Water-soluble tetrapodal N,O ligands incorporating soft N-heterocycles for the selective complexation of Am(III) over Ln(III)

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A series of four water-soluble N,O-tetrapodal ligands derived from ethylenediamine, bearing hard acetate groups and soft N-heterocycles, either pyridine or pyrazine, was developed to study the impact of the softness of N-donors on the complexation properties with trivalent f ions. Two novel ligands of enhanced soft character, bearing three pyridines (L^{3py}) or three pyrazines (L^{3pz}), were synthesized and the related lanthanide complexes were studied in solution. The ligand containing three pyridylmethyl moieties L^{3py} gives complexes with a coordination similar to EDTA, *i.e.* a hexadentate coordination mode as indicated by NMR and luminescence decays ($q = 3$) and stability constants in the range log $\beta_{110} = 6.99$–9.3 (La–Lu). On the other hand, the softest molecule L^{3pz} forms much less stable complexes with log $\beta_{110} = 4.0$–4.4 (La–Eu). The selective back-extraction of Am(III) from organic solutions containing 4f and 5f elements was tested with the four water-soluble complexing agents. The ligand L^{3pz} demonstrates poor stripping ability and selectivity. In contrast, the three ligands L^{py}, L^{pz} and L^{3py} give interesting back-extraction results with Eu/Am separation factors ranging from 36 to 46, which are significantly higher than with HEDTA. This exemplifies the role of the N-heterocycle softness in enhancing the separation between Am(III) and Eu(III). Interestingly, the pyrazine-based ligand, L^{pz}, demonstrates the best stripping properties, with a distribution factor that approaches that of HEDTA in the same conditions ($D_{Am} \approx 0.3$). This molecule is a good compromise between softness and hardness and forms complexes still stable at pH 3 due to its low basicity.

Introduction

The separation of trivalent actinides (An(III)) from trivalent lanthanides (Ln(III)) is a key step in the partitioning and transmutation strategy, which is one of the scenario being seriously considered for the future management of nuclear waste. The aim is to separate long-lived α-emitting minor actinides from spent nuclear fuel and to transmute them by nuclear fission into shorter-lived isotopes. Indeed, the transmutation of the minor actinides will only be possible after separation from the abundant fission products lanthanides having large neutron capture cross sections.[1,2]

This separation is one of the most challenging issues owing to the very similar physicochemical properties of An(III) and Ln(III). Indeed, lanthanides and transplutonium actinides both exist predominantly in their trivalent oxidation state in solution. These cations are hard acids in the Pearson classification (HSAB for hard and soft acids and bases)[3] with close ionic radii (*e.g.* 1.066 for Eu(III) and 1.090 for Am(III), CN = 8).[4] Their interactions with inorganic and organic ligands are therefore predominantly determined by electrostatic and steric factors. Even if both An(III) and Ln(III) are considered to be hard acids in HSAB theory, the higher spatial expansion of the 5f actinide orbitals with respect to the 4f lanthanide orbitals opens possibilities to discriminate them through their relative hardness. Therefore, numerous extractants containing nitrogen[5] or sulfur[6] functionalities which are softer than oxygen donors have been developed to favor An(III) over Ln(III) complexes. Several of these soft molecules extract selectively Am(III) from Am(III)–Ln(III) mixtures.[7]

Among heterocyclic N-donors, pyridine and pyrazine significantly differ in their soft character and have been inserted in tripodal[8,9] or tetrapodal[10,11] chemical architectures to test the effect of the softness of the ligand on its extraction ability and selectivity. We have recently reported[12] two tetrapodal ligands derived from ethylenediamine bearing both hard and soft donors, L^{py} and L^{pz} (see Scheme 1). These ligands bear (i) two hard acetate groups to provide stability to the trivalent f-element complexes and (ii) two N-heterocyclic soft groups to provide Am(III) *versus* Eu(III) selectivity. The complexation with Am(III) and Ln(III) is efficient in water: for instance log β_{110}(Eu) = 11.6 (L^{py}) and 9.4 (L^{pz}). Moreover, they show significant selectivities for Am(III) over Eu(III): $K_{selectivity}$(Am/Eu) = β_{110}(Am)/β_{110}(Eu) = 60 (L^{py}) and 500 (L^{pz}). These ligands only differ in their N-donor moieties and the related complexes have the same structures in water. Therefore the difference in the stability constants is correlated to the softness of the N-heterocycle and the results indicate an

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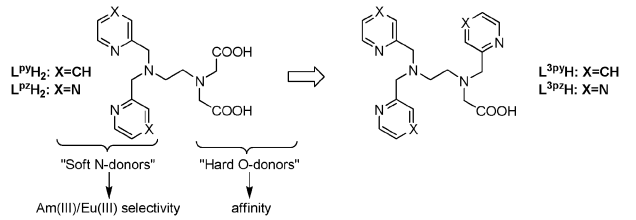


Scheme 1 Design of the ligands.

