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Design of Macrocyclic Ligands for the Selective Extraction of f-Group Elements

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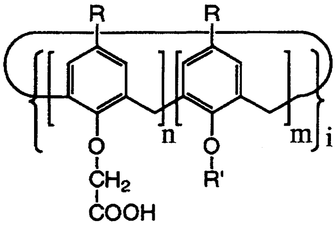
The relationship between the molecular structure of [1.$_6$]metacyclophanes (calix[6]arenes) and the extractability of trivalent lanthanides and americium was studied by solvent extraction from weekly acidic aqueous into chloroform solutions. The ligands differ in number and position of the ionophilic carboxymethoxy- and (diethylcarbamoyl)methoxy-groups, as well as in their hydrophobicity. The separation of Am(III) from Ln(III) is achieved due to cooperative binding of different ionophilic groups. The separation factor, $D_{\mathrm{Am(III)}}/D_{\mathrm{Nd(III)}}$, is 15 for an unsymmetrically substituted ligand (**4**) and 61 for an symmetric ligand (**6**) bearing the same ionophilic groups. Extraction constants were calculated for the ligands and compared with reference data.

Among the [1.$_n$]metacyclophanes, calix[n]arenes[1,2] are attractive ligands for solvent extraction,[3] mainly due to the possibilities to introduce various ionophilic groups in a certain geometric arrangement within the molecule, to pre-organize the conformation, to balance the hydrophobic and ionophilic characters, and to obtain high yields in the synthesis. While calix[4]arenes bearing monodentate groups can extract metal ions with lower coordination numbers well,[4] metal ions which require high coordination numbers or larger cations are extracted to a lower extent from acidic solutions.[5] Possibilities to overcome this problem are the introduction of bidentate groups, e.g. to the upper rim which provides a larger cavity compared with the 'lower rim',[6—8] or of crown moieties to the calix[4]arene molecule.[9,10] Another approach, aimed at the extraction of f-element ions, consists of using calix[6]arenes with monodentate groups attached to the phenolic oxygen atoms (Scheme 1), because calix[6]arenes extract Ln(III) from weekly acidic solutions into chloroform or into toluene better than do the calix[4]arenes and non-cyclic analogue.[11—15] It has recently been shown,[16] that substituting three of the six acid groups in reference ligand **2** by amide groups gives ligand **6**, which shows a pronounced difference in extractability towards Am(III) and Ln(III) (Ln = Nd, Eu, Tb, Dy, Er, Yb) from aqueous solutions of pH 2 to 3.5, which can be applied for ion separation. In this paper, we characterize the extraction equilibria of ligands **1** to **6** by a slope analysis, calculate the extraction constants and discuss the influence of the molecular structure on the extraction and selectivity.



No.	R	R′	n	m	i
1	t-bu	$-CH_2COOH$	6	0	1
2	t-oct	$-CH_2COOH$	6	0	1
3	t-bu	$-CH_3$	3	3	1
4	t-bu	$-CH_2CON(Et)_2$	3	3	1
5	t-oct	$-CH_3$	1	1	3
6	t-oct	$-CH_2CON(Et)_2$	1	1	3

Scheme 1. Ligands investigated in terms of this work.

Experimental

Materials. The parent calix[6]arenes complied with the NMR-, mass and IR spectral-, mp-, and el. anal. data.[1,14,17,18] New compounds were identified based on spectroscopic evidence. Air-sensitive reactions were carried out under a N_2-atmosphere using transfer techniques. NMR-spectra were recorded at 250 MHz (^{1}H) and 63 MHz (^{13}C), and if not stated otherwise at room temperature with $CDCl_3$ as the solvent. Mass spectra were measured in the EI or FAB mode, as indicated. TLC was carried out on Merck Silica gel $60F_{254}$. All solvents were distilled and chemicals were of p.a. grade. The terms 'lower' and 'upper' rim refer to the ionophilic and hydrophobic side of the macrocycle, respectively.

Reference compounds **1** and **2** were prepared from the parent calix[6]arenes according to common procedures[19] involving a treatment with NaH/ethyl bromoacetate in THF followed by exhaustive hydrolysis of the ester groups with 15% tetramethylammonium hydroxide in refluxing THF/water. Ligand **4** was synthesized in three steps from the trimethoxytris[(ethoxycarbonyl)methoxy] precursor

