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CMPO-substituted calix[6]- and calix[8]arene extractants for the separation of An^{3+}/Ln^{3+} from radioactive waste

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Abstract—Three calix[6]arene derivatives (**1a**–**c**) and two calix[8]arene derivatives (**2a**,**b**), with six and eight CMPO residues, respectively, attached to the narrow/lower rim via ether links, were synthesised. Preliminary liquid–liquid extraction studies for Eu(III) and Am(III) from aqueous nitric acid to *o*-nitrophenylhexyl ether reveal remarkable properties with respect to efficiency and selectivity, especially for the *tert*-butylcalix[6]arene derivative with a $–(CH_2)_3–$ spacer.

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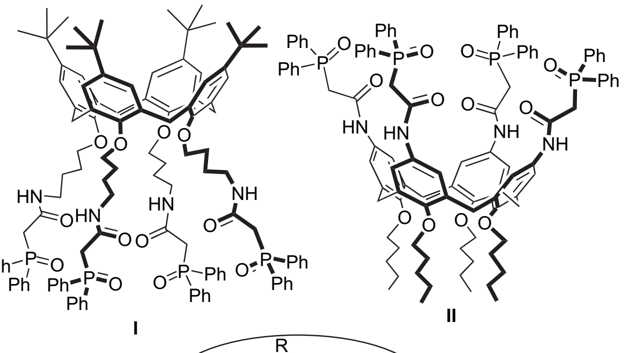
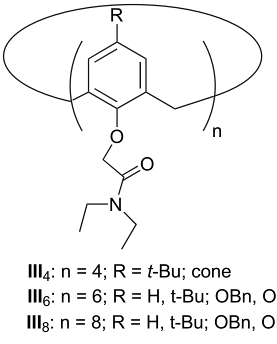
1. Introduction

The separation of actinides (An) from lanthanides (Ln) is an urgent and important problem for the management of waste resulting from the reprocessing of fuels of nuclear plants. In fact, spent nuclear fuel contains moderate amounts of long-lived minor actinides (Np, Am, Cm) together with many fission products, among which lanthanides represent one of the major components.[1] The transmutation of actinides into short-lived radionuclides has been proposed for the conditioning of such waste,[1–3] which requires their separation from lanthanides. Organophosphorous ligands like CMPO (carbamoylmethyl-phosphine oxide), used in the TRUEX process, phosphine oxides or dialkylphosphoric acids (TALSPEAK) are quite efficient extractants for An from acidic media. The introduction of CMPO binding groups onto the lower[4] or upper[5,6] rim of calix[4]arenes (**I**, **II**), as well as onto other polyvalent scaffolds,[7,8] increases not only the extraction efficiency of trivalent metal ions by more than 2 orders of magnitude, but also improves the selectivity, in some cases.[9] The original idea of pre-organising four CMPO functional groups on a calix[4]arene fixed in the cone conformation[4,5] was further strengthened by the fact that blocking the calix[4]arene platform in a 'rigid cone' led to an increase (about 10-fold) in extraction ability, although not in selectivity.[6] On the other hand, we have recently shown for a series of calixarene-based amide ligands, that not only the efficiency of alkali and alkaline-earth metal ion complexation greatly changes, passing from the calix[4]arene to the calix[6]- and calix[8]arene scaffold but also the selectivity





III_4: n = 4; R = *t*-Bu; cone
III_6: n = 6; R = H, t-Bu; OBn, OMe
III_8: n = 8; R = H, t-Bu; OBn, OMe