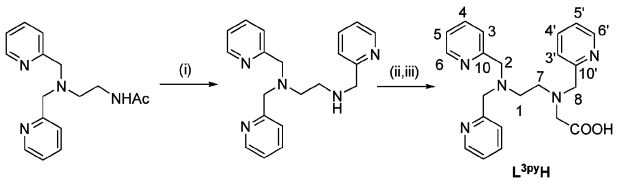
enhancement of the selectivity when the two pyridine groups are replaced by two pyrazine groups.

In this paper, the synthesis and lanthanide complexation properties of two novel ligands with increased soft character in comparison to L^{py} and L^{pz} are presented. In order to increase the soft character of the latter ligands, one of their acetate arms was replaced by one methylpyridyl group in L^{py} or one methylpyrazinyl group in L^{pz} to obtain the two novel complexing molecules L^{3py} and L^{3pz} (Scheme 1). The four N,O tetrapodal ligands presented in Scheme 1 afford a series of hydrophilic N,O ligands with a range of soft character, which allows us to evaluate the impact of the softness on the complexation of f-elements. Furthermore, they are good candidates for the selective back-extraction of Am(III) from organic solutions containing 4f and 5f elements, as they efficiently complex trivalent f cations in aqueous solution. Back-extraction experiments are presented and show that, whereas the three ligands L^{py}, L^{pz} and L^{3py} are able to selectively strip Am(III) from the organic phase, L^{3pz} which bears three methylpyrazinyl moieties is probably too soft to efficiently complex f-elements in water at pH 3. Moreover it appears that L^{pz} is a good compromise between hardness and softness because it provides enough affinity for Am(III) at pH 3 to significantly strip this ion from the organic phase and an interesting selectivity ($SF_{Am/Eu}$ = 40–50).

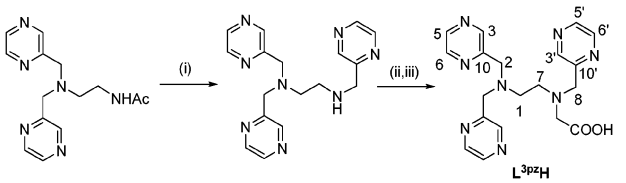
Results and discussion

Synthesis of the N,O ligands

L^{3py} and L^{3pz} are softer analogues of L^{py} and L^{pz} containing one acetate function and three pyridyl or pyrazinyl groups. These functions are introduced on an ethylenediamine bridge. The synthetic procedures are summarized in Schemes 2 and 3. The ligands L^{3py} and L^{3pz} were obtained from *N*,*N*-bis(2-pyridylmethyl)*N*′-acetylethylenediamine and *N*,*N*-bis(2-pyrazinylmethyl)*N*′-acetylethylenediamine, respectively. The syntheses of these two precursors were described in a previous report for the synthesis of L^{py} and L^{pz}, from *N*-acetylethylenediamine and 2-(chloromethyl)pyridine or 2-(chloromethyl)-pyrazine.[12] The key step in the synthesis of L^{3py} and L^{3pz} is the monosubstitution of the second aliphatic nitrogen atom, which was achieved by a reductive amination using 2-pyridine- or 2-pyrazinecarbaldehyde and sodium borohydride. Subsequent reaction with ethylchloroacetate in the presence of potassium carbonate followed by the deprotection of the ethyl ester groups gave the expected ligands L^{3py} and L^{3pz} in 19% and 9% yield, respectively. Cleavage of the ethyl ester groups was performed under acidic conditions for L^{3py} and by saponification for L^{3pz}.



Scheme 2 Synthesis of $L^{3py}H$. *Reagents and conditions*: (i) a. HCl (1 M), b. pyridine-2-carbaldehyde, $NaBH_4$, CH_3OH, 55%, (ii) $ClCH_2COOEt$, K_2CO_3, CH_3CN, 70%, (iii) HCl (2 M), H_2O, 50%.



Scheme 3 Synthesis of $L^{3pz}H$. *Reagents and conditions*: (i) a. HCl (1 M), b. pyrazine-2-carbaldehyde, $NaBH_4$, CH_3OH, 27%, (ii) $ClCH_2COOEt$, K_2CO_3, CH_3CN, 49%, (iii) KOH, EtOH–H_2O, 81%.

L^{3py} was obtained as the corresponding hydrochloride salt: $L^{3py}H{\cdot}4HCl{\cdot}2H_2O{\cdot}EtOH$ (1 equivalent of ethanol was also detected in the proton NMR spectra). L^{3pz} was obtained as the potassium salt: $L^{3pz}K{\cdot}4.5H_2O$. The ligands L^{3py} and L^{3pz} were fully characterized by NMR, ESMS and elemental analysis. The proton and carbon NMR spectra of the two ligands in D_2O indicate the presence of a unique species in which the two methylpyridine or methylpyrazine arms connected to the same nitrogen atom are equivalent.