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(**3a**) of **3** via intermediates **3b** and **3c**, similarly as described for ligands **5** and **6**.[16] Shaking of an aqueous 10 M $NaClO_4$ solution (1 M = 1 mol dm^{-3}) with **3a** in $CHCl_3$ followed by phase separation and removal of $CHCl_3$, drying of the obtained $NaClO_4$ complex, treatment of the complex with 6.7 equivalents (equiv) Me_3SiI per 1 equiv of calixarene in refluxing $CHCl_3$ for 20 h followed by cooling, quenching with water, washing with HCl and water, drying, and crystallizing from MeOH gave 5,11,17,23,29,35-hexa-*t*-butyl-37,38,39-trihydroxy-40,41,42-tris[(ethoxycarbonyl)methoxy]calix[6]-arene **3b**. Yield 80%; TLC (CH_2Cl_2 : acetic acid 95 : 5): $R_f = 0.63$; ^{1}H NMR δ_H = 0.89 (15 H, s), 1.06—1.11 (15 H, m), 1.18—1.32 (33 H, m), 3.49—3.56 (10 H, s+m), 4.17 (10 H, br m), 4.5—4.6 (4 H, m), 6.5 (1 H, s), 6.75—7.1 (12 H, m), 7.21 (1 H, s), 8.85 (1 H, s); ^{13}C NMR δ_C = 13.94 and 14.14 (CH_3 of ester), 31.14, 31.3, 31.51, 31.6, 32.46 (Ar–*CH₂*–Ar and –CH_3 of Bu^t), 33.92, 34.12, 34.26 (Bu^t), 60.92 (O–CH_2–CH_3), 69.34, 69.72 (O–CH_2–C-(O)); 124.2, 125.87, 126.2, 127.17, 127.61, 132.88, 133.17, 133.95, 143.29, 146.92, 148.68 (C_{Ar}); 169.45 (C=O); MS *m/z* (EI) 1230 (L^+; 100%), 1252 (LNa^+; 10).

3b was treated with 12 equiv each of K_2CO_3, NaI and chloroacetamide in CH_3CN under reflux for 12 h, cooled, quenched, dried in vacuo, washed (water, $Na_2S_2O_5$, 0.1 M HCl), dried, and recrystallized twice from hexadecane to give 5,11,17,23,29,35-hexa-*t*-butyl-37,38,39-tris[(diethylcarbamoyl)methoxy]-40,41,42-tris[(ethoxycarbonyl)methoxy]calix[6]arene **3c**. Yield 65%; TLC ($CHCl_3$: ethanol 9 : 1), $R_f = 0.36$; ^{1}H NMR δ_H = 1.07 (br m) and 1.15 (s) and 1.26 (bs) and 1.36 (s) (Σ 81H), 3.46 (18H, at 250 MHz br d+br m, at 400 MHz br s), 4.24 (br s) and 4.6 (24 H, at 250 MHz br m, at 400 MHz 4.45 (s) and 4.61 (s)), 6.8—7.26 (12 H, br m); ^{13}C NMR δ_C = 12.72 and 14.01 (CH_3 of ester), 29.44, 31.23 (Ar–CH_2–Ar and CH_3 of Bu^t), 33.91 (Bu^t), 40.07 (b) and 40.79 and 41.43 (N–CH_2), 60.6 (O–CH_2–CH_3), 70.62 (b), 71.95 (O–CH_2–C(O)); 127.11, 132.17, 145.56, 152.93 (b, C_{Ar}); 167.37, 169.09 (C=O); MS *m/z* 1571 (100%).

Partial hydrolysis of **3c** with 15% tetramethylammonium hydroxide in refluxing THF/water gave 5,11,17,23,29,35-hexa-*t*-butyl-37,38,39-tris[(diethylcarbamoyl)methoxy]-40,41,42-tris(carboxymethoxy)calix[6]arene **4**. Yield 95%; mp 156—157 °C. Found: C, 72.22; H, 8.30; N, 2.09%. Calcd for $C_{90}H_{123}O_{15}N_3$: C, 72.69; H, 8.34; N, 2.83%. IR ν_{max} (KBr) 1643 and 1750 (C=O), 3416 cm^{-1} (OH); ^{1}H NMR δ_H = 0.94—1.28 (m) and 1.43 (s) (60H), 3.42 (16 H, m), 4.32—4.65 (12 H, m), 7.0 (12 H, m), 9.2 (br s OH); ^{13}C NMR δ_C = 12.82, 12.99, 14.2, 14.41, 30.26, 31.25, 31.30, 34.17, 40.66, 41.29, 41.73, 69.77, 71.22, 71.58, 125.45 (br), 132.31, 132.43, 132.8, 146.71, 167.89, 170.44; MS *m/z* (FAB$^+$) 1488 (LH^+; 100%), 1510 (LNa^+; 12).

Two-Phase Solvent Extraction Procedure. The extraction of ^{241}Am at tracer levels from diluted HNO_3 was carried out at 296 K with phase volumes of 3 ml each on a magnetic stirring plate in a glove box for 4 h at 400 rpm, followed by liquid scintillation counting (model LSC 6500, Beckmann Instr.) of the aqueous phase. The specific activity was 1 kBq ml^{-1} (3.3×10^{-8} M) before extraction. The oxides (> 99.9%) of Nd, Eu, Tb, Dy, Yb, and Er were converted to perchlorate stock solutions (pH 2.5) for further dilution. The extraction experiments were carried out at 298 K for 4 h at 100 rpm using an overhead shaker in a thermostated box. The aqueous phase for lanthanide extraction contained either 1×10^{-4} moles per liter (M) of Nd(III) (single element extraction) or 6 lanthanides (Nd+Eu+Tb+Dy+Yb+Er, 1×10^{-4} M each, competitive extraction). Buffers were not used so as to avoid possible complexation of the extractants with the buffer components. The pH-values given in the figures are the equilibrium values, measured with a Ross combination electrode. The phase volumes were 4 ml each for extraction and 3 ml each for stripping. The extractant concentration ranged from 0.1 to 10 mM, as indicated in the captions. The solvent was chloroform (p.a.), washed and saturated with water. Complete stripping of the lanthanides from the organic phases was achieved with 10 mM DTPA at pH 5 (mass balance 100%). Nearly quantitative stripping (> 95%) was found to be possible with 0.01 M HCl. Lanthanide concentrations in the aqueous and stripping solutions were analyzed by ICP-AES (model IRIS/AP, TJA). The data are averages of at least 3 measurements. No extraction took place by chloroform in the absence of calixarenes. Extraction equilibria were attained within 30 min. of magnetic stirring, as tested with ligand **1**.

