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New systems based on 2,2′-dipyridyl-6,6′-dicarboxylic acid diamides for Am–Eu separation

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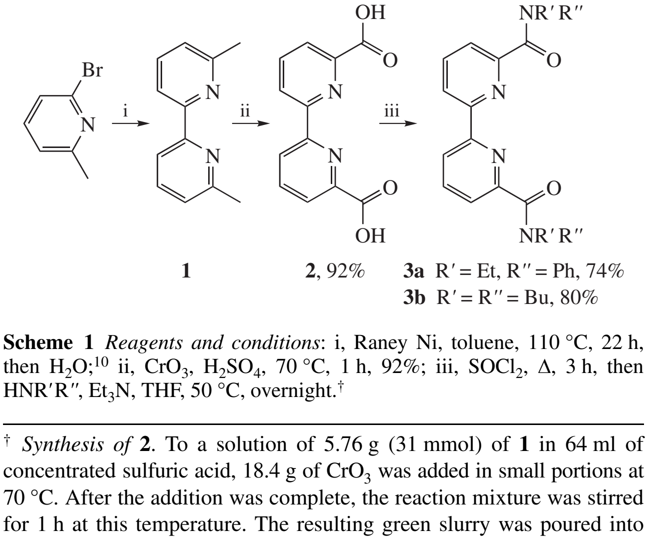
New synergistic extraction mixtures based on 2,2′-dipyridyl-6,6′-dicarboxylic acid diamides and chlorinated cobalt dicarbolide were proposed as highly effective for americium–europium separation in acidic media.

The separation of minor actinides (particularly, americium and curium) from rare earth elements is very important for reducing actinide waste volume. There are many polynitrogen compounds, which extract americium much more than europium from solutions with pH 2–4. Note that compounds such as *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine, tris(pyridyl)triazine, bis(benzimidazolyl)pyridines, tripyridine and bis(triazinyl)-pyridines have good separation factor for Am–Eu up to 1 M nitric acid, but all of them are unstable in nitric acid.[1,2] The main goal of this investigation was to find the reagent that possesses a high separation factor (SF) for actinides *vs.* lanthanides even in acidic media.

The reagents that possess high extraction ability together with high hydrolytic stability were found among dicarboxylic acids (malonic[3] and dipicolinic[4–6]) amides. The latter type of amides are the most promising agents for nuclear technology due to their high stability toward acid hydrolysis and radiolysis.[7] In 1994, Rais and Tachimori found during the study of extractive properties of mixtures of chlorinated cobalt dicarbolide (CCD) and phenanthroline that this mixture is suitable for separating Am from Eu with separation factors up to 36 at pH 3.5.[8] Mixtures of tetraalkyl or dialkyldiaryl dipicolinic diamides (DPAs) with CCD extract cesium, actinides and lanthanides from acidic solutions and strontium after addition of polyethylene glycol.[4–6] However, the $SF_{Am/Eu}$ lies in the range 2–5.4 for different DPAs–CCD compositions.[6] We propose 2,2′-dipyridyl-6,6′-dicarboxylic acid diamides as a substance of choice for Am/Eu separation. These compounds have an additional pyridine ring comparing to DPA, so they can coordinate metal ions as tetradentate ligands. Moreover, an additional nitrogen coordination centre can increase the selectivity of americium/lanthanides separation.[9]

The 2,2′-dipyridyl-6,6′-dicarboxylic acid diamides **3a** and **3b** were prepared in high yields starting from 2-bromo-6-picoline (Scheme 1).[†]



1 **2**, 92% **3a** R′ = Et, R″ = Ph, 74%
3b R′ = R″ = Bu, 80%

Scheme 1 *Reagents and conditions*: i, Raney Ni, toluene, 110 °C, 22 h, then H_2O;[10] ii, CrO_3, H_2SO_4, 70 °C, 1 h, 92%; iii, $SOCl_2$, Δ, 3 h, then HNR′R″, Et_3N, THF, 50 °C, overnight.[†]

The extraction behaviour of 2,2′-dipyridyl-6,6′-dicarboxylic acid diamides is very similar to that of DPA. We studied the extraction of americium and europium with 0.03 M **3a** in F-3[‡] from aqueous solutions with various concentrations of nitric acid. The distribution ratios (*D*) of americium were 0.01, 0.33 and 0.76 for extraction from 0.2, 0.5 and 1.0 M nitric acid, respectively. Thus, the extraction ability of pure diamide increases with increasing nitric acid concentration, which is common for DPAs, but the $SF_{Am/Eu}$ is much more for the diamide **3a** than for that of DPA.[6]

[†] *Synthesis of* **2**. To a solution of 5.76 g (31 mmol) of **1** in 64 ml of concentrated sulfuric acid, 18.4 g of CrO_3 was added in small portions at 70 °C. After the addition was complete, the reaction mixture was stirred for 1 h at this temperature. The resulting green slurry was poured into 100 g of crushed ice. The white precipitate of **2** was filtered off, washed with water and dried. ^1H NMR ([$^2H_6$]DMSO) δ: 8.16 (d, 1H), 7.99 (t, 1H), 7.89 (d, 1H).

Synthesis of **3a**,**b**: 10 ml of $SOCl_2$, 2.0 g (8.2 mmol) of **2** and a drop of DMF were refluxed for 3 h. Excess $SOCl_2$ was removed under reduced pressure, and the resulting solid was dried. Solid residue was dissolved in dry THF (120 ml). This solution was added dropwise to a mixture of 2.22 ml (17.2 mmol) of HNR′R″, 8.3 ml (59 mmol) of NEt_3 and THF (20 ml) at 50 °C. The resulting mixture was stirred overnight at this temperature, then poured into water (70 ml) and extracted with $CHCl_3$ (2×150 ml). Combined organic extracts were washed with water (2×120 ml) and dried over Na_2SO_4. Rotary evaporation of organic solution yielded **3**.

