Assessing the mechanism of the synergistic action of calixarenes and Co-dicarbollides in lanthanide extractions†

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The extraction pathway of lanthanide ions from simulated nuclear waste solutions and the synergistic effects of a calixarene and a cobalt dicarbollide anion (CD) have been investigated on a model system by the combined use of electrospray ionization MS, FTMS ICR, together with ^{1}H and ^{11}B high field NMR spectroscopy techniques. Moreover, the extracting capabilities of the calixarene/BrCD mixture were determined by liquid–liquid extraction tests. An enhanced extraction efficiency of the calixarene/BrCD mixture with respect to the calixarene alone was observed. MS analysis allowed the assessment of a supramolecular ternary association, while the NMR data gave information on the calixarene binding sites for lanthanide ions. Herein, we report the experimental evidence of the formation of a ternary *lanthanide/calixarene/Co-dicarbollide* aggregate, which allowed us for the first time to assess the mechanism of the synergistic action of calixarenes and CD anions in lanthanide ion extraction.

In the fascinating framework of supramolecular chemistry, calixarenes play a primary role as receptors of a large variety of molecular and ionic guest systems, as extensively reviewed in the literature.[1] In the past few years, calixarenes functionalized with metal-binding groups have shown outstanding extraction properties for metal ions of paramount interest for environmental control: the extraction of Cs, Sr, actinides and lanthanides from acidic nuclear waste solutions can be cited as examples.[2] In particular, the separation of actinides (An) from lanthanides (Ln) is an urgent and important problem in the management of waste resulting from the reprocessing of fuels from nuclear plants.[3] Spent nuclear fuels contain moderate amounts of long-lived minor actinides (Np, Am, Cm) and many fission products, among which Lns represent some of the major components. The selective extraction of minor actinides and their subsequent transmutation into short lived or non-radioactive isotopes is a vital process in the management of waste.[4–7] This extraction process, however, needs efficient, chemically-selective and radiochemically-resistant ligands.[8] Therefore, in the last few decades, great efforts have been made in developing efficient extractants for application in new separative processes.[9–11] A large number of cation extractants based on calixarenes, in which pre-organization has been shown to favour specificity of extraction, have been extensively studied, either alone or in mixtures, with synergistic agents such as lipophilic Co-dicarbollide anions.[12–14] Thanks to a synergistic effect among the components, the extraction efficiency of calixarene-based ligands is strongly improved by the addition of lipophilic Co-bis-dicarbollide anions. However, no clear explanation for this improved extraction efficiency has been proposed at a molecular level.

In the presence of a lipophilic synergiser, the extraction process (Fig. 1) with these macrocycles, at present, is believed to consist of these basic steps: (i) the neutral calixarene ligand binds the metal ion, forming a positively-charged lipophilic adduct at the water/organic phase interface; (ii) the Cs salt of Co-bromodicarbollide provides a hydrophobic counterion that is able to form a lipophilic ion pair with the Ln-calixarene adduct; (iii) Cs^{+} ions migrate to the aqueous phase while the ternary non-covalent association Ln-calixarene-dicarbollide is extracted in the organic layer. Despite the fact that these steps seem reasonable, no experimental evidence in the literature supports the extraction pathways outlined above.[15]

In the present article, the extraction process is simulated by using model components: (i) $La(NO_3)_3$, as a representative lanthanide species in spent fuel solutions, (ii) hexakis(3-*N*-(6-carboxymethylpicolinamide)propyl)calix[6]arene (Calix, **1**), the extracting agent, and (iii) dicarbollide anions (Scheme 1). In particular, Co-bis(dicarbollide) (CD) and bromo-substituted Co-bis(dicarbollide) anions (Br_nCD) are used. Moreover, higher extraction coefficients have been measured for the mixture Calix/Br_nCD.

The extraction mechanism presented in Fig. 1 has been experimentally proved using electrospray ionization mass spectrometry (ESI-MS), together with ^{1}H and ^{11}B nuclear magnetic resonance spectroscopy (NMR). The experimental evidence for the formation of a ternary adduct La^{3+}/Calix/Br_nCD will be discussed. We think that these findings will be particularly helpful in developing new classes of more efficient extracting agents for technologically relevant applications.