Data Treatment. The distribution ratio (*D*), defined as the ratio between the metal concentration in the organic and in the aqueous phase at equilibrium, serves as a measure of extractability and of the stability of the complexes, which formed between ligand and metal. Because the solubility of the extractants in aqueous solutions is very low (e.g. less than 2×10^{-5} M ligand **1** dissolves in pure water) and their distribution constant between chloroform and water are high (e.g. $\log K = 3.15$ for **1** at pH 6), complex formation occurs at the liquid–liquid interface and complexation in the aqueous phase can be neglected in the data treatment. Dimerization of ligands **3** to **6** could not be observed in the NMR- and IR-spectra up to 10 mM concentrations. Moreover, from the low dimerization constant of the reference compound **2**[14] in $CHCl_3$ it is expected that for ligands **3**—**6**, which have with fewer acid groups than **2**, the dimer concentration is less than 1% of the monomer concentration over the investigated concentration range.

The extraction equilibria can be written according to the following equations, where a solid line denotes the species in the organic phase:

$$M^{3+} + \overline{H_6L} \rightleftarrows \overline{MH_3L} + 3H^+$$
$$\log K_{ex} = \log D - \log c_L - 3{\cdot}\text{pH}, \qquad \text{(I)}$$

$$M^{3+} + 2\overline{H_3L} \rightleftarrows \overline{ML{\cdot}H_3L} + 3H^+$$
$$\log K_{ex} = \log D - 2{\cdot}\log c_L - 3{\cdot}\text{pH}. \qquad \text{(II)}$$

The extraction constants (K_{ex}) were calculated according to Eqs. I and II.

Due to the low ionic strength in the investigated solutions, the activity coefficients were not taken into account in the calculations. The concentration of the uncomplexed ligand in the organic phase (c_L) was calculated from the initial ligand concentration and the measured concentration of complexed Ln(III) in the organic phase. In the case of Am(III) extraction, the initial ligand concentration can be regarded as the equilibrium concentration, due to the trace concentration of Am(III). The separation factors (S_f) are the quotients of the distribution ratios.

Results and Discussion

Figure 1 shows the extraction of ^{241}Am(III) into chloroform by reference compound **2**[13—15] bearing six –COOH groups, as a function of the pH of the aqueous phase. Three protons are exchanged per metal ion according to the slope of 3, in agreement with the metal-ion charge. The extractability of Am(III) by ligand **2** is slightly better compared with the less-hydrophobic ligand **1**, as concluded from the values of $pH_{0.5}$ (50% extraction) 2.13 for ligand **2** and 2.35 for ligand **1**. In case of Ln(III), the extractability is also higher with ligand

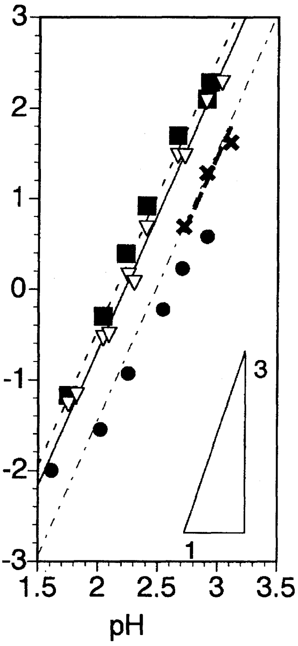


Fig. 1. Distribution ratios *D* of Am(III) (■, ▽, ●) in the extraction from aqueous to chloroform solutions by ligand **2** at different pH values. Included are data for the extraction of Nd(III) (✖) by ligand **1**. Concentration of ligand **2**: 5 mM (■), 3 mM (▽), 2 mM containing 2% 1-octanol (●), calcd for 5 mM (- - -), 3 mM (——), 0.5 mM ligand (—•—•—); Concentration of ligand **1**: 0.5 mM (✖), calcd for 0.5 mM (- - -); Aq phase (Am series): ^{241}Am(III) 1 kBq ml^{-1}, HNO_3 (vari. concn); Org. phase: 5 mM or 3 mM ligand as indicated; series (●) contains 2% 1-octanol and 2 mM ligand instead. Solid lines were calculated from K_{ex}. Nd series: competitive extraction, 6 × 0.01 mM Ln(III), 0.5 mM ligand, data fitted with K_{ex}.[11]