Keywords: Actinides/lanthanides separation; CMPO; Calixarenes; Conformational properties; Radioactive waste treatment; Actinides complexation.
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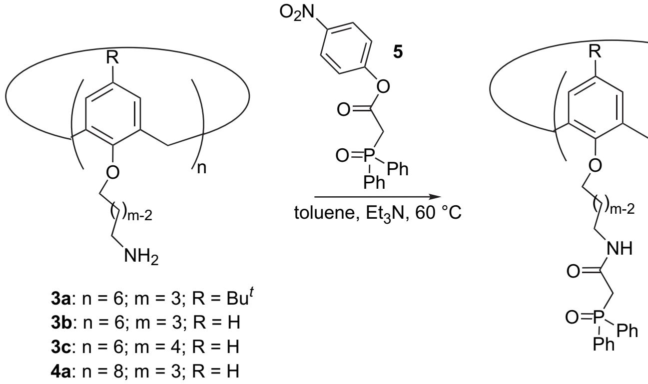
within and between group IA and IIA cations is affected.[10,11] For example, while the tetramide of *p-tert*-butylcalix[4]arene (**III$_4$**) has a slight preference for Sr^{2+} over Na^+ complexation, the amides of *p-tert*-butylcalix[6]arenes (**III$_6$**) and –calix[8]arenes (**III$_8$**) present a high selectivity[11,12] for Sr^{2+} over Na^+, which makes them promising candidates for the selective removal of strontium radionuclides from radioactive wastes.[13] Therefore, it seems attractive to introduce CMPO binding sites/groups on the larger and more flexible calix[6]- and calix[8]arene scaffolds in order to study how the enlargement of the macrocyclic scaffold and the increase of the number of ligating functions influence the efficiency in trivalent metal ion complexation and the An^{3+}/Ln^{3+} selectivity. We report in this paper the synthesis of the new ligands and results of An(III) liquid–liquid extraction experiments.

2. Synthesis and structures of the ligands

In order to attach CMPO binding groups at the lower rim of calix[6]- and calix[8]arenes we needed the hexaamino- (**3**) and octaamino- (**4**) calixarene derivatives. These compounds were synthesised according to known procedures.[14] Reaction of compounds **3** and **4** with the *p*-nitrophenyl active ester **5** in toluene at 60 °C gives the CMPO ligands **1** and **2** in 46–78% yields (Scheme 1). The introduction of the CMPO units on the calixarene skeleton was confirmed by the presence of the correct molecular peaks in the mass spectra (ESI-MS), of the typical doublet at δ 3.5–3.4 (J=10–14 Hz) for the $POCH_2CO$ protons in the ^1H NMR spectra and by elemental analyses. In the mass spectra, clear peaks of the mono- and/or di-sodium complexes were obtained. The ^1H NMR spectra of these compounds in $CDCl_3$ are usually very broad at rt. Only octamer **2b** shows a sharp spectrum under these conditions with the appearance of several singlets and doublets for the methylene bridges ($ArCH_2Ar$) and for the aromatic protons of the calixarene, indicating the presence of different conformations slowly interconverting on the NMR timescale. On the other hand, **2b** shows, in DMSO-d_6, even at rt a rather sharp spectrum, which becomes even sharper at 80 °C showing a singlet around δ 3.85 for the methylene bridges, which indicates a fast interconversion between different conformers. This indicates that the presence of several slowly interconverting conformers in $CDCl_3$ at rt, is due, not only to the presence of bulky groups both at the upper and lower rim, but also to the formation of NH$\cdots$O=P (O=C) hydrogen bonds between the CMPO functions.[15] All the spectra of compounds **1**–**2** were therefore recorded in CD_3OD or DMSO-d_6 (see Section 5). Moreover, the spectrum of *p-tert*-butyl hexamer **1a** is much broader than those of its *p*-H-analogues **1b** or **1c** even in DMSO at 100 °C, indicating that the presence of large substituents at both rims of the calixarene skeleton decreases the rate of conformational interconversion especially for this compound.

3. Liquid–liquid extraction studies

Aqueous solutions of Am^{3+} and Eu^{3+} with different concentrations of HNO_3 were extracted with 10^{-3} M solutions of the various ligands in NPHE (*o*-nitrophenylhexyl ether). Since in the case of *p*-H calixarenes **1b**, **1c** or **2a** a precipitate formed at the interphase, extraction experiments, with these compounds, were performed at a ligand concentration of 10^{-4} M. For ligand **1b**, however, at $c(HNO_3)$=2–4 M a precipitate was still observed. This seems to indicate that *tert*-butyl or benzyloxy groups at the upper rim of these large macrocycles considerably help to solubilise the complexes. The distribution coefficients ($D_M=[M]_{org}/[M]_{aq}$) for the extraction experiments are reported in Table 1 and compared with those of compounds **I** and **II**. For all the newly synthesised CMPO ligands **1** and **2**, both D_{Eu} and D_{Am} remarkably increase with increasing HNO_3 concentration in the water layer, in agreement with what was observed with the lower rim substituted calix[4]arene-based CMPO ligands **I**, while the *D*-values for upper rim derivatives of type **II** usually show a maximum for $c(HNO_3)$=2 M. This increase can be explained by the assumption that the nitrate anion is co-extracted together with Am(III) and Eu(III) thus increasing the D_M according to the equation $D_M=K_{ex}[L]^m[NO_3^-]^n$. Interestingly, the data also show that for all the ligands D_{Am} is higher than D_{Eu}. The most efficient ligand seems to be **1a**, but considering that **1b** and **2a** were studied at 10 times higher dilution than **1a**, their D_{Am} values are also rather high. Although these preliminary tests do not allow to determine D_{Am} (and consequently $S_{Am/Eu}$) precisely at $c(HNO_3)$>1 M, it is evident that compound **1a** shows an interesting Am^{3+} over Eu^{3+} selectivity ($S_{Am/Eu}$>3), which seems to increase with