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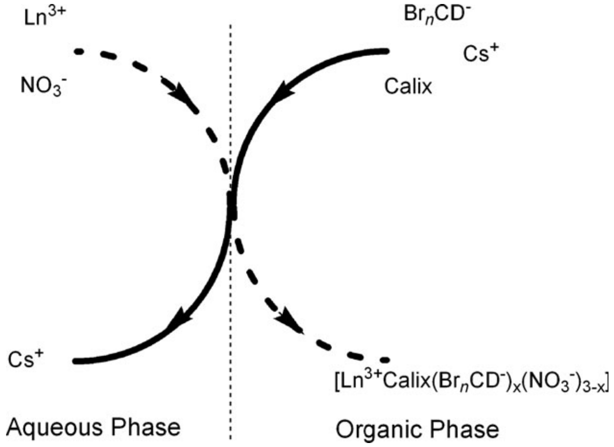
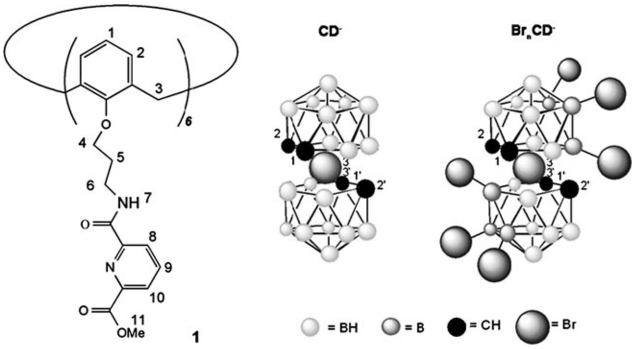


Fig. 1 A proposed mechanism for the extraction of Ln ions by a calixarene ligand and a CD synergiser.



Scheme 1 The molecular structures and atom numbering of Calix (**1**), Co-dicarbollide (CD) and Co-bromodicarbollide (Br_6CD).

Experimental

General

Lanthanum nitrate was obtained from Sigma-Aldrich, and Co-bis(dicarbollide) and bromo-substituted Co-bis(dicarbollide) were purchased from Katchem Ltd., Prague. Different degrees of Br substitution (n = 6, 7 and 8) were detected in the commercially available Br-dicarbollide (see the ESI†). The synthesis of 37,38,39,40,41,42-hexakis{3-[(pyridine-6-methoxycarbonyl-2-carboxy)-amino]-propoxy}calix[6]arene (**1**) was undertaken by a literature method.[16]

Extraction tests

The extracting properties of **1** were established by liquid–liquid extraction experiments. For the radioactive tests, the aqueous phase consisted of a nitric acid solution spiked with ^{241}Am, used as a representative of actinides, and ^{152}Eu, used as representative of lanthanides. For ESI-MS analyses, an aqueous phase of trivalent lanthanum nitrate was prepared in de-ionized water containing nitric acid at pH 4.5. The lanthanum concentration was set as 4×10^{-2} M. The organic phase was prepared by dissolving the calixarene and the dicarbollide anion in nitrobenzene at a concentration of 1×10^{-2} and 1.5×10^{-2} M, respectively. A 1 : 1.5 ligand-to-synergiser ratio was maintained during the experiments.

The extraction experiments were performed by contacting 500 μl of each of the two phases, previously prepared in a single-use microtest tube, for 1 h. In the case of samples for ESI-MS analyses, the phases were shaken for 15 h. Subsequently, the sample was centrifuged for 10 min in order to obtain complete phase separation. Next, an aliquot of the each phase was withdrawn and analysed by γ spectrometry or by mass spectrometry. All of these operations were carried out at room temperature.

Physical measurements

After the extraction experiments, an aliquot of both the aqueous and organic phase was withdrawn, transferred into micro-test tubes, diluted 1 : 50 in MeOH and analysed by ESI-MS.

The ESI-MS experiments were performed using a Bruker Esquire 3000+ spectrometer equipped with an ESI source and a quadrupole ion trap detector (QIT). Acquisition parameters: needle: 3.5 kV, N_2 flow rate: 12 L h^{-1}, cone voltage: 10 to 60 V, infusion rate: 4 μL min^{-1}. Scan rate and range: 13 000 (m/z) s^{-1} over the mass range m/z 200–3000.

