



Communication

Anionic alkyl diglycoldiamides with covalently bonded cobalt bis(dicarbollide)(1–) ions for lanthanide and actinide extractions

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ABSTRACT

Ionic diamides composed of a N,N'-dialkyl diglycolyl complexing group and two cobalt bis(dicarbollide)(1–) anions were synthesized with the aim to develop efficient extraction agents for liquid–liquid extraction of polyvalent cations, i.e. lanthanides and actinides from high-level activity nuclear waste. Compounds of general formulation $[(N,N-(8-CH_2-CH_2O)_2-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})-3,3'-Co)(N,N'-R)NCOCH_2)_2O]Na_2$, where R = *n*-C₄H₉, *n*-C₈H₁₇, *n*-C₁₂H₂₅ and 1-C₆H₄-4-CH₃ (**1–4**), were prepared and characterized by combination of ¹¹B ¹H, ¹³C NMR spectroscopy, ESI-MS, HPLC and other techniques. Effects of different nitrogen substitution in the structures of **1–4** on the extraction properties were tested. The study resulted in the observation that the compounds are significantly (2–3 orders in magnitude) more efficient extractants for Eu(III) and Am(III) than synergic mixtures of organic N,N'-tetra *n*-octyl diglycolic acid diamide (TODGA) and chlorinated cobalt bis(dicarbollide) at the same concentrations of both groups. Low polar mixtures of *n*-dodecane (D) and hexyl methyl ketone (HMK) can be applied as an auxiliary solvent for extraction, replacing thus the polar and less environmentally friendly nitro-, fluoro- and chloro- solvents used in the current dicarbollide liquid–liquid extraction process.

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1. Introduction

Spent nuclear fuel produces high-active liquid waste. One of the possibilities how to reduce the volume of the spent nuclear waste is the reprocessing consisting of the separation of the most dangerous radionuclides, particularly minor actinides (^{241,243}Am, ²⁴⁵Cm, ²³⁷Np) responsible for the long-term radiotoxicity [1]. Several hydrometallurgical processes based on the use of extractants containing amidic groups have been designed during the last decades for the extraction of trivalent α-emitters. The currently most studied processes are based on malonamides (DIAMEX process) [1–5] or (N,N-dialkyl-carbamoylmethyl)-dialkyl phosphine oxides (CMPO) (TRUEX process) [5–10] as the organic ionophores. More recently, another efficient extractant, N,N,N',N'-tetra(*n*-octyl)-3-oxapentane-1,5-diamide (tetra-*n*-octyl-diglycolamide, TODGA) [11,12], has appeared among them to attain great attention due to good efficiency and high stability (ARTIST process). All these organic ionophores are able to bind tightly the M³⁺ cations in chelate complexes by donor atoms of the uncharged ligand. Usually, nitrates are co-extracted as counter-ions, which can result in the decrease of extraction efficiency.

Halogen derivatives of the singly charged cobalt bis(dicarbollide)(1–) ion [(1,2-C₂B₉H₁₁)-3-Co(III)][–] were designed more than

30 years ago for efficient extraction of ¹³⁷Cs⁺ and ⁹⁰Sr²⁺ (in the presence of synergist polyethylene glycol) from highly acidic nuclear waste, for more information see the recent review [13]. This robust liquid–liquid extraction procedure has been later developed into an industrial process currently called “UNEX” [14,15]. Considering the use of halogen protected cobalt bis(dicarbollide) without functional groups, difficulties still persist in the extraction of trivalent α-emitters, although some synergic mixtures with polydentate ligands were designed and tested [13,14].

In past years we have focused on covalent combinations of cobalt bis(dicarbollide) ion with functional groups that are able to bond trivalent lanthanides and actinides, particularly these containing CMPO functions, where the markedly high effect of covalent bonding of was observed [16–20]. In this paper we report in preliminary fashion on another new and efficient family of compounds consisting of molecular scaffold resembling organic TODGA molecule, but bearing two ionic cobalt bis(dicarbollide) groups. Reported are also basic effect of nitrogen modifications on the synthesis along with the first results from the extraction studies.