2[14] compared with **1**, although complexes with different stoichiometry are extracted into chloroform by ligands **1** and **2** : 1 : 2 and 1 : 1 Ln(III) : ligand respectively. The difference in extraction by ligands **1** and **2** is not sufficient for the separation of Am(III) and Ln(III), as can be seen from the values of $pH_{0.5}$ being 2.13 (Eu^{3+}) and 2.07 (Nd^{3+}) for ligand **1**. This is also illustrated by the data for Nd(III) extraction by ligand **1** (Fig. 1); the data were fitted by the previously calculated value of $\log K_{ex} = -0.91$.[11]

Figure 1 includes extraction data obtained when the org. phase contained 2% of 1-octanol, which was tested as a solvent modifier. However, due to competitive binding of metal and 1-octanol to the –COOH groups, the distribution ratios of Am(III) decrease. A similar decrease of *D* was observed for Ln(III).

From the values of the distribution ratio of Am(III) as a function of the ligand concentration in the range of 0.25 to 5 mM ligand at pH 2.9, which gives a slope of 1.0, the extraction constant according to Eq. I was calculated for the 1 : 1-complex. The result is given in Table 1. The value of $\log K_{ex} = -4.14$ is slightly higher than those for Ln(III), which are extracted according to the same mechanism,[14] ranging from $\log K_{ex} = -4.53$ (Nd, Pr) to -5.35 (Y). The value of $K_{ex,\ Am}$ was used to calculate the solid line in Fig. 1.

The distribution ratios of Am(III) for the extraction by the calix[6]arenes **1** and **2** are more than 10-times higher at a given pH, compared with calix[4]arenes bearing four COOH groups at the 'lower' rim, which is explained by the high coordination numbers of trivalent f-elements and the size of the macrocyclic cavity.[5,20] It has been shown, that Ac^{3+} behaves similar to Am^{3+} in the extraction by ligand **1** with respect of pH-dependency and stoichiometry.[21]

In order to achieve separation between Am(III) and Ln(III), different ionophilic groups were introduced into the calix[6]arenes in unsymmetric (ligands **3**, **4**) and symmetric arrangements (ligands **5**, **6**).

Figure 2 shows the extraction of Am(III) and six lanthanides by ligand **3**, bearing only three (instead of six) –COOH groups. The distribution ratio of Am(III) decreases by 2 orders of magnitude, compared with extraction by **2**, while the extraction of Ln(III) is decreased by more than 3 orders of magnitude. Although the distribution ratios of Am(III) and Ln(III) differ by a separation factor (S_f) of more than 30, the extractability is low at pH < 3. Above pH 3, the separation factors are smaller due to the converging slopes for Ln(III) and Am(III). Three protons are exchanged for each Ln(III), and 2 for Am(III). The presence of 2% of 1-octanol in the org. phase decreases the extractability of Am(III), similar as in case of ligand **2**.

It was previously observed that alkali ions increase the extraction of heavy metal ions by calix[4]arenes bearing –COOH groups due to a specific interaction between the co-

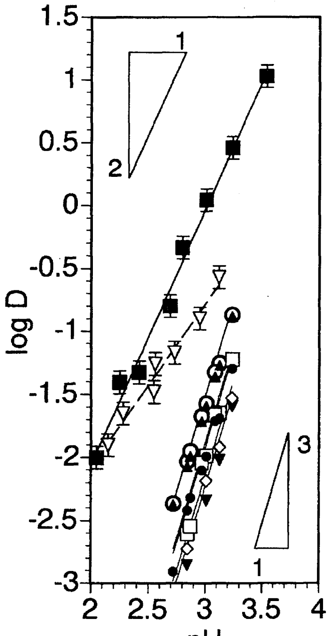


Fig. 2. Distribution ratios of trivalent Am (■, ▽) and Ln (Nd ▲, Eu ○, Tb □, Dy ●, Er ◇, Yb ▼) in the extraction by ligand **3**. Aq phase: ^{241}Am(III) (1 kBq ml^{-1} in HNO_3), or 0.6 mM $Ln(ClO_4)_3$ (0.1 mM of each Ln(III) in $HClO_4$ (vari. concn)); Org. phase: chloroform contg. 3 mM ligand; series (▽) contains 5 mM ligand and 2% 1-octanol.

extracted alkali ion and the phenolic oxygen atoms in small cyclophanes, e.g. in the systems of Ln(III) and Na^+,[11,13,15,22,23] Cu(II) and Na^+,[24] Am(III) and Na^+,[5,12] Am(III) and K^+ with a [1.0.1.0.1.0.1.0]metacyclophane.[5] On the other hand, Na^+ was found to decrease the extraction of Au(III) and Pd(II) by calix[4]arene derivatives due to competition for the binding sites,[4] and of Ln(III) by ligand **2**.[15] Evidence for Na^+-binding was observed in the mass spectrum of ligand **3**, despite its larger cavity size compared with the calix[4]arene. Therefore, the influence of 5×10^{-2} M of Na^+ or K^+ on the extraction of Ln(III) by ligand **3** was investigated. It was found that alkali salts at this concentration exert no significant influence on the distribution ratio. However, a concentration of 10^{-2} M Na^+ in the aq phase, which is a 5×10^5 excess over Am(III), reduces the distribution ratio of Am(III) by a factor of ca. 2.5 in the extraction by ligand **6**.[16] The slope of 2 in the plot of $\log D$ vs. pH for Am(III) in Figs. 2 and 6 is probably caused by traces of Na^+ in the ligand due to the synthesis procedure, and reflects the exchange of two protons plus one Na^+ for Am^{3+}, which is also present in trace amount.