Protonation of the ligands

All potentiometric studies were performed in KNO_3 0.1 M at 298 K. The protonation constants of L^{3py} and L^{3pz} could be obtained from the titrations of the free ligands with KOH and HNO_3. They are defined in eqn (1) and listed in Table 1, together with the values previously reported with their analogues L^{py} and L^{pz}.[12]

$$K_i = [H_iL]/[H_{i-1}L][H^+] \quad (1)$$

The titration of $L^{3py}H{\cdot}4HCl$ is indicative of three acidic sites. The first protonation ($\log K_1$ = 8.18) occurs at the most basic nitrogen, *i.e.* the aliphatic nitrogen atom adjacent to the acetate function. As expected, this $\log K$ value is lower than the

Table 1 Protonation constants of the four ligands and stability constants of their lanthanide complexes LnL from potentiometric measurements in water KNO_3 0.1 M at 298 K. β_{110} = [ML]/[M][L]

	L^{3py}	L^{py} [a]	L^{3pz}	L^{pz} [a]
$\log K_1$	8.18(7)	9.60(6)	7.18(9)	9.35(8)
$\log K_2$	5.08(6)	5.46(8)	2.3(2)	2.5(1)
$\log K_3$	3.23(9)	3.4(1)	—	—
$\log \beta_{110}$ (La)	6.99(9)	9.86(6)	4.0(3)	8.30(7)
$\log \beta_{110}$ (Nd)	8.1(1)	11.46(1)	—	8.90(2)
$\log \beta_{110}$ (Eu)	8.76(2)	11.62(4)	4.4(3)	9.37(9)
$\log \beta_{110}$ (Dy)	8.74(6)	11.89(2)	—	9.6(1)
$\log \beta_{110}$ (Lu)	9.3(1)	13.05(6)	—	9.77(1)
$\log \beta_{110}$ (Am)	—	13.4(2)	—	12.1(1)

[a] Ref. 12.

corresponding value found for L^{py}, because of the withdrawing effect of the methylpyridyl group attached to this nitrogen atom. The other two protonations give similar log$K$ values to L^{py} and can therefore be assigned to nitrogen atoms of pyridines (logK_2 = 5.08 and logK_3 = 3.23). Moreover, the log$K$ value of the carboxylate group of the NCH_2COO^- fragment is expected to be lower than 2.7 like in EDTA or other polyaminocarboxylate ligands. As for L^{py}, the second aliphatic nitrogen atom of L^{3py} does not protonate in our experimental conditions (pH > 2.5).

The titration of $L^{3pz}H$ is indicative of only two acidic sites, as observed for $L^{pz}H_2$. The first protonation (logK_1 = 7.18) also occurs at the aliphatic nitrogen atom adjacent to the acetate function and is significantly lowered in comparison to L^{3py}, because the electron withdrawing effect of the methylpyrazinyl group is larger than the electron withdrawing effect of the methylpyridyl group. The second log$K$ value can hardly be assigned to the second aliphatic nitrogen atom as in L^{pz} because the strong electron withdrawing effect of the methylpyrazinyl group directly attached to this nitrogen atom would significantly affect this value to give a much lower log$K$ value than the one found for L^{pz} (logK_2 = 2.5). Therefore, this second log$K$ can be assigned to the protonation of the carboxylate function.

As expected, the ligands containing pyridines are much more basic than the ligands containing pyrazines. Indeed, the pyridine group is much more basic than the pyrazine group: the pK_a of 2-methylpyridine is 5.96 whereas the pK_a of 2-methylpyrazine is only 1.65.[13] Moreover the withdrawing effect of methylpyridyl and methylpyrazinyl groups significantly decreases the basicity of the nitrogen atoms to which they are connected. Furthermore, as this effect is much larger with pyrazine than pyridine, the attachment of one methylpyridyl or one methylpyrazinyl group instead of one methylcarboxylate group decreases the pK_a value of the most basic site, *i.e.* the tertiary amine nitrogen atom adjacent to the acetate function, by 1.4 and 2.2 units, respectively. Consequently the two ligands L^{3py} and L^{3pz} are less basic than their analogues with two N-donors L^{py} and L^{pz}.

Potentiometric studies of the lanthanide complexes

The lanthanide complexes of L^{3py} have been studied by potentiometric titration for five representative cations of the 4f series, namely La(III), Nd(III), Eu(III), Dy(III) and Lu(III).

Typical titration curves are shown in Fig. 1. For every cation, these data could be fitted according to the formation of a unique metallic species, namely LnL^{2+} for pH values inferior to 7. The corresponding stability constants are given in Table 1. Above pH 7, the curves are characteristic of the formation of hydroxo complexes. Nevertheless, a hysteresis exists between the direct titration with KOH and the back titration with HNO_3 in this high-pH region and prevented us from determining reliable thermodynamic constants for the hydrolysis reactions. The metal titrations were fitted in the pH-range 2.5–7 (no hysteresis) with the formation of LnL^{2+}.