2. Results and discussion

In our previous papers we reported on the synthesis of reactive building blocks comprising ammonium groups attached on the ionic cobalt bis(dicarbollide) cage [16,17,21], the methods based on

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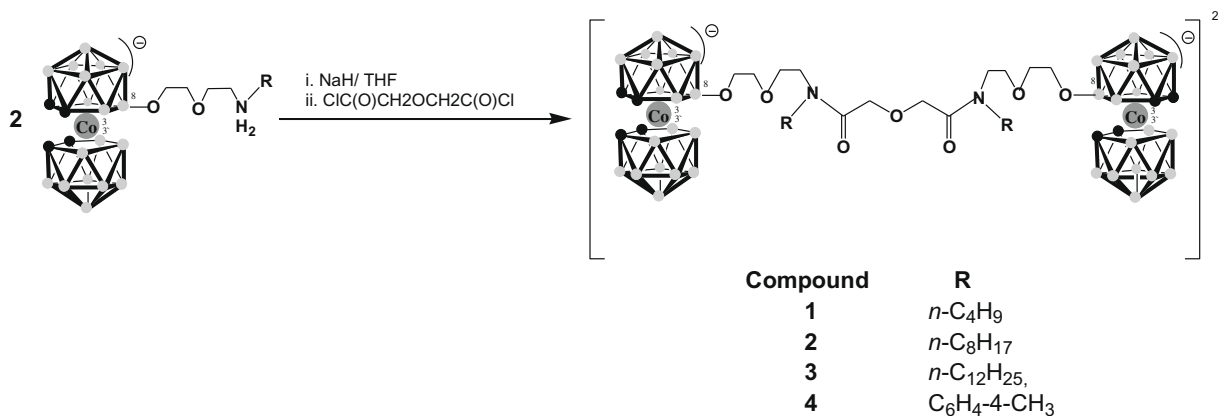
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ring opening of the reactive dioxane cobalt bis dicarbollide derivative are also summarized in a recent review article [22]. The series of compounds bearing alkylammonium group connected to cage via diethylene glycol chain proved, upon deprotonation with NaH, to react smoothly with diglycolyl acid dichloride to produce good yields of the corresponding N,N-diglycolic acid diamides (see Scheme 1). These compounds of general formula $[(N,N-(8-CH_2-CH_2O)_2-1,2-C_2B_9H_{10})(1',2'-C_2B_9H_{11})-3,3'-Co)(N',N'-R)NCOCH_2)_2O]Na_2$, therefore contain two hydrophobic cobalt bis(dicarbollide) anions in the molecule along with two alkyl/aryl ($R = n-C_4H_9, n-C_8H_{17}, n-C_{12}H_{25},$ and $1-C_6H_4-4-CH_3$) (**1–4**, see Scheme 1 and Table 1) substituents bonded at the amidic nitrogen atoms. The compounds were characterized by combination of ^{11}B , 1H and ^{13}C NMR spectroscopy and ESI-MS and other methods their purity was also assayed by HPLC methods [23,17] being better than 98%.

Extraction of trivalent cations ($^{152}, ^{154}Eu, ^{241}Am$) from aq. nitric acid solution was studied, using 2-octanone/dodecane (HMK, D, 1:1) as diluent. Table 1 contains selected data for the series of four compounds differing in alkyl/aryl substituents at the two amidic nitrogen centres. Here we report basic data measured at low concentrations of the extractants (10^{-3} M) used throughout this study in order to compare their properties even in the low acidity range. Detailed report of the extraction properties will appear in a following full paper. From the results can be seen, that all compounds are exceptionally efficient extractants. The increased length of the alkyl chain leads to a slight decrease in extraction efficiency. The highest distribution ratios were observed for *n*-butyl

group in **1**, but the difference from *n*-alkyl/aryl substituted species (**1–4**) is still relatively unimportant. Most of compounds show increased selectivity for Eu^{3+}/Am^{3+} , which is in the range 4–7 and slightly increases with HNO_3 concentrations. Exception can be found for the toluidine substituted derivative **4**, which shows no selectivity, apparently due to presence of two weakly basic nitrogen centres in the structure.

