 ± 0.04	2.04 ± 0.05
F-3	3.73	22.3	0.91 ± 0.02	1.00 ± 0.04
PhNO₂	4.28	35.0	1.13 ± 0.03	1.04 ± 0.06

separation factor $SF_{Am/Eu}$ in line with the theoretical prediction.

Conclusions

In the present work, we verified the theoretical prediction made earlier[1] by means of DFT simulation that the tridentate O,N,O-donor cyclic dilactams **D** belonging to the family of pyridine-2,6-dicarboxamides are much more selective and efficient extractants for the separation of actinides and lanthanides than pyridine-2,6-dicarboxamides **C** with an open structure due to a higher degree of "ligand preorganization". Three new ligands of this type were synthesized. Extraction experiments showed that, in line with the data from the DFT simulation, these ligands have 5–6-fold higher selectivity for the separation of an Am^{3+}/Eu^{3+} pair and provide distribution coefficients D which are by three orders of magnitude higher than those for the related parent ligands with an open structure. Determination of the solvate numbers (SNs) for Eu^{3+} and Am^{3+} cations by slope analysis showed that the stoichiometry of complexes, in the form of which these ions pass from the aqueous into the organic phase, depends to a considerable extent on the polarity of the organic solvent. Strongly polar solvents ($\varepsilon > 20$) extract these cations mainly in the form of 1:1 complexes $LM(NO_3)_3$ having the largest dipole moments ($\mu = 18.6$–19.7 D) according to the DFT simulation. The low-polarity solvents ($\varepsilon \leq 10$) extract these cations mainly in the form of less polar 2:1 complexes $L_2M(NO_3)_3$ ($\mu = 1.6$ D). For solvents of intermediate polarity, fractional values of the solvate numbers were obtained which suggests the coexistence of complexes $LM(NO_3)_3$ and $L_2M(NO_3)_3$ in the organic phase.

From the results obtained in this work and from the extensive literature data, it is clear that the most important characteristics of the extractants, the distribution coefficient D and the separation factor $SF_{Am/Eu}$, are determined not only by the structure of the ligands, but also to a considerable extent by the effects of solvent, acid concentration and, to a lesser extent, by several other factors. The accumulated experience in the quantum chemical modeling of extraction processes[45] indicates a need to take into account such effects in calculations. In this paper, a rather rough gas phase approximation is used in which these effects are not taken into consideration. Despite this fact, very good agreement between the calculated and experimental values is obtained. In this connection, it is rather important to understand why this approximation works well in this particular case and in our earlier work.[1] The reason seems to be that in this case we consider the complexes of europium and americium whose molecules are completely identical in their shape. They differ very little in geometric parameters and dipole moments, and the electronic configurations of their central ions are the same. As a consequence, the solvate shells of these complexes must also have a very close structure, and the effects of the medium, which can be very significant in value, must be very close or coincident, which allows one to ignore them without losing the prediction accuracy. Naturally, such a simplified approach has very narrow limits of applicability. It should also be emphasized that the evaluation of solvent effects at the level of the continuum models (PSM, COSMO) also has certain limitations, and the need to develop more adequate cluster models is very relevant. Despite this, the high efficiency of quantum chemical modeling of actinide and lanthanide extraction and separation using the approaches and methods which already exist is beyond doubt.

Acknowledgements

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