The extraction data for Ln(III) at different concentrations of ligand **3** are plotted in Fig. 3, where c_L is the concentration of an uncomplexed ligand. The slope of 2 indicates the stoichiometry of the extracted complex to be 1 : 2 (metal : ligand), which may be a sandwich complex. The same stoichiometry has been observed with ligand **1**.[11] On the other hand, 1 : 1-complexes with Ln(III) are extracted by ligand **2**.[14] This difference may be attributed to the different hydrophobicity of the complexes of **1** and **2**, the conformational freedom of the ligands and the ligand–solvent interaction. The extraction constants were calculated from these data and are given in Table 1. They were used to calculate the lines for Ln(III) in Fig. 2. The order of extractability is the same as with ligand **1**, following the order of decreasing ion radii.###

The following structural features are assumed to be responsible for the low extraction by ligand **3** from acidic solutions: (i) The number of oxygen donor atoms available for coordination doesn't match the high coordination numbers and geometry (e.g. tri-capped trigonal prismatic) of trivalent f-elements, and (ii) the cavity formed by the ionophilic groups in **3** is not closed, but allowing interaction of the metal ion with water, which competes with the extraction. Therefore, the three methoxy groups were substituted by (diethylcarbamoyl)methoxy groups in ligand **4**, providing more donor atoms and a more closed cavity. The distribution ratios are plotted vs. the pH in Fig. 4. The values of D are higher by a factor of 10 (at pH 3) for Am(III) and Ln(III), compared with ligand **3**. The separation of Am(III) from Ln(III) in weekly acidic media can therefore effectively be accomplished by ligand **4**. The order of extraction of Ln(III) follows the order of ion radii.

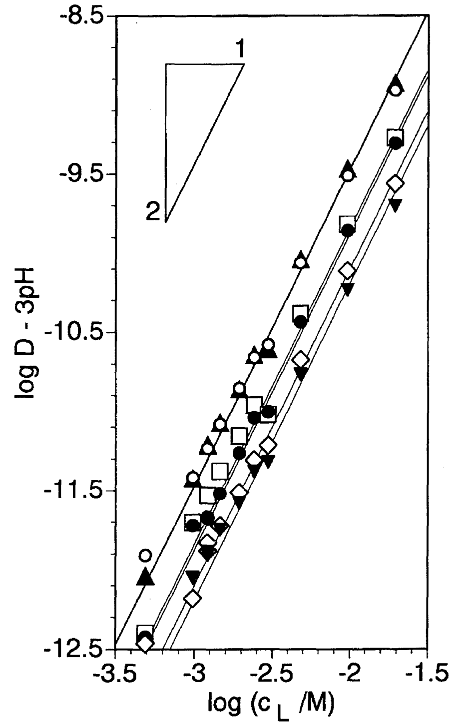


Fig. 3. Extraction of trivalent Ln at various concentrations of ligand **3**. Aq phase: 0.6 mM $Ln(ClO_4)_3$ (Ln = Nd(▲)+Eu(○)+Tb(□)+Dy(●)+Er(◇)+Yb(▼), 0.1 mM each in $HClO_4$), pH 3.0—3.3; Org. phase: chloroform contg. 5 to 20 mM ligand, c_L is the concentration of uncomplexed ligand.

The slope of the plot $\log D$ vs. pH in Fig. 4 is 3 for Am(III). It is also 3 for Nd(III) when the concentration ratio between ligand and metal is high, e.g. 5 mM : 0.05 mM, but decreases from the expected value of 3 to less than 3 when the ligand:metal ratio decreases from above 8 : 1 to below 5 : 1. This phenomenon was observed for the extraction of

Table 1. Values of $\log (K_{ex}/dm^3\ mol^{-1})$ for the Extraction from Water to Chloroform

	Am[c]	Nd[d]	Nd[c]	Eu[d]	Tb[d]	Dy[d]	Er[d]	Yb[d]	Eqn.
Ligand **2**	−4.14	−4.53[e]	−4.60[e]	−4.63[e]			−5.28[e]		I
Ligand **3**		−5.48		−5.47	−5.84	−5.88	−6.10	−6.19	II
Ligand **4**	−2.92	−4.12	−4.11	−4.29	−4.53	−4.65	−4.87	−4.94	II
Ligand **6**	−2.52	−4.31	−4.55	−4.56	−4.77	−4.96	−5.24	−5.18	II

c) from single element extraction; d) from competitive extraction of 6 lanthanides; e) from Ref. 14.