The data in Table 2 clearly show that covalent bonding of the cobalt bis(dicarbollide) ion has remarkably high (2–5 orders in magnitude) positive effect on the extraction efficiency for lanthanides/actinides, as compared to extractions with the organic TODGA or its synergic mixtures with chlorinated cobalt bis(dicarbollide). This effect is highest up to one molar HNO_3 concentration, but remains still markedly high even at 4 M acid. The data in Table 2 suggest about differences in the extraction behaviour of compound **2** and the organic TODGA. In the case of TODGA, the extractability increases with increasing HNO_3 concentrations. This can be attributed to co-extraction of NO_3^- ion together with lanthanide/actinide cation, and therefore the effective extraction is achieved only under highly acidic conditions [11,12]. In opposite, the efficiency of extractants **1–4** with cobalt bis(dicarbollide) ions decreases with increased acidity, what seems to indicate mechanism based on ion-exchange. The advantage is the significantly faster extraction kinetics observed for compound **2** covalently bound to cobalt bis(dicarbollide) cage, where the equilibrium is reached within approx. 20 min. compared to more than 24 h necessary for the synergic mixtures. A drawback is a low solubility in nonpo-



Scheme 1.

Table 1
Dependence HNO_3 concentration on extraction with extractants **1–4**.

Compound	Efficiency	$c(HNO_3)$ [M]					
		0.01	0.1	1	2	3	4
1	D_{Eu}	>100	>100	40.6	3.16	1.11	0.478
	D_{Am}	>1000	>1000	8.83	0.618	0.189	0.070
	$SF_{Eu/Am}$			4.60	5.12	5.85	6.82
2	D_{Eu}	>100	>100	19.5	1.71	0.607	0.268
	D_{Am}	>1000	>1000	5.91	0.364	0.108	0.041
	$SF_{Eu/Am}$			3.29	4.69	5.62	6.57
3	D_{Eu}	>100	>100	10.5	0.843	0.285	0.117
	D_{Am}	>1000	>1000	3.16	0.198	0.057	0.020
	$SF_{Eu/Am}$			3.32	4.26	5.03	5.77
4	D_{Eu}	>100	>100	25.6	1.83	0.573	0.165
	D_{Am}	>100	>100	28.1	1.82	0.513	0.132
	$SF_{Eu/Am}$			0.91	1.00	1.12	1.25

1×10^{-3} M extractant in HMK/D (1:1); $^{152}Eu, ^{154}Eu$ and ^{241}Am tracers, variable nitric acid concentration.

Table 2

Comparison of Eu(III) and Am(III) extraction of organic TODGA (tetra-*n*-octyl-diglycolamide), the synergic mixture of TODGA with chloroprotected cobalt bis(dicarbollide) and compound **2** with covalently bound cobalt bis(dicarbollide) anions.

Compound	Efficiency Selectivity	c(HNO ₃) [M]					
		0.01	0.1	1	2	3	4
TODGA	D_{Eu}	<0.001	<0.001	0.001	0.013	0.033	0.041
	D_{Am}	<0.001	<0.001	<0.001	0.006	0.008	0.009
	$SF_{Eu/Am}$				2.17	4.13	4.56
TODGA + cobalt bis(dicarbollide)-Cl ₆ [*]	D_{Eu}	>100	>100	0.084	0.009	0.006	0.008
	D_{Am}	>100	37.1	0.021	0.003	0.003	0.003
	$SF_{Eu/Am}$			4.00	3.00	2.00	2.67
2	D_{Eu}	>100	>100	19.5	1.71	0.607	0.268
	D_{Am}	>100	>100	5.91	0.364	0.108	0.041
	$SF_{Eu/Am}$			3.29	4.69	5.62	6.57

1×10^{-3} M extractant in HMK/D (1:1); ca 5×10^{-7} M ¹⁵²Eu, ¹⁵⁴Eu or ²⁴¹Am tracers, variable nitric acid concentration.

* 1×10^{-3} M TODGA + 2×10^{-3} M cobalt bis(dicarbollide)-Cl₆ = [(1,2-C₂B₉H₈Cl₃)₂-3,3'-Co]⁻ at the same extraction conditions described above.

lar solvents such as aliphatic hydrocarbons, nevertheless, mixtures of HMK and dodecane still represent an ecologically acceptable variant of possible diluents.