The FTMS ICR experiments were performed with an APEX II (Bruker Daltonics) instrument; magnet: 4.7 T. Acquisition parameters: broadband acquisition mode, 512 k time-domain data points, zero filling to 1024 k, m/z range: 115–3500, acquisition time 0.4 s, resolution > 10.000 FWHM.

NMR experiments were performed: ^{1}H NMR (500 MHz, Bruker AVANCE), T = 320 K, chemical shift reference = internal TMS (tetramethylsilane); ^{11}B NMR (128 MHz, Bruker ARX 400 equipped with multinuclear broadband reverse probe), T = 305 K, chemical shift reference = external $BF_3(EtO)_2$. The samples (5×10^{-3} M 1 : 1 mixture of $CDCl_3 : CD_3CN$) were transferred into NMR tubes of low boron content (<0.01 ppm). Spectral assignments were supported by {^{11}B–^{11}B} 2D COSY experiments.

Results and discussion

Extraction results

The extracting properties of **1** were extensively studied in experimental conditions of interest for nuclear reprocessing applications by means of liquid–liquid extraction tests.[16] It was observed that the ligand suffers from protonation at higher acidities. However, it was demonstrated that the addition of the dicarbollide anion strongly improved the extraction efficiency and that it is possible to reach the desired values of D_M (metal ion distribution coefficient = $[M]_{org}/[M]_{aq}$ at equilibrium) at the target pH value by varying the dicarbollide concentration.[16,17] It was verified that the enhanced extracting capability of the Calix/Br$_n$CD mixture with respect to calixarene alone was not due to the extracting capability of the synergiser.[16]

The experimental conditions for the extraction tests performed on La^{3+} aqueous solutions were chosen after some preliminary radioactive extraction experiments. Since nitrobenzene was used as a diluent in the preliminary extraction tests for the ESI experiments but no data for **1** in nitrobenzene was available in the literature, the ligand behaviour in this diluent was established. The distribution coefficients for Am^{3+} and Eu^{3+} with a 1 : 1.5 ligand-to-synergiser ratio were much greater values than the 10^3 at $0.01\ M < [H^+] < 1\ M$. However, the acidity of the aqueous phase was decreased (pH 4.5) in order to maximize the presence of La^{3+}-containing species in the organic extract.

ESI-MS and NMR results

After the extraction tests, both the aqueous and organic phases were analyzed by electrospray ionization mass spectrometry (ESI-MS). The spectra of the organic extracts showed the formation of ternary La^{3+}/Calix/Br_nCD adducts with different stoichiometries (Table 1).

Fig. 2 shows, as an example, the peaks corresponding to the double charge multicomponent association of La^{3+}, Calix and Br_nCD (1 : 1 : 3 ratio) observed in the organic phase after the extraction of La^{3+} with the Calix/Br_nCD mixture. The assignment of the species detected was confirmed by the simulation of the isotopic clusters corresponding to the ternary complexes and by collision-activated decomposition (CID) mass spectrometry experiments (MSˆ2).

The main La^{3+} adducts observed by ESI-MS experiment on the organic extracts are gathered in Table 1. Other peaks detected in the full scan spectrum and not reported in Table 1 are due to clusters containing Calix, Br_nCD and environmental Na^+ ions only. Interestingly, no adducts containing Cs ions were observed in the spectrum, consistent with the migration of Cs^+ into the aqueous phase (see Fig. 1).

The elemental composition of the multicomponent associations at *m*/*z* 1486.6 and 1526.1 were determined by FTMS-ICR spectra with a resolution ≥ 10 000. The experimental and calculated spectrum of the peak at 1486.6 are displayed in Fig. 3. The corresponding molecular formulae, $[C_{112}H_{123}N_{12}O_{24}B_{18}Br_7CoLa]^{2+}$ and $[C_{112}H_{122}N_{12}O_{24}B_{18}Br_8CoLa]^{2+}$, derived by peak matching with associated errors ≤7 ppm, are consistent with $[La(Calix)(Br_7CD)]^{2+}$ and $[La(Calix)(Br_8CD)]^{2+}$, respectively. Fig. 4 reports the MSˆ2 spectrum of the ion at *m*/*z* 2385.2, attributed to the 1 : 1 : 3-type Ln/calixarene/dicarbollide association of composition $[LaNa_2(Calix)(Br_7CD)_3]^{2+}$ or $[LaNa_2(Calix)(Br_8CD)(Br_7CD)(Br_6CD)]^{2+}$. The fragment ions at *m*/*z* 1936.1, 1486.6 and 1040.9 are assigned to $[LaNa(Calix)(Br_7CD)_2]^{2+}$ or $[LaNa(Calix)(Br_6CD)(Br_8CD)]^{2+}$, $[La(Calix)(Br_7CD)]^{2+}$ and $[La(Calix\text{-}CH_3)^-]^{2+}$, respectively.