3a: n = 6; m = 3; R = Bu^t
3b: n = 6; m = 3; R = H
3c: n = 6; m = 4; R = H
4a: n = 8; m = 3; R = H
4b: n = 8; m = 3; R = OBn

1a: n = 6; m = 3; R = Bu^t, η = 66%
1b: n = 6; m = 3; R = H, η = 59%
1c: n = 6; m = 4; R = H, η = 78%
2a: n = 8; m = 3; R = H, η = 55%
2b: n = 8; m = 3; R = OBn, η = 46%

Scheme 1. Synthesis of ligands **1** and **2**.

Table 1. D_M values and selectivity $S_{Am/Eu}$ for the extraction of Am^{3+} and Eu^{3+} from an aqueous solution into a NPHE solution of ligands **1** and **2** and **I–II** at different HNO_3 concentrations (*T*=25 °C)

Ligand	[L] (M)		[HNO_3] (M)						
			0.001	0.01	0.1	1	2	3	4
1a	10^{-3}	D_{Eu}	0.29	0.56	5.1	26.4	27.7	35.5	26.6
		D_{Am}	0.44	0.82	11.1	>100	>100	>100	>100
		$S_{Am/Eu}$	1.5	1.5	2.2	>3	>3	>3	>3
1b	10^{-4}	D_{Eu}	1.6	0.6	1.2	5.9	[a]	[a]	[a]
		D_{Am}	2.8	0.9	2.1	20.6	[a]	[a]	[a]
		$S_{Am/Eu}$	1.7	1.5	1.7	3.5			
1c	10^{-4}	D_{Eu}	0.47	0.25	0.56	3.0	nd	nd	10.6
		D_{Am}	0.85	0.34	0.95	4.5	nd	nd	20.7
		$S_{Am/Eu}$	1.8	1.4	1.7	1.5			1.9
2b	10^{-3}	D_{Eu}	[b]	7.8	9.2	21.9	nd	nd	nd
		D_{Am}	[b]	14.6	18.3	32.8	nd	nd	nd
		$S_{Am/Eu}$		1.9	2.0	1.5			
2a	10^{-4}	D_{Eu}	3.8	5.6	4.2	10.7	12.5	14.7	32
		D_{Am}	3.8	7.1	12.6	12.6	18.0	>100	[b]
		$S_{Am/Eu}$	1	1.3	3.0	1.2	1.4	>6	
I[6]	10^{-3}	D_{Eu}	nr	nr	28	33	44	48	nr
		D_{Am}	nr	nr	48	51	61	63	nr
		$S_{Am/Eu}$			1.7	1.5	1.4	1.3	
II[9]	10^{-3}	D_{Eu}	nr	nr	2.3	30	52	37	19
		D_{Am}	nr	nr	19	195	275	150	100
		$S_{Am/Eu}$			8.3	6.5	5.3	4.0	5.26

nd: not determined; nr: not reported.

[a] Important precipitation at the interphase.

[b] Content of the aqueous layer too low to allow a precise determination of *D*.

an increase of the HNO_3 concentration. Calix[6]arene-CMPO ligand **1a** is slightly more selective than the analogous derivative based on the calix[4]arene scaffold **I**, having a spacer, which is longer by one methylene group, while the extraction efficiency of the calix[4]arene derivative with the same C_3 spacer is distinctly lower.[4] Interestingly, ligand **1a** having six CMPO arms or the octameric CMPO ligands **2** are much more efficient than dendritic octa-CMPO derivatives.[16] The efficiency and selectivity obtained with the novel calix[6]arene-CMPO ligand **1a** seem close to the upper rim substituted calix[4]arene **II**.