3. Conclusions

We proved in preliminary fashion, that compounds bearing two hydrophobic cobalt bis(dicarbollide) (1-) anions replacing two alkyl groups in the structure of TODGA-like extractants are synthetically feasible. Introduction of the hydrophobic anionic clusters into molecule led to significant increase in the extraction efficiency for the group separation of lanthanides and actinides given by a cooperative action of the complexing and ionic groups present within single ligating moiety. As we have shown, the $D_{M(III)}$ values in 1M HNO₃ are several orders of magnitude higher compared with synergic mixture of both components present at the same concentrations. The higher efficiency is a bit at the expense of low solubility of the ionic extractants in low polar hydrocarbons, but possibility of use of HMK/D mixture still represents an ecologically reasonable alternative of the auxiliary solvent, significantly better than the use nitrobenzene or fluorinated solvents necessary for processes employing synergic mixtures of organic ionophores and chlorinated bis(dicarbollide) [13–15].

4. Experimental

For purpose of this article, the basic reaction conditions are given valid for the whole series of compounds **1–4**. Under typical experiments, the zwitterionic ammonium derivatives [(8-RNH₂-(CH₂-CH₂O)₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)-3,3'-Co]⁰ (R = *n*-C₄H₉, *n*-C₈H₁₇, *n*-C₁₂H₂₅, -C₆H₄-4-CH₃) prepared by known general procedure [16,17] [22] (3.6 mmol) were dried in vacuum at 60 °C for 12 h, then dissolved in THF (100 ml) and treated with solid NaH (95%, 360 mg, 14.4 mmol). The slurry was stirred at room temperature for 2 h, and then diglycolyl acid dichloride (95%, Aldrich 210 μL, 1.8 mmol) in THF (10 ml) was dropwise added from syringe during 60 min. The content of the reaction flask was heated at 60 °C (bath temperature) until the spot of starting species almost disappeared on TLC (16–48 h). Ethanol (3 ml) was carefully added to the reaction mixture followed by acetic acid (0.2 ml) and the volatiles were removed in vacuum. The crude products were dissolved in CH₂Cl₂ and chromatographed on silica gel column (25 × 2.5 cm I.D., high purity silica gel Aldrich) and eluted with CH₂Cl₂ to remove small amount of the unreacted ammonium derivative and then with CH₂Cl₂-CH₃CN mixture (3:1) to elute the products. The resulting orange solids were re-crystallized from

CH₂Cl₂-hexane. Yields: Na₂**1** 1.14 g (57%); Na₂**2**: 1.97 g (88%), Na₂**3**: 1.72g (70%); Na₂**4**: 1.05 g (48%) and R_F (TLC on silica gel plates Silufol in CH₂Cl₂: CH₃CN, 3:1): 0.28, 0.33, 0.39 and 0.03, respectively. The spectral and other data for compounds characterization are given below. For analyses the anions were converted to the tetramethyl-ammonium salts by metathesis.

4.1. Data for characterization of compounds **1–4**

Na₂**1**; [(N,N-(8-CH₂-CH₂O)₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)-3,3'-Co)(N',N'-C₄H₉)NCOCH₂]₂-O]Na₂: m.p. 263–267 °C; Anal. Calc. for C₃₆H₁₀₄O₇N₄B₃₆Co (1212.28) (Me₄N)₂, H, 8.65; C, 35.67. Found H, 8.56; C, 34.98%. ¹¹B NMR (acetone-d₆, 128 MHz) δ (ppm) (J_{B-H} , Hz) 23.11 (2B, s), 4.65 (2B, d) (140), 0.35 (2B, d, B10') (168), -2.67 (2B, d, B10) (170), -4.27 (4B, d, B4',7') (159), -7.26, -7.97 (12B, 2d, B 4, 7, 9, 12, 9',12') (overlap), -17.32 (4B, d, B5',11') (177), -20.30 (4B, d, B5, 11) (187), -21.93 (B6') (overlap), -28.60 (2B, d, B6) (197); ¹H NMR: (acetone-d₆, 400 MHz) δ (ppm) 4.801, 4.754 (2 s, 4H, C(O)-CH₂-O), 4.227 (s, 8H, CH_{carb.}), 3.591 (m, 8H, CH₂-O), 3.539 (m, 4H, CH₂-N), 3.536 (br.s, 4H, CH₂-N), 3.484 (m, 4H, CH₂-O), 1.645 (m, 4H, CH₂), 1.34 (m, 4H, CH₂), 0.937 (t, $J(H-H)$ = 7.2 Hz, 6H, CH₃); ¹³C NMR{1H} (acetone-d₆, 100 MHz) δ (ppm) 171.64 (C=O), 72.95 (CH₂-O), 69.273 (CH₂-O), 54.51 (CH_{carb.}), 47.95 (CH₂-N), 47.32 (CH_{carb.}), 46.70 (CH₂-N), 29.65 (CH₂), 20.51 (CH₂), 14.11 (CH₃); M.S. (ESI⁻) 1084.36 (100%), 1093.24 (2%) [M+Na-2H]²⁻, calc. 1093.27.