However, extraction of La(III) is lower, ranging between Er(III) and Eu(III), Ref. 6. The order is slightly different from the order of extractability by the analogous tetrakis(carboxymethoxy)calix[4]arene in the presence of excess Na^+, showing a maximum at Eu^{3+}.

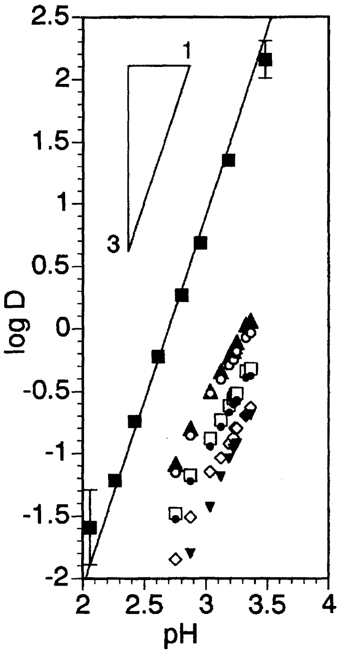
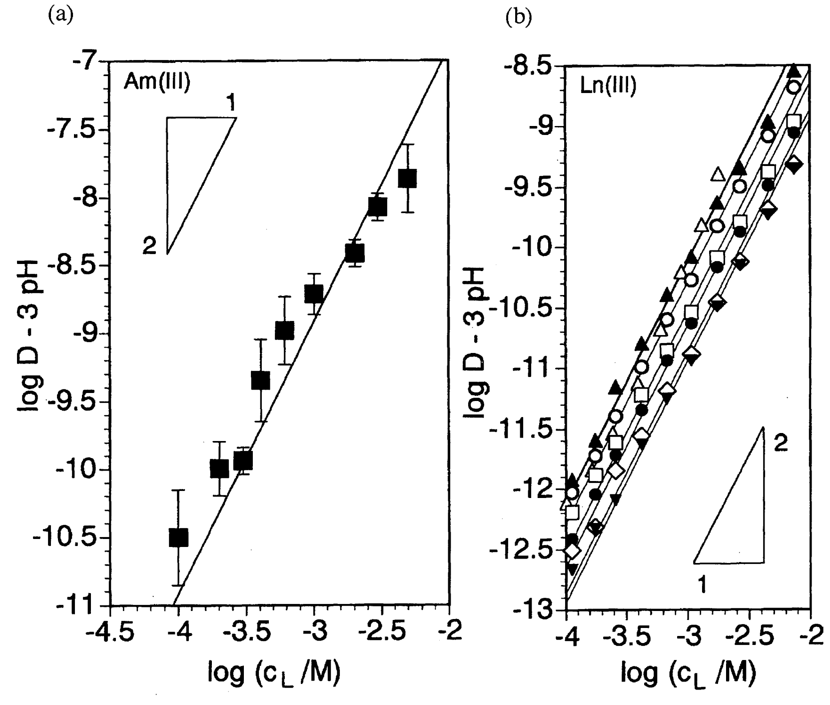


Fig. 4. Distribution ratios of trivalent Am and Ln in the extraction by ligand **4**. Aq phase: ^{241}Am(III) (■) (1 kBq ml^{-1} in HNO$_3$), or 0.6 mM Ln(ClO$_4$)$_3$ (Ln = Nd(▲)+Eu(○)+Tb(□)+Dy(●)+Er(◇)+Yb(▼), 0.1 mM each in HClO$_4$), pH 3.0—3.3; Org. phase: chloroform contg. 3 mM ligand. The solid line for Am(III) was calculated from K_{ex}.

Ln(III) with the ligands **1**, **4**, [####] and **6**. The latter plot is included in Fig. 7 for the ligand:metal ratio 100 : 1 (see below). On the other hand, the slope is 3 in Fig. 2 due to the low extractability of Ln(III), resulting in a high ligand:metal ratio in the org. phase. It was confirmed that the slope of 2 is not caused by a coextracted anion by measuring the distribution ratio at different concentrations of ClO$_4^-$. The plot of ($\log D - 2{\cdot}\log c_L - 2$pH) vs. log[ClO$_4^-$] shows no significant concentration dependency.

Figures 5a and 5b show the extraction by ligand **4**, expressed as log D–3pH, as a function of the concentration of uncomplexed ligand for Am(III) and Ln(III), respectively. [#####] The stoichiometry of the extracted complex is 1 : 2 for Am(III), as concluded from the slope of 2. The extraction constant (Table 1) was calculated according to Eq. II and used to draw the solid line in Fig. 4. In case of Ln(III), the slopes are also 2 in both the single element (Nd) and competitive extraction. The extraction constants for Nd(III) (Table 1) as calculated from the data of the single element and of the competitive extraction agree well with each other. The separation factor calculated from K_{ex} ranges from 15 (Am/Nd) to 105 (Am/Yb).

In order to understand the influence of the extractant


(a)

(b)

Fig. 5. Extraction of trivalent Am (left, 5a) and Ln (right, 5b) at various concentrations of ligand **4**. Aq phase: ^{241}Am(III) (1 kBq ml^{-1} in HNO$_3$), or 0.6 mM Ln(ClO$_4$)$_3$ (Ln = Nd(▲)+Eu(○)+Tb(□)+Dy(●)+Er(◇)+Yb(▼), 0.1 mM each in HClO$_4$), pH 2.6—3.2 (for Am), pH 3.0—3.4 (Ln); symbol △ indicates single element extraction of Nd (0.1 mM); Org. phase: chloroform contg. 0.1 to 10 mM ligand.