Extraction experiments for compound **1a** were also performed in the presence of the lipophilic dicarbollide anion (BrCosan), which is known to facilitate cation extraction.[17,18]

The results reported in Table 2 indicate that dicarbollide highly facilitates the extraction of M^{3+} ions into the organic phase. Especially at low nitric acid concentration ($[HNO_3] \leq 0.1$ M) the D_M values increased by up to 2 orders of magnitude (cf. Tables 1 and 2). Surprisingly, D_{Eu} slightly decreases under these conditions at high nitric acid concentration ($[HNO_3] \geq 0.1$ M).

4. Conclusions and outlook

Calix[6]- and calix[8]arenes, bearing at their lower rim six or eight CMPO functions attached via alkylether groups, are easily prepared in reasonable to good yields using well-established synthetic protocols. Although the ligands are less preorganised than calix[4]arene derivatives, the increased number of CMPO functions leads to remarkable properties for the extraction of Eu and Am from aqueous nitric acid to *o*-nitrophenylhexyl ether. Such properties are superior to those shown by dendritic octa-CMPO-derivatives of calix[4]arenes. The extraction studies are presently extended to other calixarene scaffolds and to other organic solvents.

5. Experimental

5.1. General remarks

Melting points were determined with an electrothermal apparatus in sealed capillaries under nitrogen. ^1H and ^{13}C NMR spectra were recorded with Bruker spectrometers AC300 (^1H: 300 MHz, ^{13}C: 75 MHz) or AMX400 (^1H: 400 MHz) with TMS as an internal standard. Mass

Table 2. D_M values and $S_{Am/Eu}$ for the extraction of Am^{3+} and Eu^{3+} from an aqueous solution ([BrCosan]=3×10^{-3} M) into a NPHE solution of ligand **1a** at 25 °C at different [HNO_3]

	[HNO_3] (M)						
	0.001	0.01	0.1	1	2	3	4
D_{Eu}	31.9	46.0	40.8	33.6	39.6	36.8	28.5
D_{Am}	>100	>100	>100	>100	>100	>100	>100
$S_{Am/Eu}$	>3	>2	>2	>3	>2	>2	>3

spectra were obtained in the ESI mode with a Micromass 4LCZ spectrometer (capillary voltage = 3 kV, cone voltage = 60 V, extractor voltage = 3 V, source block temperature = 80 °C, desolvation temperature = 150 °C, cone and desolvation gas (N$_2$) flow rates = 1.6 and 8 l/min, respectively). TLC was performed on precoated silica gel Merck 60 F$_{254}$. All the reactions were carried out under nitrogen.

5.2. General procedure for the synthesis of CMPO derivatives

To a solution of amino calix[*n*]arene (0.2 mmol) in dry toluene (40 ml) were added *p*-nitrophenyl (diphenylphosphoryl)-acetate (1.5 equiv per amino group) and triethylamine (1.5 equiv per amino group). The mixture was stirred overnight at 60 °C. Then toluene was evaporated under reduced pressure and dichloromethane (50 ml) was added. The organic phase was washed several times with 10% NaOH (5×40 ml) and dried with anhydrous magnesium sulfate. The dichloromethane was evaporated under reduced pressure to obtain the pure product.

5.2.1. 37,38,39,40,41,42-Hexakis{3-[(diphenylphosphoryl)-acetamide]-propoxy}-*p*-*tert*-butylcalix[6]arene (1a). Yield: 66%. Mp: 133–134 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, 373 K): δ=7.89–7.13 (m, 60H, PhH), 6.89 (br s, 12H, ArH), 3.80 (br s, ArCH$_2$Ar), 3.45 (d, J=14.0 Hz, 12H, POCH_2CO), 3.40 (br s, 12H, OCH_2CH$_2$CH$_2$), 3.12 (br s, 12H, OCH$_2$CH$_2$CH_2), 1.37 (br s, 12H, OCH$_2$CH_2CH$_2$), 1.05 (br s, 54H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz, 300 K): δ=164.2 (CO), 156.3 (Ar$_{ipso}$), 144.4 (Ar$_{para}$), 134.0–128.3 (Ph and Ar), 70.1 (OCH$_2$CH$_2$CH$_2$), 39.1 (OCH$_2$CH$_2C$H$_2$), 30.9 (C(CH$_3$)), 34.8 (C(CH$_3$)), 33.5 (CH$_2$P), 29.4 (ArCH$_2$Ar), 29.3 (OCH$_2C$H$_2$CH$_2$). ESI-MS (+): m/z=2790 (100%) [M+Na]$^+$. $C_{168}H_{192}N_6O_{18}P_6$ (2769.26): calcd C 72.87, H 6.99, N 3.03; found C 72.80, H 6.96, N 3.08.