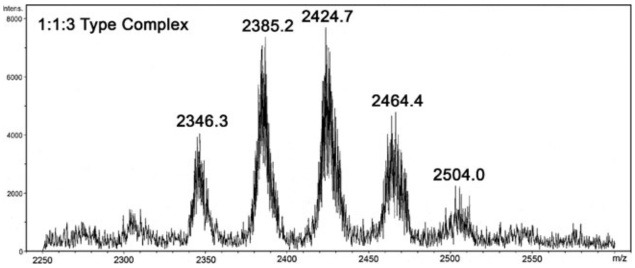


Fig. 2 The negative ion polarity ESI-MS spectrum of the ternary complex La^{3+}/Calix/Br_nCD (1 : 1 : 3) containing Br_nCD anions with different degrees of bromination.

The fragmentation pattern is characterized by the sequential loss of neutral $NaBr_n$CD, confirming the strong interaction of La^{3+}, Calix and Br_nCD^- within their ternary association. As a matter of fact, the latter can be interpreted as the basic aggregation core of the larger clusters reported in Table 1 (*e.g.* 1 : 1 : 2- and 1 : 1 : 3-type adducts). This conclusion is substantiated by the finding that the MSˆ2 experiments on the precursor ions at *m*/*z* 1895.8 and 1447.7 (corresponding to 1 : 1 : 2- and 1 : 1 : 1-type associations) gave the same general fragmentation pattern.

The base peak in Fig. 4 at *m*/*z* 1040.9 corresponds to a complex rearrangement within the multicomponent association under collision activation. Indeed, the fragment at *m*/*z* 1040.9 can be formally obtained from the precursor ion by the neutral loss of two pre-formed $NaBr_n$CD moieties and methylated Br_nCD, in turn generated by an ion–molecule reaction with Calix under CID conditions. The doubly-charged ion at *m*/*z* 1040.9 was, in turn, allowed to decompose in an MSˆ3 experiment. The main fragments were at *m*/*z* 1859.6 (single charge), corresponding to the loss of $C_{11}H_{13}N_2O_3^+$ (221 Da) from one picolinamide arm $[CH_2CH_2CH_2NH(CO)PyCOOCH_3]$ of Calix, and the doubly-charged fragment at *m*/*z* 930.8, originating from the neutral loss of 220 Da, once again consistent with the release of one side chain from the calixarene ligand.

Table 1 La^{3+} complexes detected by ESI-MS in the organic phase after extraction experiments (peaks due to clusters containing Calix, Br_nCD and environmental Na^+ are not reported)

Species (ratio)	Designation	*m*/*z*
La^{3+}/Calix/Br_nCD^-	$[La(Calix)(Br_6CD)]^{2+}$	1447.7
(1 : 1 : 1)	$[La(Calix)(Br_7CD)]^{2+}$	1486.6
	$[La(Calix)(Br_8CD)]^{2+}$	1526.0
La^{3+}/Calix/Br_nCD^-	$[LaNa(Calix)(Br_6CD)_2]^{2+}$	1895.8
(1 : 1 : 2)	$[LaNa(Calix)(Br_7CD)(Br_6CD)]^{2+}$	1896.6
	$[LaNa(Calix)(Br_7CD)_2]^{2+}$	1936.1
	$[LaNa(Calix)(Br_8CD)(Br_6CD)]^{2+}$	
	$[LaNa(Calix)(Br_7CD)(Br_8CD)]^{2+}$	1975.6
	$[LaNa(Calix)(Br_8CD)_2]^{2+}$	2014.5
La^{3+}/Calix/Br_nCD^-	$[LaNa_2(Calix)(Br_7CD)_2(Br_6CD)]^{2+}$	2346.3
(1 : 1 : 3)	$[LaNa_2(Calix)(Br_8CD)(Br_6CD)_2]^{2+}$	
	$[LaNa_2(Calix)(Br_7CD)_3]^{2+}$	2385.2
	$[LaNa_2(Calix)(Br_8CD)(Br_7CD)(Br_6CD)]^{2+}$	
	$[LaNa_2(Calix)(Br_7CD)_2(Br_8CD)]^{2+}$	2424.7
	$[LaNa_2(Calix)(Br_8CD)_2(Br_6CD)]^{2+}$	
	$[LaNa_2(Calix)(Br_7CD)(Br_8CD)_2]^{2+}$	2464.4
	$[LaNa_2(Calix)(Br_8CD)_3]^{2+}$	2504.0