Na₂**2**, [(N,N-(8-CH₂-CH₂O)₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)-3,3'-Co)(N',N'-C₈H₁₇)NCO-CH₂]₂O]Na₂: m.p. 177–181 °C; Anal. Calc. for C₄₄H₁₂₀O₇N₄B₃₆Co (1324.50) (Me₄N)₂, H, 9.13; C, 39.90. Found H, 9.02; C, 39.46%. ¹¹B NMR (acetone-d₆, 128 MHz) δ (ppm) (J_{B-H} , Hz) 23.25 (2B, s, B8), 4.27 (2B, d, B8') (140), 0.44 (2B, d, B10') (147), -2.41 (2B, d, B10) (143), -4.27 (4B, d, B4',7') (144), -7.24, -8.19 (12B, 2d, B 4, 7, 9, 12, 9',12') (overlap), -17.27 (4B, d, B5',11') (137), -20.27 (4B, d, B5, 11) (137), -21.93 (B6') (overlap), -28.47 (B6) (139). ¹H NMR: (acetone-d₆, 400 MHz) δ (ppm) 4.529 (br s, 4H, C(O)-CH₂-O), 4.238 (s, 8H, CH_{carb.}), 3.637 (m, 8H, CH₂-O), 3.508 (t, 4H, $J(H-H)$ = 3.6 Hz, CH₂-O), 3.434 (br.s, 4H, CH₂-N), 3.318 (br.s, 4H, CH₂-N), 1.67 (m, 4H, CH₂), 1.601 (m, 4H, CH₂), 1.316 (m, 16H, CH₂), 0.891 (t, 6H, CH₃). ¹³C NMR{1H} (acetone-d₆, 100 MHz) δ (ppm) 171.62 (C=O), 73.15 (CH₂-O), 69.76 (CH₂-O), 69.46 (CH₂-O), 69.22 (CH₂-O), 54.6 (CH_{carb.}), 48.07 (CH₂-N), 47.32 (CH_{carb.}), 32.06 (CH₂), 28.11 (CH₂), 27.81 (CH₂), 27.53 (CH₂), 27.54 (CH₂), 14.45 (CH₃); M.S. (ESI⁻) 1198.83 (100%), 1201.83 (10%) [M+Na-2H]²⁻, calc. 1201.88.

Na₂**3**, [(N,N-(8-CH₂-CH₂O)₂-1,2-C₂B₉H₁₀)(1',2'-C₂B₉H₁₁)-3,3'-Co)(N',N'-C₁₂H₂₅)NCO-CH₂]₂O]Na₂: m.p. 173–177 °C; Anal. Calc. for C₅₂H₁₃₆O₇N₄B₃₆Co (1436.72) (Me₄N)₂, H, 9.54; C, 43.47. Found