[####] Data of log D vs. pH for ligands **1** and **4** at various ligand : metal ratios are unpublished results.

[#####] The value of 3·pH is subtracted from values of log D in the plot vs. log c_L for Ln(III), because the ligand : metal ratio is high due to the low extractability of Ln(III) under the conditions applied for the concentration dependency, so that the slope in the plot of log D vs. pH is 3.

structure on the selectivity, we designed and investigated the symmetrical calix[6]arenes **5** and **6** in more detail. As recently reported, a good separation between Am(III) and Ln(III) is achieved with **6**.[16] As a counter-balance to the ionophilic groups at the 'lower' rim of the ligand, hydrophobic branched alkyl groups, such as 1,1,3,3-tetramethylbutyl (*t*-octyl) groups at the 'upper' rim, are introduced. This improves the solubility in less-polar solvents,[14] compared with *t*-butyl groups. Figure 6 shows a plot of log *D* vs. pH for ligand **5**, the symmetrical similarity to **3** bearing three –COOH groups. From the slope of 2 observed for Am(III) it is concluded that only two –COOH groups contribute to the binding. Despite the higher hydrophobicity of **5** and probably also of its metal complexes in comparison with **3**, the extractability of Am(III) is lower, as reflected by the $pH_{0.5}$ values (3.28 for **5** and 3.02 for **3**). A more restricted rotational freedom of the phenyl rings around the methylene bridges may be responsible for that behaviour. As can be seen in Fig. 6, the extractability of Ln(III) by ligand **5** is also lower compared with ligand **3**.

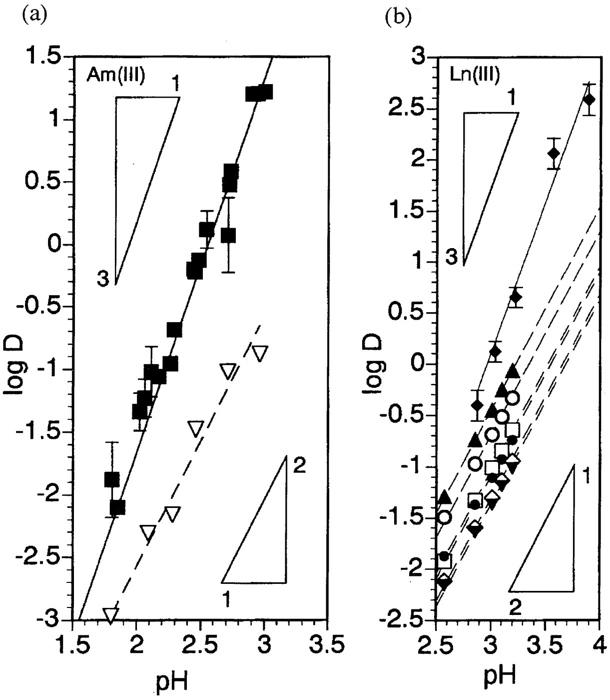


Fig. 7. Distribution ratios of trivalent Am (left, 7a) and Ln (right, 7b) with ligand **6**. Aq phase: ^{241}Am(III) (■) (1 kBq ml^{-1}, HNO_3), or 0.6 mM $Ln(ClO_4)_3$ (competitive extraction, Ln = Nd(▲)+Eu(○)+Tb(□)+Dy(●)+Er(◇)+Yb(▼), 0.1 mM each), or 0.05 mM $Nd(ClO_4)_3$ (single element extraction (◆)), $HClO_4$; Org. phase: chloroform contg. 3 mM or 5 mM (only ◆) ligand **4**. The solid lines were calculated from K_{ex}. Symbol ▽ in Fig. 7a shows the lower extraction of Am(III) by **5** for comparison.

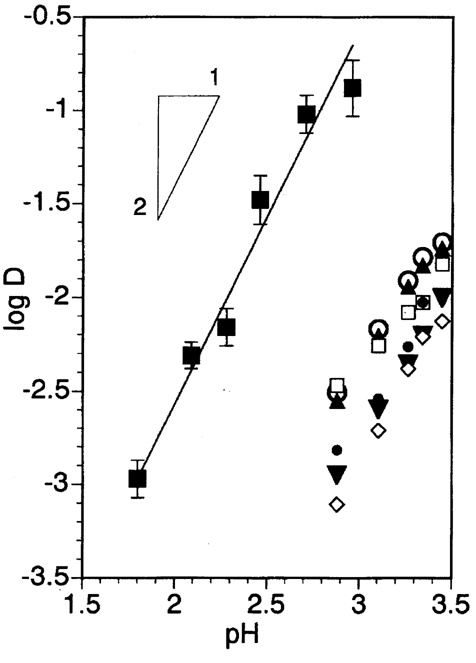


Fig. 6. Distribution ratios of trivalent Am and Ln in the extraction by ligand **5**. Aq phase: ^{241}Am(III) (■) (1 kBq ml^{-1} in HNO_3), or 0.6 mM $Ln(ClO_4)_3$ (Ln = Nd(▲)+Eu(○)+Tb(□)+Dy(●)+Er(◇)+Yb(▼), 0.1 mM each, in $HClO_4$ (vari. concn)); Org. phase: chloroform contg. 3 mM ligand.