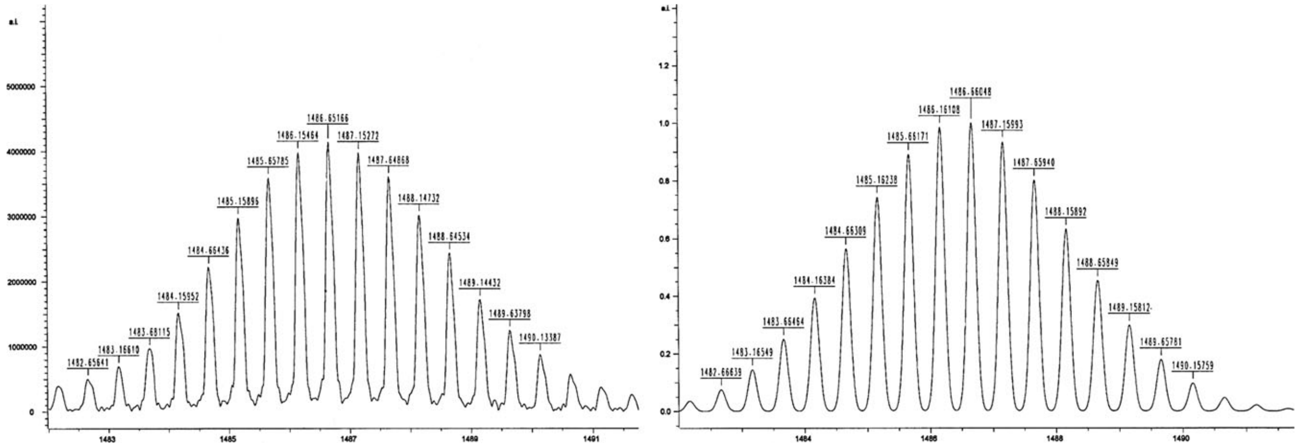


Fig. 3 Experimental FTMS ICR high resolution spectrum (left) and calculated spectrum (right) of the peak at m/z 1486.6.

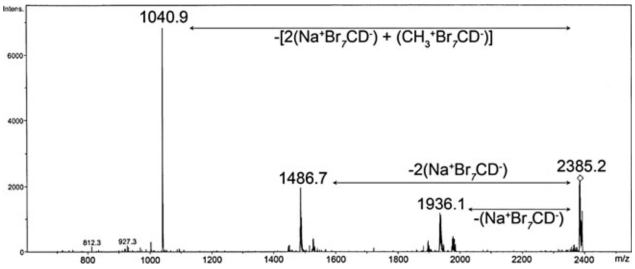


Fig. 4 MSˆ2 spectrum of the precursor ion at m/z 2385.2, corresponding to $[LaNa_2(Calix)(Br_7CD)_3]^{2+}$ or $[LaNa_2(Calix)(Br_8CD)(Br_7CD)(Br_6CD)]^{2+}$.

The MSˆ2 experiments suggest that: (i) the La^{3+}/Calix associations are stable against dissociation, indicating the great strength of the La^{3+}/Calix interaction; (ii) the non-covalent forces that hold the complexes together are likely to be largely governed by electrostatic interactions,[18] which are favoured in solventless conditions.

ESI-MS analyses of the aqueous phase after the extraction showed several peaks containing Cs^+, confirming the transfer of caesium ions from the organic to the aqueous phase to counterbalance the La^{3+} ions. The dicarbollide anion acts as a counterion to the positively-charged La^{3+}/Calix adducts and favours extraction of the neutral complexes due to its high lipophilicity, thus reducing the unfavourable co-extraction of the more hydrophilic nitrate ions.