5.2.2. 37,38,39,40,41,42-Hexakis{3-[(diphenylphosphoryl)-acetamide]-propoxy}calix[6]arene (1b). Yield: 59%. Mp: 136–138 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, 363 K): δ=7.78–7.42 (m, 60H, PhH), 6.82 (d, J=7.56 Hz, 12H, ArH$_{meta}$), 6.70 (t, J=7.56 Hz, 6H, ArH$_{para}$), 4.07 (br s, 12H, ArCH_2Ar), 3.45 (d, J=10.1 Hz, 12H, POCH_2CO), 3.38 (br s, 12H, OCH$_2$CH$_2$CH_2), 2.48 (br s, 12H, OCH_2CH$_2$CH$_2$), 1.47 (br s, 12H, OCH$_2$CH_2CH$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz, 300 K): δ=165.2 (CO), 158.6 (Ar$_{ipso}$), 133.9–128.2 (Ph and Ar), 122.4 (Ar$_{para}$), 73.1 (OCH$_2$CH$_2$CH$_2$), 39.7 (OCH$_2$CH$_2C$H$_2$), 32.3 (CH$_2$P), 30.6 (ArCH$_2$Ar), 30.5 (OCH$_2C$H$_2$CH$_2$). ESI-MS (+): m/z=2454 (100%) [M+Na]$^+$. $C_{144}H_{144}N_6O_{18}P_6$ (2432.61): calcd C 71.10, H 5.97, N 3.45, P 7.64; found C 71.08, H 5.94, N 3.49, P 7.61.

5.2.3. 37,38,39,40,41,42-Hexakis{4-[(diphenylphosphoryl)-acetamide]-butoxy}calix[6]arene (1c). Yield: 78%. Mp: 146–147 °C. ^{1}H NMR (CD$_3$OD, 400 MHz, 300 K): δ=7.8–7.4 (m, 60H, PhH), 7.2–6.8 (m, ArH), 3.90 (br s, 12H, ArCH_2Ar), 3.44 (br s, 24H, POCH_2CO and OCH_2CH$_2$CH$_2$CH$_2$), 3.18 (br s, 12H, OCH$_2$CH$_2$CH$_2$CH_2), 1.40–1.31 (m, 24H, OCH$_2$CH_2CH_2CH$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz, 300 K): δ=164.02 (CO), 156.3 (Ar$_{ortho}$), 134.0–128.1 (Ph and Ar), 123.2 (Ar$_{para}$), 71.9 (OCH$_2$CH$_2$CH$_2$CH$_2$), 38.6 (OCH$_2$CH$_2$CH$_2C$H$_2$), 31.2 (CH$_2$P), 30.5 (ArCH$_2$Ar), 26.9 and 25.6 (OCH$_2C$H$_2C$H$_2$CH$_2$). ESI-MS (+): m/z=2538 (100%) [(M+Na)]$^+$. $C_{150}H_{156}N_6O_{18}P_6$ (2516.77): calcd C 71.59, H 6.25, N 3.34; found C 71.65, H 6.32, N 3.45.