H, 9.42; C, 42.92%. ^{11}B NMR (acetone- d_6 , 128 MHz) δ (ppm) ($J_{\text{B-H}}$, Hz) 23.29 (2B, s, B8), 4.46 (2B, d, B8') (155), 0.47 (2B, d, B10') (141), -2.48 (2B, d, B10) (146), -4.24 (4B, d, B4',7') (154), -7.36, -7.91 (12B, 2d, B4, 7, 9, 12, 9',12') (overlap), -17.32 (4B, d, B5',11') (153), -20.25 (4B, d, B5, 11) (153), -21.96 (B6') (overlap), -28.17 (2B, d, B6) (139); ^1H NMR: (acetone- d_6 , 400 MHz) δ (ppm) 4.748 (q, 4H, C(O)-CH $_2$ -O), 4.236 (s, 8H, CH $_{\text{carb.}}$), 3.691 (br. t, 8H, CH $_2$ -O), 3.592 (m, 4H, CH $_2$ -O), 3.351 (m, 4H, CH $_2$ -N), 3.351 (br. q, 4H, CH $_2$ -N), 1.667 (m, 4H, CH $_2$), 1.604 (m, 4H, CH $_2$), 1.362 (m, 4H, CH $_2$), 1.306 (m, 24H, CH $_2$), 0.892 (t, 6H, CH $_3$); ^{13}C NMR{ ^1H } (acetone- d_6) δ (ppm) 171.63 (C=O), 73.16 (CH $_2$ -O), 69.45 (CH $_2$ -O), 69.21 (CH $_2$ -O), 54.72 (CH $_2$ -O), 48.22 (CH $_2$ -N), 47.31 (CH $_{\text{carb.}}$), 32.68 (CH $_2$), 28.11 (CH $_2$), 28.34 (CH $_2$), 28.13 (CH $_2$), 27.85 (CH $_2$), 23.37 (CH $_2$), 14.44 (CH $_3$); M.S. (ESI $^-$) 1309.08 (100%), 1315.00 (1%) [M+Na-H] $^{2-}$, calc. 1315.01.

Na $_2$ 4, [(N,N-(8-CH $_2$ -CH $_2$ O) $_2$ -1,2-C $_2$ B $_9$ H $_{10}$)(1',2'-C $_2$ B $_9$ H $_{11}$)-3,3'-Co) (1-N',N'-C $_6$ H $_4$ -4-CH $_3$),NCOCH $_2$) $_2$ O]Na $_2$: m.p. 269–273 °C; *Anal.* Calc. for C $_{42}$ H $_{100}$ O $_7$ N $_4$ B $_3$ Co (1280.32) (Me $_4$ N) $_2$ 4, H, 7.87; C, 39.40. Found H, 7.78; C, 39.88%. ^{11}B NMR (acetone- d_6 , 128 MHz) δ (ppm) ($J_{\text{B-H}}$, Hz) 23.44 (2B, s, B8), 4.62 (2B, d, B8') (128), 0.44 (2B, d, B10') (137), -2.40 (2B, d, B10) (146), -4.39 (4B, d, B4',7') (155), -7.17, -8.0 (12B, 2d, B 4, 7, 9, 12, 9',12') (overlap), -17.22 (4B, d, B5',11') (159), -20.25 (4B, d, B5, 11) (159), -21.95 (2B, d, B6') (overlap), -28.26 (2B, d, B6) (140); ^1H NMR: (acetone- d_6 , 400 MHz) δ (ppm) 7.48 (br. s, 4H, Ar), 7.256 (br. s, 4H, Ar), 4.22 (s, 4H, CH $_{\text{carb.}}$), 4.128 (s, 4H, CH $_{\text{carb.}}$), 3.936 (br.s, 4H, C(O)CH $_2$ -O), 3.624 (br.t, 12H, CH $_2$ -O), 3.49 (m, 4H, CH $_2$ -N), 2.352 (s, 6H, CH $_3$); ^{13}C NMR (acetone- d_6 , 100 MHz) δ (ppm) 171.60 (C=O), 131.49 (ArC), 128.93 (ArC), 72.54 (CH $_2$ -O), 69.50 (CH $_2$ -O), 67.86 (CH $_2$ -O), 54.54 (CH $_{\text{carb.}}$), 49.87 (CH $_2$ N), 47.39 (CH $_{\text{carb.}}$), 21.17 (CH $_3$); M.S. (ESI $^-$) 1152.92 (100%), 1159.72 (1%) [M+Na-2H] $^{2-}$, calc. 1159.77.

The extraction experiments were performed in closed screwed top test tubes using 1ml of each phase and shaking of 1 h on a horizontal shaker in a thermostated box at 25 ± 0.1 °C. After shaking, the test tubes were centrifuged and aliquots of each phase (0.5 mL) were measured using single-channel γ analyzer with NaI (TI) well-type detector. The distribution of Eu(III) and Am(III) was studied using $^{152,154}\text{Eu}$ and ^{241}Am in trace amount (radiochemical purity). All reagents and solvents used were of analytical reagent grade.