In a parallel sense, NMR experiments provided a picture of association phenomena in solution. A titration of Calix with $La(NO_3)_3$ and Br_nCD up to the ratio La : Calix : Br_nCD of 1 : 1 : 1 was followed by ^1H NMR. The results are summarized in Table 2 as complexation-induced chemical shift variations $\Delta\delta = \delta_{observed} - \delta_{free}$ (in Hz).

Table 2 Chemical shift changes (in Hz) upon adding Br_nCD^- and/or La^{3+} to a solution of Calix in $CD_3CN/CDCl_3$. Positive changes represent deshielding (see Scheme 1 for atom numbering)

	Calix/Br_nCD^-	La^{3+}/Calix	La^{3+}/Calix/Br_nCD^-
H(1)	—	−21	−16
H(2)	—	−35	−50
CH_2 (3)	—	−56	−39
CH_2 (4)	—	+48	+78
CH_2 (5)	—	+51	+100
CH_2 (6)	—	+48	+78
NH(7)	—	+109	[a]
H(8)	—	−12	−70
H(9)	—	+20	+22
H(10)	—	+8	+8
OMe(11)	—	+40	+53

[a] Not determined due to excessive broadening.

Table 2 shows that no chemical shift changes were observed when comparing the spectrum of Calix with that of a 1 : 1 mixture of Calix/Br_nCD (second column), implying that the addition of Br_nCD to the solution gave rise neither the conformational modification of the calixarene molecule nor complexation phenomena. The figures reported in the third column show significant deshielding of the NH proton of the picolinamide moiety upon complexation with La^{3+}. Similar deshielding was observed for the H9, H10, OCH_3 and CH_2 groups of the alkyl chains, thus indicating that the picolinamide moiety is the binding site of the La^{3+} ions. The aromatic ring H1, H2 and methylene bridge protons 3 undergo shielding as a result of the conformational change due to La^{3+}/Calix complexation. The overall picture emerging from the chemical shift titrations indicates that the picolinamide side chains of Calix act as binding groups for La^{3+} ions, while the macrocycle undergoes conformational rearrangements. The values reported in the fourth column show that the addition of Br_nCD to the La^{3+}/Calix system does not inhibit the binding capacity of Calix towards La^{3+}, and also introduces small but significant Calix-cosane interactions. The latter are therefore detectable only in the presence of La^{3+}, consistent with a stable ternary association.

The role of the Br_nCD anion in the complexation process was further investigated by ^{11}B NMR spectroscopy. ^{11}B has magnetic and electrical quadrupole moments.[19] The interaction between the electrical quadrupole moment, Q, of each ^{11}B nucleus and any electrical field gradient existing at the nuclear site affects the NMR lineshape. When the extreme narrowing condition is fulfilled, the longitudinal and transversal relaxation times, T_1 and T_2, are equal, and the linewidth at half-height, $\nu_{\frac{1}{2}}$, of the quadrupolar nuclei in solution is given by eqn (1):

$$\nu_{\frac{1}{2}} = \frac{3}{10}\pi\left(\frac{2I+3}{2I-1}\right)\chi^2\tau_c \qquad (1)$$

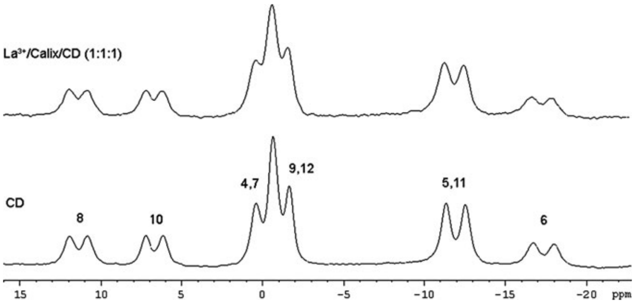


Fig. 5 ^{11}B NMR spectra of CD and La^{3+}/Calix/CD in $CD_3CN : CDCl_3$ 1 : 1 ($T = 305$ K). For the atom numbering, see Scheme 1.