5.2.4. 49,50,51,52,53,54,55,56-Octakis{3-[(diphenylphosphoryl)acetamide]-propoxy}calix[8]arene (2a). Yield: 55%. Mp: 180 °C (dec). ^{1}H NMR (CD$_3$OD, 400 MHz, 300 K): δ=7.70–7.31 (m, 80H, PhH), 7.25–7.11 (m, 16H, ArH$_{meta}$), 6.82–6.70 (m, 8H, ArH$_{para}$), 3.93 (br s, 16H, ArCH_2Ar), 3.51 (br s, 16H, POCH_2CO), 3.30 (s, 16H, OCH_2CH$_2$CH$_2$), 3.13 (br s, 16H, OCH$_2$CH$_2$CH_2), 1.60 (br s, OCH$_2$CH_2CH$_2$). ^{13}C{^{1}H} NMR (CD$_3$OD, 75 MHz, 300 K): δ=167.2 (CO), 156.7 (Ar$_{ipso}$), 135.7–129.0 (Ph and Ar), 125.5 (Ar$_{para}$), 72.5 (OCH$_2$CH$_2$CH$_2$), 38.6 (OCH$_2$CH$_2C$H$_2$), 32.3 (CH$_2$P), 31.4 (ArCH$_2$Ar), 31.0 (OCH$_2C$H$_2$CH$_2$). ESI-MS (+): m/z=1643.6 (100%) [M+2Na]$^{2+}$. $C_{192}H_{192}N_8O_{24}P_8$ (3243.48): calcd C 71.10, H 5.97, N 3.45; found C 71.18, H 5.90, N 3.54.

5.2.5. 5,11,17,23,29,35,41,47-Octakis[phenylmethoxy]-49,50,51,52,53,54,55,56-octakis{3-[(diphenylphosphoryl)-acetamide]-propoxy}calix[8]arene (2b). Yield: 46%. Mp: 129–130 °C. ^{1}H NMR (DMSO-d_6, 400 MHz, 353 K): δ=7.75–7.36 (m, 80H, PhH), 7.03–7.01 (m, 40H, OCH$_2$BnH), 6.17 (m, 16H, ArH$_{meta}$), 4.56 (br s, 16H, OCH_2Bn), 3.85 (br s, 16H, ArCH_2Ar), 3.63 (t, J=6.1 Hz, 16H, OCH_2CH$_2$CH$_2$), 3.41 (d, J=14.0 Hz, 16H, POCH_2CO), 3.13–3.10 (m, 16H, OCH$_2$CH$_2$CH_2), 1.71 (t, J=6.4 Hz, 16H, OCH$_2$CH_2CH$_2$). ^{13}C{^{1}H} NMR (DMSO-d_6, 75 MHz, 300 K): δ=164.2 (CO), 153.8 (Ar$_{ipso}$), 136.7–127.2 (Ar, Ph and Bn), 114.2 (Ar$_{para}$), 71.2 (OCH$_2$CH$_2$CH$_2$), 68.7 (OCH$_2$Bn), 39.1 (OCH$_2$CH$_2C$H$_2$), 32.5 (CH$_2$P), 30.9 (ArCH$_2$Ar), 30.0 (OCH$_2C$H$_2$CH$_2$). ESI-MS (+): m/z=2068 (100%) [M+2Na]$^{2+}$. $C_{248}H_{240}N_8O_{32}P_8$ (4092.47): calcd C 72.79, H 5.91, N 2.74; found C 72.70, H 5.98, N 2.82.

5.3. Extraction experiments

Liquid–liquid extraction experiments were performed by dissolving the ligand at the desired concentration (10^{-4} or 10^{-3} M) in NPHE (*o*-nitrophenylhexyl ether) and mixing the organic phase with an aqueous phase containing Am(III) and Eu(III) nitrates at different HNO$_3$ concentrations. Am(III) and spiked Eu(III) nitrate aqueous solutions were prepared in order to have a radioactivity in the range 1500–2000 kBq/l. Liquid–liquid extraction experiments were performed by shaking the same volumes of organic and aqueous phases, at the appropriate HNO$_3$ concentration, inside closed tubes placed in a thermostated cell (25±0.2 °C) for 1 h. Complete separation of the phases was ensured by spinning the tubes in a centrifuge for 5 min. Then, aliquots of aqueous and organic phases were removed for analysis by γ-spectrometry (Eurysis Mesures, Strasbourg). The measurement times were adapted to obtain a reproducibility of ±5%. The distribution coefficients, D_M, were determined as the ratio of cation γ-activity in the organic phase to cation γ-activity in the aqueous phase. The selectivity for Am(III) over Eu(III) is expressed as $S_{\mathrm{Am/Eu}} = D_{\mathrm{Am}}/D_{\mathrm{Eu}}$.

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