Titrations conducted with the pyrazine-based ligand L^{3pz} indicate the formation of complexes with low stability in comparison to L^{3py}. Furthermore, precipitation occurs for

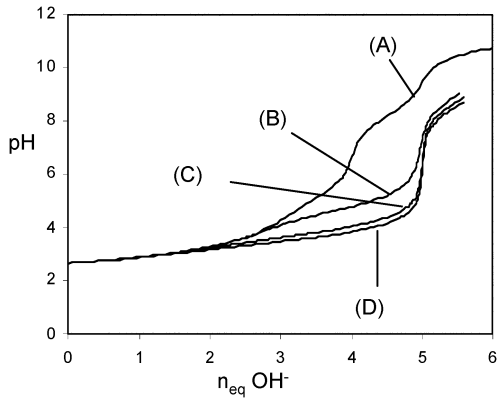


Fig. 1 Alkalimetric titrations of solutions containing 10^{-3} M $L^{3py}H{\cdot}4HCl$ with 0 or 1 equiv. $Ln(NO_3)_3$ in water and 0.1 M KNO_3 at 298 K. (A) L^{3py}, (B) LaL^{3py}, (C) EuL^{3py}, (D) LuL^{3py}.

pH > 6 with La and Eu. The titration curve with 1 Eu(III) equiv. is presented in Fig. 2 and could be fitted in the pH-range 2.7–6 (no precipitate) with the formation of the complex $(EuL^{3pz})^{2+}$ with log β_{110} = 4.4. At pH 6, 45% of the complex is formed and 55% of the cation is still free. Therefore the stability constant is calculated with a lower number of points than for L^{3py}, which explains the higher uncertainty associated with this particular value. Other lanthanide complexes of L^{3pz} were not studied because of experimental difficulties due to the precipitation of the complexes.

The evolution of the stability constants as an inverse function of the cation ionic radii, related to the hardness of the ion, is represented in Fig. 3 for the four N,O ligands. As expected, the series of complexes show an increase of the complex stability when the ionic radius of the cation decreases, according to the well-known electrostatic trend. Indeed the net complexation reaction of a Ln(III) ion with a ligand L is the result of two successive steps corresponding to dehydration followed by the combination of the partially desolved partners. The compensation effect assumes that the free energy for the dehydration process is negligible at room temperature because $\Delta H_{dehyd} \approx T\Delta S_{dehyd}$.[14] Therefore the global free energy of the complexation process is dominated by the enthalpy-driven combination step, leading to increased formation constants

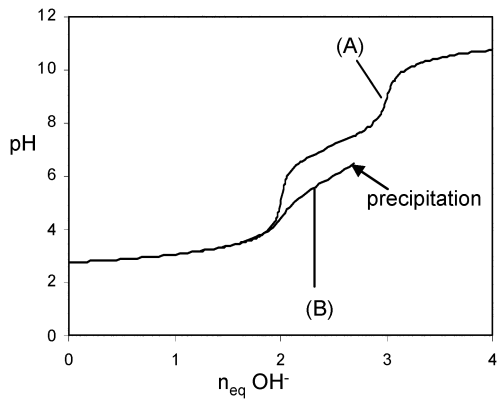


Fig. 2 Alkalimetric titrations of solutions containing 10^{-3} M $L^{3pz}H + 2HNO_3$ with 0 or 1 equiv. $Eu(NO_3)_3$ in water and 0.1 M KNO_3 at 298 K. (A) L^{3pz}, (B) EuL^{3pz}.

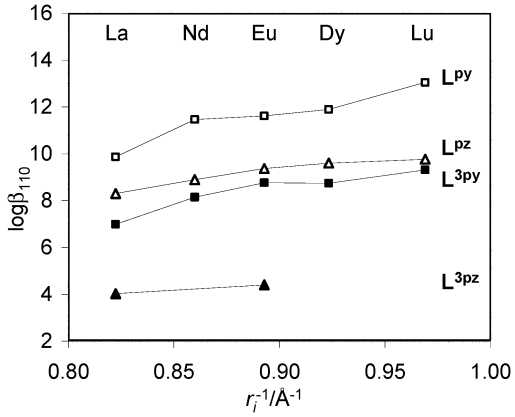


Fig. 3 Evolution of the stability constants, log β_{110} of ML complexes as an inverse function of the cation ionic radii.

with increasing charge density (or hardness) on the cation.[15] For the two pyridine-based ligands, the increase of the stability constants across the 4f series is common and of the same order of magnitude as EDTA: L^{py} ($\log \beta_{Lu} - \log \beta_{La} \approx 3.2$, 32%); L^{3py} ($\log \beta_{Lu} - \log \beta_{La} \approx 2.3$, 33%). The electrostatic trend is less marked for the pyrazine-based ligands, L^{pz} ($\log \beta_{Lu} - \log \beta_{La} \approx 1.5$, 18%) and L^{3pz} ($\log \beta_{Eu} - \log \beta_{La} \approx 0.4$, 10%). This tendency can be attributed to their softer character which produces smaller electrostatic interactions and therefore a smoother electrostatic evolution of the stability constants across the 4f series.