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References

- [1] C. Madic, M. Lecomte, P. Baron, B. Boullis, *Comptes Rendus Phys.* 3 (2002) 797–811.
- [2] C. Madic, M.J. Hudson, J.O. Liljenzin, J.P. Glatz, R. Nannicini, A. Facchini, Z. Kolarik, R. Odoj, *Prog. Nucl. Energy* 40 (2002) 523–526.
- [3] D. Serrano-Purroy, B. Christiansen, J.P. Glatz, R. Malmbeck, G. Modolo, *Radiochim. Acta* 93 (2005) 357–361.
- [4] A.P. Paiva, P. Malik, *J. Radioanal. Nucl. Chem.* 261 (2004) 485–496.
- [5] B. Christiansen, C. Apostolidis, R. Carlos, O. Courson, J.P. Glatz, R. Malmbeck, G. Pagliosa, K. Romer, D. Serrano-Purroy, *Radiochim. Acta* 92 (2004) 475–480.
- [6] J.N. Mathur, M.S. Murali, K.L. Nash, *Solvent Extr. Ion Exc.* 19 (2001) 357–390.
- [7] G.R. Choppin, *Solvent Extr. Res. Dev. Jpn.* 12 (2005) 1–10.
- [8] T. Fujii, K. Aoki, H. Yamana, *Solvent Extr. Ion Exc.* 24 (2006) 347–357.
- [9] R.S. Herbst, J.D. Law, T.A. Todd, *Sep. Sci. Technol.* 37 (2002) 1321–1351.
- [10] S. Belair, C. Lamouroux, M. Tabarant, A. Labet, C. Mariet, P. Dannus, *Solvent Extr. Ion Exc.* 22 (2004) 791–811.
- [11] S.A. Ansari, P.N. Pathak, V.K. Manchanda, M. Husain, A.K. Prasad, V.S. Parmar, *Solvent Extr. Ion Exc.* 23 (2005) 463–479.
- [12] S.A. Ansari, P.N. Pathak, M. Husain, A.K. Prasad, V.S. Parmar, V.K. Manchanda, *Radiochim. Acta* 94 (2006) 307–312.
- [13] J. Rais, B. Grüner, in: Y. Marcus, A.K. SenGupta (Eds.), *Solvent Extraction, Ion Exchange*, Marcel Dekker, New York, 2004, pp. 243–334.
- [14] T.A. Luther, R.S. Herbst, D.R. Peterman, R.D. Tillotson, T.G. Garn, V.A. Babain, I.V. Smirnov, E.S. Stoyanov, N.G. Antonov, *J. Radioanal. Nucl. Chem.* 267 (2006) 603–613.
- [15] J.D. Law, R.S. Herbst, D.R. Peterman, R.D. Tillotson, T.A. Todd, *Nucl. Technol.* 147 (2004) 284–290.
- [16] B. Grüner, J. Plešek, J. Bába, I. Císařová, J.F. Dozol, H. Rouquette, C. Viñas, P. Selucký, J. Rais, *New J. Chem.* 26 (2002) 1519–1527.
- [17] P. Selucký, J. Rais, M. Lučaníková, B. Grüner, M. Kvíčalová, K. Fejfarová, I. Císařová, *Radiochim. Acta* 96 (2008) 273–284.
- [18] B. Grüner, M. Kvíčalová, *J. Organomet. Chem.* 694 (2009) 1678–1689.
- [19] H.H. Dam, D.N. Reinhoudt, W. Verboom, *Chem. Soc. Rev.* 36 (2007) 367–377.
- [20] L. Mikulášek, B. Grüner, C. Danila, V. Böhmer, J. Časlavský, P. Selucký, *Chem. Commun.* (2006) 4001–4003.
- [21] V. Šícha, J. Plešek, M. Kvíčalová, I. Císařová, B. Grüner, *Dalton Trans.* (2008) 851–860.
- [22] A.A. Semioshkin, I.B. Sivaev, V.I. Bregadze, *Dalton Trans.* (2008) 977–992 (A review).
- [23] B. Grüner, Z. Plzák, *J. Chromatogr. A* 789 (1997) 497–517.