Eventually, ligand **6** which is similar to **4** shows a high extraction power towards Am(III), as seen in Fig. 7a. The value of $pH_{0.5}$ at 3 mM ligand concentration is 2.55 for **6**, lower than the value of 2.71 for ligand **4** and only slightly higher than the value of 2.22 for reference compound **2**, which shows the highest extraction but the lowest selectivity towards Am(III). The slope of log *D* vs. pH is 3 indicating that 3 –COOH groups participating in binding to the Am^{3+} ion, similar to ligands **4** and **2**. Figure 7b shows the corresponding data for the competitive and single element extraction of Ln(III) by 3 and 5 mM solutions of ligand **6**, respectively. The slopes of log *D* vs. pH change from 2 to 3 at high ligand : metal ratio as seen in case of Nd(III) in the single element extraction as described for ligand **4**. The order of extraction is the same as with ligands **1**, **3**, and **4**. The separation factors range from 61 (Am/Nd) to 457 (Am/Yb) as calculated from K_{ex}. It is concluded that an amide group is nearly as effective as a –COOH group in binding to Am(III), but less effective in binding to Ln(III).

The influence of the concentration of ligand **6** in the organic phase on the extraction of Am(III) and Ln(III) is plotted in Figs. 8a and 8b. The stoichiometry of the extracted complex as concluded from slope analysis for Am(III) and for Ln(III) is 1 : 2 (metal : ligand), the structure probably being a sandwich type. In competitive Ln(III) extraction the slope of $\log D - 3\text{pH}$ vs. $\log c_L$ is 2.0, as in single-element extraction (Fig. 8b). The values of K_{ex} (Table 1) were applied to calculate the solid lines for Am(III) and Ln(III) in Fig. 7.

In summary, the extraction of Am(III) decreases in the order of ligand **6** > **4** > **3** > **5**. The extraction of Ln(III) decreases in the order of ligands **4** > **6** > **3** > **5**. The separation factors between Am(III) and Ln(III) are higher with **6**, compared with **4**. At pH > 3, ligand **5** could also be used for the group separation. The selectivity within the group of lanthanides(III) is similar with ligands **6**, **4**, and **3**. The com-

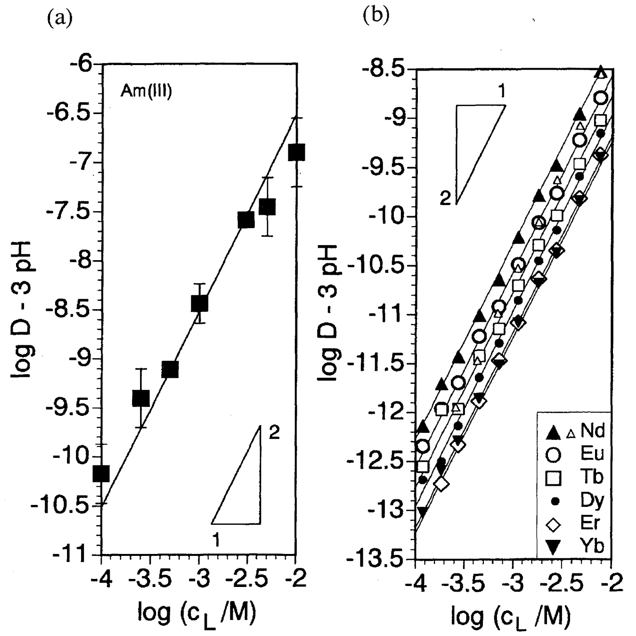


Fig. 8. Extraction of trivalent Am (left, 8a) and Ln (right, 8b) at various concentrations of ligand **6**. Aq phase: see Fig. 7, pH 2.7—3.1 (for Am), pH 3.0—3.4 (Ln); symbol △ indicates single element extraction of Nd (0.1 mM); Org. phase: chloroform contg. 0.1 to 10 mM ligand.

plexes formed by extraction of Am(III) and Ln(III) with ligands **3**, **4**, and **6** have the stoichiometry 1 : 2 (metal : ligand), different from the 1 : 1-complexes formed between Am(III) and the ligands **1** and **2** and between Ln(III) and ligand **2**.

Conclusions

This paper demonstrates the usefulness of macrocyclic extractants for the separation of trivalent f-elements, which is difficult to achieve by means of conventional mono- or bidentate extractants. It is shown that mainly the simultaneous presence of –COOH and amide groups, and to a smaller extent the geometric arrangement of these groups contribute to extractability and selectivity for Am(III). The ligands show high chemical stability, giving the same results after several extraction/back extraction cycles. Preliminary tests also indicate high radiolytic stability.

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