As expected the two novel ligands, L^{3py} and L^{3pz}, bearing three N-donor sites and only one O-donor acetate group show lower affinities for the hard lanthanide cations than their analogues with two acetate moieties. The replacement of one acetate arm in L^{py} by one methylpyridyl group induces a loss of 2.9 log units in the stability constants, whereas the replacement of one acetate arm in L^{pz} by one methylpyrazinyl group has an even more dramatic effect, loss of 5 log units in the stability constants.

The three ligands L^{py}, L^{pz} and L^{3py} demonstrate significant affinities for Ln(III) in water (10^8–10^{11} for Eu(III)) whereas the softest ligand L^{3pz} forms lanthanide complexes of quite low affinity (10^4). This indicates that L^{3pz} is too soft to efficiently compete with the water molecules, which have a large affinity for the hard lanthanide cations. For instance, ligands containing only pyrazine groups like tpza[8] or tpzen[11] have very low affinities for lanthanides preventing the study of their complexation properties in water, whereas their pyridine analogues have larger complexation efficiency even in water.[8,16] L^{3pz} has an intermediary behavior between these ligands bearing exclusively N-donors and the three other molecules presented in this paper.

Characterization of LnL^{3py} complexes

The proton NMR spectrum of the diamagnetic complex LaL^{3py} shows the presence of only one set of signals indicating the presence of one isomer without symmetry. The spectra of free L^{3py} and its lanthanum complex, LaL^{3py}, in D_2O at pD 7 are presented in Fig. 4. They were assigned with classical 2D NMR experiments. The aromatic protons are slightly shifted with respect to the free ligand. The spectrum of the lanthanum complex evidences the loss of symmetry upon the ion complexation. In particular, the two methylpyridyl arms connected to the same nitrogen atom are no longer equivalent: for instance H_6 gives two different doublets in the NMR spectrum of the complex. The methylene signals of protons H_2, H_8 and H_9 are split into well-resolved AB patterns. Each methylene of the ethylenediamine bridge, H_1 and H_7, is also split into a doublet and a triplet (ABXY system with $J_{AB} \approx J_{XY} \approx J_{AX} \approx 13$ Hz and $J_{AY} \approx J_{BY} \approx J_{BX} \approx 0$). The formation of only one complex was confirmed by the spectra obtained either in excess of ligand or in excess of cation. Indeed, the same set of signals was obtained for the complex, in slow exchange with the ligand in default of cation. Exchange correlations between the signals of the protons (especially H_6) of the two methylpyridine arms connected to the same nitrogen atom are detected in the EXSY spectrum (mixing time 100 ms). This feature can be explained by the successive steps: decomplexation of the cation followed by the interconversion of these two arms and new coordination of the cation.

The hydration numbers (q) of the europium and terbium cations in the complexes of L^{3py} were obtained from the measurement of the luminescence lifetimes of the excited-states of the complexes (τ) in H_2O and D_2O (see Table 2). The numbers of coordinated water molecules were calculated using the equation of Parker and co-workers[17] and are 3 within the experimental errors (see Table 2). They are similar to the values obtained previously for L^{py} and L^{pz}.[12] These values are very close to the values found for $Ln(EDTA)^-$ complexes. Indeed, depending on the empirical equations used, the hydration number of the lanthanide ion in $Ln(EDTA)^-$ complexes was found to be between 2.6 and 3.0 for Eu and between 2.8 and 2.9 for Tb.[17,18] This indicates that the novel molecule L^{3py} acts as a hexadentate ligand like the parent molecule EDTA, and affords two aliphatic nitrogen atoms, three aromatic nitrogen atoms of pyridines and only one oxygen donor of a carboxylate. Three water molecules complete the Ln(III) coordination sphere to obtain an overall coordination number of 9.

Unfortunately, the lanthanide complexes of L^{3pz} could not be studied in solution because of the occurrence of precipitation at low concentration. Therefore the coordination behavior of

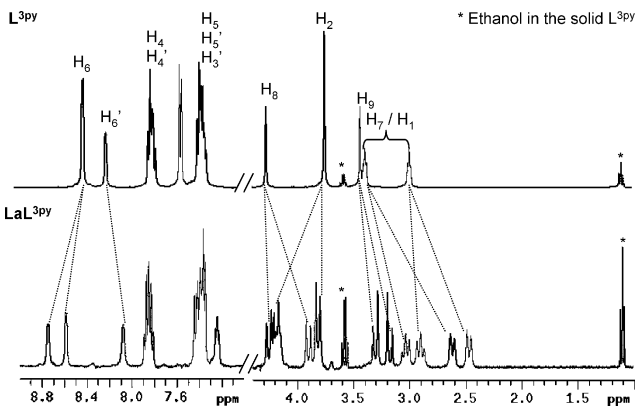


Fig. 4 400 MHz ^{1}H NMR spectra of L^{3py} and LaL^{3py} in D_2O (pD = 7.0) at 298 K.