Compound **3a** was additionally washed with small portion of EtOAc, mp 182–184 °C. ^1H NMR ($CDCl_3$) δ: 7.63 (d, 1H), 7.46 (t, 1H), 7.17 (d, 1H), 7.07 (m, 5H, Ph), 4.01 (q, 4H, CH_2), 1.24 (t, 6H, Me). ^{13}C NMR ($CDCl_3$) δ: 153.57, 143.43, 136.88, 128.77, 127.55, 126.44, 124.21, 121.53, 45.51, 12.77. IR (KBr, ν/cm^{-1}): 1639 (amide I). Found (%): C, 74.50; H, 5.90; N, 12.32. Calc. for $C_{28}H_{26}N_4O_2$ (%): C, 74.65; H, 5.82; N, 12.44.

Compound **3b** was additionally dried at 80 °C at 0.1 Torr for 4 h. ^1H NMR ($CDCl_3$) δ: 8.42 (d, 1H), 7.89 (t, 1H), 7.60 (d, 2H), 3.54 (t, 2H, *cis*-CH_2), 3.36 (t, 2H, *trans*-CH_2), 1.69 (m, 4H), 1.44 (q, 2H, *cis*-CH_2), 1.11 (q, 2H, *trans*-CH_2), 1.00 (t, 3H, *cis*-Me), 0.74 (t, 3H, *trans*-Me). ^{13}C NMR ($CDCl_3$) δ: 168.68, 154.63, 153.92, 137.65, 123.45, 121.30, 48.69, 45.66, 31.11, 29.63, 20.29, 19.76, 13.90, 13.55. Found (%): C, 72.15; H, 9.18; N, 12.19. Calc. for $C_{28}H_{42}N_4O_2$ (%): C, 72.07; H, 9.07; N, 12.01.

[‡] *meta*-Nitrobenzotrifluoride (F-3) was used as a diluent.

Table 1 Am and Eu extraction from nitric acid solutions. Solvent: 0.03 M diamide + 0.01 M CCD in F-3.

$[HNO_3]$/mol dm^{-3}	Diamide	D_{Am}	D_{Eu}	$SF_{Am/Eu}$
0.2	**3a**	85	2.1	40
0.3	**3a**	24	1.1	22
	3b	1.9	0.10	19
0.5	**3a**	8.5	0.46	18
	3b	0.76	0.03	25
1.0	**3a**	2.1	0.24	8.8

The distribution ratios of metals extracted with the mixture of **3a** and CCD significantly increase compared with pure diamide. Thus, the synergistic effect takes place when diamides are used in the mixture with CCD. The practical application demanded the distribution ratios of Am to be much higher than 1, and *D* of Eu lower than 1. Such conditions were reached when the diamide–CCD ratio was about 2:1 or 3:1 (Figure 1). Increasing the CCD concentration with constant diamide leads to increasing distribution ratios but lowers separation factors.

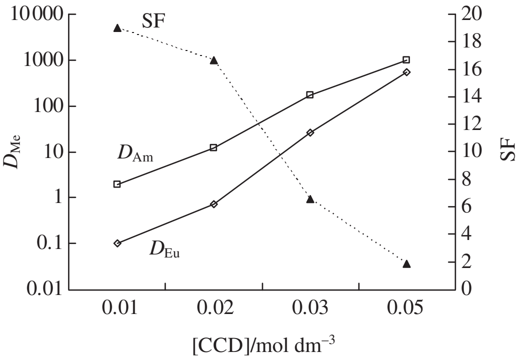


Figure 1 Am and Eu extraction from 0.3 M nitric acid. Solvent: 0.03 M **3b** + CCD in F-3.

It is known that the extraction properties of all diamide extractants are strongly dependent on their structures, namely, the nature of substituents in the amide moiety. We studied diamide **3a**, which has alkyl and aryl substituents at the amidic nitrogen, and diamide **3b** with only alkyl substituents. Table 1 indicates that metal distribution ratios for **3a** are about ten times higher than those for **3b**. The same dependence on structure was previously found for DPAs and bidentate neutral organophosphorous compounds (carbamoylphosphine oxides). This effect of increasing the extraction ability of an organic compound when an alkyl substituent is replaced by an aryl one, is known as the effect of anomalous aryl strengthening.

Table 2 Am and Eu extraction from nitric acid solutions. Solvent: **3a** + 0.01 M CCD in F-3.

[**3a**]/ mol dm^{-3}	0.2 M HNO_3			0.3 M HNO_3			0.5 M HNO_3		
	D_{Am}	D_{Eu}	SF	D_{Am}	D_{Eu}	SF	D_{Am}	D_{Eu}	SF
0.01	14.3	1	14	1.5	0.28	5.4	0.63	0.14	4.5
0.02	—	—	—	—	—	—	6.6	0.45	15
0.03	85	2.1	40	24	1.1	22	8.5	0.46	18

The americium–europium separation factor depends on the diamide–CCD ratio and the concentration of nitric acid. The highest separation ratios can be achieved for extraction from dilute nitric acid (*e.g.*, 0.2 M HNO_3). Increasing nitric acid concentration leads to decreasing separation factors up to 20 in 0.5 M HNO_3 (Table 2), that is sufficient for effective separation.

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