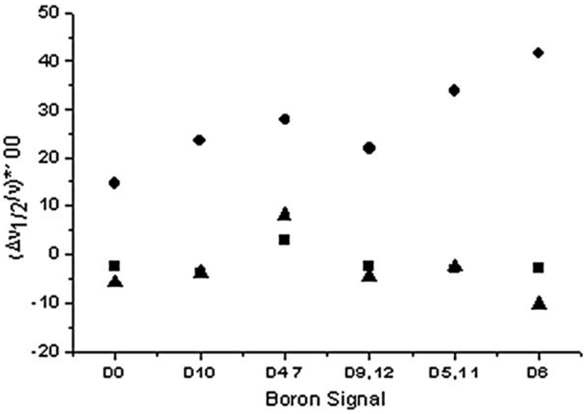


Fig. 6 A plot of the relative variation of linewidth ($\Delta\nu/\nu$) × 100 for all the ^{11}B NMR signals of samples ($\Delta\nu = \nu_{\text{observed}} - \nu_{\text{CD}}$). The quantity ($\Delta\nu/\nu$) × 100 is defined as $[(\nu_{\text{sample}} - \nu_{\text{reference}})/\nu_{\text{reference}}] \times 100$. ■: Calix/CD; ▲: La^{3+}/CD; ◆: La^{3+}/Calix/CD.

where I represents the nuclear spin quantum number, τ_c the correlation time and χ the nuclear quadrupole coupling constant. χ in turn can be written as:[20]

$$\chi = \frac{e^2 Q q_{zz}}{h} \tag{2}$$

where q_{zz} represents the electric field gradient. Therefore, $\nu_{\frac{1}{2}}$ is directly proportional to q_{zz}. The latter is related to unsymmetrical charge distribution at the quadrupolar nucleus. All boron sites are "fingerprinted" by the quadrupolar parameters that provide information on atomic arrangements, chemical bonding and complexation processes.[21,22] The linewidth analysis was carried out on CD samples as they showed spectra more resolved than the Br$_n$CD samples. ^{11}B proton-coupled NMR spectra of a CD solution, the Calix/CD mixture, the La^{3+}/CD mixture and the La^{3+}/Calix/CD mixture in $CD_3CN : CDCl_3$ 1 : 1 were acquired. The ^{11}B NMR chemical shift showed poor sensitivity to intermolecular interactions. On the contrary, the $\nu_{\frac{1}{2}}$ of the ^{11}B signals, which are highly influenced by relaxation phenomena, were affected by the complexation and thus were a sensitive probe for binding (see Fig. 5). Indeed, a remarkable growth in the ^{11}B linewidths were selectively detected in the case of the ternary association La^{3+}/Calix/CD, as displayed in Fig. 5.

This finding suggests that a ternary association is actually formed in solution and clearly visualizes the enhanced effect of the simultaneous presence of the host (Calix), synergiser (CD) and La^{3+} ions. Moreover, $\nu_{\frac{1}{2}}$ variations of the ^{11}B signals upon complexation were selectively observed for B5, B11 and B6, as visualized in Fig. 6, and indicates that CD may play a direct role in the extraction process, thus exceeding that of a generic lipophilic counterion. This issue is being currently investigated.

Conclusions

In conclusion, the combined use of ESI-MS, and ^{1}H- and ^{11}B-NMR spectroscopy allowed us to gain experimental evidence for the formation of a ternary association, La^{3+}/Calix/Br$_n$CD, which is expected to play a key role in the extraction process of lanthanoids and possibly actinoid radionuclides from nuclear waste solutions. ESI-MS experiments on both organic and aqueous phases allowed the characterization of ternary and multicomponent associations of La^{3+}, host and synergiser, and the tracking of Cs$^+$ and La^{3+} ions, providing information on the fate of the metal and nitrate ions, and the role of the carbollides during the extraction process. The exact mass determinations obtained by FTMS ICR provided an unambiguous assessment of the nature of the multicomponent clusters. ^{1}H NMR spectroscopy allowed the identification of the site of binding for La/Calix and for the separation of binding effects from conformational changes. The ^{11}B NMR data of a model synergiser confirmed the role of the carbollide as a counterion of the complex, proving the fact that the ligand is able to form a strong adduct with the metal cation in the presence of the synergiser. More generally, it was demonstrated for the first time by the combined use of NMR and mass spectrometry techniques the key role of lipophilic Co-dicarbollide synergisers in the ligand-mediated extraction of metal(III) ions from simulated radioactive wastes. Details of the ternary complexes described above can be exploited for the rational design of new or improved extracting systems.

Acknowledgements

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