Table 2 Luminescence lifetimes and calculated hydration numbers (q)

	τ_{H_2O}/ms	τ_{D_2O}/ms	q^a
EuL^{3py+}	0.29(1)	1.34(1)	2.9(2)
TbL^{3py+}	0.91(3)	2.05(2)	2.8(2)

[a] The hydration numbers, q, were calculated using the equation of Parker and co-workers:[17] $q = A_{Ln}(1/\tau_{H_2O} - 1/\tau_{D_2O} - \alpha_{Ln})$, with $A_{Tb} = 5$ ms, $A_{Eu} = 1.2$ ms, $\alpha_{Tb} = 0.06$ ms^{-1} and $\alpha_{Eu} = 0.25$ ms^{-1}.

this ligand could not be compared with its analogues. As pyrazine has only a very low contribution to the stability of the lanthanide complexes,[12] other types of coordination in which more than one aminoacetate moiety is coordinated to the cation may be favored leading to insoluble polymolecular systems.

Back-extraction of Am–Ln mixtures with the ligand series

The selectivity for Am(III) over Eu(III) of the two previously reported ligands L^{py} and L^{pz} has been demonstrated in water solution by the values of the stability constants in aqueous 0.1 M KNO_3 at 298 K and makes them interesting candidates for the separation of the two families of f-elements. Indeed, soft-donor reagents can be used to separate actinides from lanthanides either as lipophilic extractant molecules or as water-soluble complexing agents.[2] For instance, the TALSPEAK process (trivalent actinide–lanthanide separation by phosphorus reagent extraction from aqueous komplexes)[19] and the DIAMEX-SANEX process[20] are based on the partitioning of lanthanides and actinides between an acidic phosphorus extractant organic solution and an aqueous phase containing a high concentration of a carboxylic acid buffer and a polyaminopolycarboxylate complexant. The four water-soluble molecules L^{py}, L^{pz}, L^{3py} and L^{3pz} were subjected to back-extraction experiments to test their ability to selectively strip Am(III) from an organic metal solution containing Am(III) and Eu(III). The ligand HEDTA, used as a selective complexing agent in the DIAMEX-SANEX partitioning process,[20] was tested in the same conditions for comparison.

The metal-containing organic solution was obtained by equilibrating an aqueous solution of lanthanides (25 mM) spiked with ^{152}Eu(III) and ^{241}Am(III) in HNO_3 3 M, with an organic solution containing the malonamide derivative DMDOHEMA (0.6 M) and the dialkyl phosphoric acid HDEHP (0.3 M) in TPH, which have been demonstrated to extract these cations in the organic phase.[21] Then, this metal-containing organic solution was contacted with 0.5 M water solutions of the ligands at pH 3 buffered with 0.4 M citric acid. The results are reported in Table 3. The distribution ratios, D_M, were calculated as the ratio of the analytical concentrations of the relevant cation in the organic and aqueous phase (eqn (2)). Therefore, the smaller D_M is, the more efficient the back-extraction is

$$D_M = [M]_{org}/[M]_{aq} \quad (2)$$

The percentage of metal ion stripped in the water phase can also be calculated from the distribution factor according to eqn (3).

$$\%_{stripped\ M} = \frac{1}{1 + D_M} \quad (3)$$

Table 3 Back-extraction results: distribution ratios, percentages of stripped ions and separation factors for the back-extraction of Eu(III) and Am(III) by ligands L^{pz}, L^{py}, L^{3py}, L^{3pz} and HEDTA[a] and conditional stability constants at pH 3 (298 K, KNO_3 0.1 M)[b]

	L^{pz}	L^{py}	L^{3py}	L^{3pz}	HEDTA
D_{Eu}	13	49	53	130	1.6
D_{Am}	0.31	1.37	1.16	8.3	0.13
$\%_{stripped\ Eu}$	7	2	2	1	38
$\%_{stripped\ Am}$	76	42	46	11	88
log β_{110}(Eu) at pH 3	2.9	2.0	1.5	0.1	6.1
log β_{110}(Am) at pH 3	5.6	3.8	—	—	6.5
$SF_{Am/Eu}$	41	36	46	15	12

[a] Aqueous phase: ligand 0.5 M, citric acid 0.4 M, pH = 3. Organic phase: 0.3 M HDEHP, 0.6 M DMDOHEMA, ^{152}Eu and ^{241}Am trace level, TPH. [b] The conditional stability constants at pH 3 were calculated from the pK and stability constants given in Table 1.

The separation factor between Am(III) and Eu(III), $SF_{Am/Eu}$, is given by eqn (4). The higher $SF_{Am/Eu}$ is, the better the selectivity of the water-soluble ligand for Am(III) with respect to Eu(III) is.

$$SF_{Am/Eu} = D_{Eu}/D_{Am} \quad (4)$$

Most of the distribution ratios given in Table 3 are above 1 indicating that a small percentage of the cations are back-extracted in the water phase. In particular, it appears that the softest molecule L^{3pz} has too low an affinity to perform significant cation back-extraction. This ligand gives the largest distribution ratios but also a poor selectivity factor, which may indicate that the pyrazine N-donors play no role in the coordination of the cations. The four other ligands give D_{Am} below 1 (L^{pz} and HEDTA) or very close to 1 (L^{py} and L^{3py}) and are thus able to strip Am(III) from the organic solution in significant amounts. The conditional stability constants at pH 3 are also reported in Table 3. These values have been calculated from the known stability constants of the Eu(III) and possibly Am(III) complexes and the log$K$ values of the ligands. As expected, large conditional stability constants give efficient back-extraction and small distribution ratios D_{Eu} or D_{Am}. The high conditional stability constant values calculated for the two ligands HEDTA and L^{pz} explain their better efficiency to strip Am(III) at pH 3. Indeed, L^{pz} shows lower affinity constants than L^{py} but is less basic, therefore, its conditional stability constants at pH 3 are higher than those of L^{py}, making the former a more efficient complexant. For the same reason, the two pyridine-based ligands L^{py} and L^{3py} give nearly the same distribution ratios, even though the stability constants of their complexes are quite different, because L^{3py} is less basic than L^{py}. As the D_{Am} values of these two ligands are very similar, this allows us to roughly estimate the conditional stability constant of L^{3py} at pH 3: log $\beta_{110}{}^{pH3}(AmL^{3py}) \approx$ log $\beta_{110}{}^{pH3}(AmL^{py}) \approx 4$, which gives an estimation of the stability constant: log $\beta_{110}(AmL^{3py}) \approx 11$. As expected, this indicates that L^{3py}, which is softer than L^{py}, has a greater selectivity for Am(III) over Eu(III) in water: $K_{selectivity}(Am/Eu) = \beta_{110}(Am)/\beta_{110}(Eu) \approx 10^{2.24} = 170$.

The three ligands L^{py}, L^{pz} and L^{3py} give interesting back-extraction results which are illustrated in Fig. 5, with separation factors ranging from 36 to 46. The SF values do not reflect the

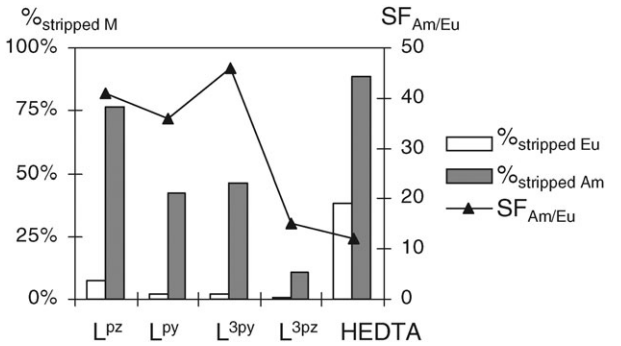


Fig. 5 Percentage of stripped ions and separation factors for the back-extraction of Eu(III) and Am(III) by 0.5 M water solutions of L^{pz}, L^{py}, L^{3py}, L^{3pz} and HEDTA at pH 3.

thermodynamic selectivity, $K_{selectivity}$(Am/Eu), determined in homogeneous water solutions. This may be due to the different media used to determine the affinity constants (homogeneous water, KNO_3 0.1 M) and to perform the back-extraction experiments (different ionic strength, presence of citric acid, extractants DMDOHEMA and HDEHP in the organic phase). In particular, the formation of ternary complexes with citric acid cannot be excluded. Nevertheless, the separation factors obtained with the three ligands containing soft N-donors, L^{py}, L^{pz} and L^{3py}, give higher SF than the ligand HEDTA, exemplifying the role of the ligand's softness in enhancing the separation between Am(III) and Eu(III).

The most interesting molecule in the series of N,O tetrapodal ligands presented here is L^{pz} which combines several advantages. L^{pz} exhibits a good selectivity for Am(III) over Eu(III). Despite its soft character it has a significant affinity for f ions due to the presence of two acetate hard donors. Finally, it is less basic than the pyridine-based ligands due to the strong withdrawing effect of the methylpyrazinyl moiety that significantly lowers the highest pK_a. Therefore L^{pz} still has an efficient conditional stability constant at pH 3 leading to a distribution ratio for Am(III) approaching the value measured with HEDTA. In this series, L^{pz} is the only molecule able to slightly strip Am(III) from Am–Eu mixtures with a good selectivity under more drastic conditions, *i.e.* at lower pH or lower ligand concentration. These results are reported in Table 4. Of course, the distribution ratios are higher than those presented in Table 3 and the back-extraction is less efficient, but the selectivity factors are in the same range: 40–50. Moreover, it can be added that working at higher pH, *e.g.* pH 4, should increase the stripping ability of this selective ligand.

Conclusion

To conclude, a series of N,O-tetrapodal ligands containing soft N-heterocycles, either pyridine or pyrazine, was developed to study the impact of the softness of the N-donor on the complexation properties with trivalent f ions. As expected, as the softness of the ligand increases, by replacing either a pyridine with a pyrazine or an acetate with a N-heterocycle, the affinity for f-elements decreases. Indeed, trivalent f-element cations are hard acids which interact mainly *via* electrostatic bonds with their ligands. The scale of affinity is the following: $L^{py} > L^{pz} \geq L^{3py} \gg L^{3pz}$. The ligand containing three pyridylmethyl moieties L^{3py} gives similar complexes to L^{py} and L^{pz} with a hexadentate coordination mode as indicated by NMR and luminescence decays ($q = 3$). The coordination behavior of the softest molecule L^{3pz} is less clear as the complexes precipitate in the mM range, which prevents detailed solution studies. Nevertheless, potentiometric titration shows that L^{3pz} complexes are much less stable than those obtained with the other three ligands.

Table 4 Back-extraction results: distribution ratios, percentages of stripped ions and separation factors for the back-extraction of Eu(III) and Am(III) by L^{pz}[a]

	$[L^{pz}]$ = 0.5 M pH = 2[b]	$[L^{pz}]$ = 0.05 M pH = 3[c]
D_{Eu}	320	650
D_{Am}	7.7	13
$\%_{stripped\ Eu}$	0.3	0.2
$\%_{stripped\ Am}$	11	7
$SF_{Am/Eu}$	42	50

[a] Organic phase: 0.3 M HDEHP, 0.6 M DMDOHEMA, ^{152}Eu and ^{241}Am trace level, TPH. [b] Aqueous phase: $[L^{pz}]$ 0.5 M, pH = 2. [c] Aqueous phase: ligand 0.5 M, citric acid 0.4 M, pH = 3.

Selective back-extraction is a promising process for the separation of minor actinides from fission products.[19] The series of water-soluble complexing agents presented in this paper was subjected to back-extraction to test their stripping ability in regard to their complexation properties for trivalent f-elements. The softest ligand L^{3pz} appears not to be an efficient stripping agent as its complexing ability is too low. Moreover, its selectivity factor is similar to that obtained with HEDTA which suggests that the pyrazine groups may not coordinate the cations in these low-affinity complexes. In contrast, the other three molecules give similar selectivity factors (~40) which are higher than that obtained with HEDTA and evidence the role of the N-heterocycles in enhancing the Am(III)–Eu(III) selectivity. The second pyrazine-based ligand, L^{pz}, demonstrates the best stripping properties. This molecule is indeed a good compromise between softness and hardness. The presence of two hard O-donors gives f-element complexes of significant stability; therefore the Am distribution ratio at pH 3 approaches that of HEDTA under the same conditions ($D_{Am} \approx 0.3$). Moreover, the two soft pyrazine groups provide a significant selectivity for Am(III) with respect to Eu(III). To obtain selective and efficient water-soluble complexing agents, soft ligands with sufficient affinity and also with a low basicity should be developed in order to maintain the stripping ability at low pH. Therefore a compromise has to be found between softness and affinity as in the pyrazine-based ligand L^{pz}.

Experimental

General details

Solvents and starting materials were purchased from Aldrich, Acros, Fluka and Alfa Aesar and used without further purification. Lanthanide salts were purchased from Aldrich and deuterium oxide (99.9 atom% D) from Euriso-Top. All

water solutions were prepared from ultrapure laboratory grade water that had been filtered and purified by reverse osmosis using a Millipore MilliQ reverse-osmosis cartridge system (resistivity 18 MΩ cm). Thin layer chromatography (TLC) was performed on aluminium oxide 60 F_{254} neutral (Merck). Flash chromatography was performed on aluminium oxide 90 active neutral (+4.9% water wt, 63–200 μm, Merck). ^{1}H NMR and ^{13}C NMR spectra were recorded at 298 K on a Mercury Varian 400 spectrometer. Chemical shifts are reported in ppm with the solvent as the internal reference and coupling constants are given in Hz. Mass spectra were acquired with a Finigan LCQ-ion trap equipped with an electrospray source. Elemental analyses were performed by the Service Central d'Analyse (Solaize, France).

L^{py}, L^{pz} and 2-pyrazinecarbaldehyde were obtained according to published procedures.[12,22]

Synthesis

***N,N,N′*-Tris(2-pyridylmethyl)ethylenediamine.** *N,N*-Bis(2-pyridylmethyl)ethylenediamine was first obtained from *N,N*-bis(2-pyridylmethyl)-*N′*-acetylethylenediamine (648 mg, 2.28 mmol) according to published procedures.[12] The crude product was used for the reductive amination: 2-pyridinecarbaldehyde (366 mg, 3.42 mmol) was added dropwise to a solution of *N,N*-bis(2-pyridylmethyl)ethylenediamine (552 mg) in dry methanol (50 mL), and the mixture was refluxed for 2 h under argon. Sodium borohydride (259 mg, 6.84 mmol) was added and the mixture was stirred at room temperature overnight, and evaporated. An aqueous solution of saturated $NaHCO_3$(100 mL) was added to the residue and the whole was extracted with dichloromethane (3 × 20 mL). The collected organic layers were dried over Na_2SO_4, filtered, and concentrated. The resulting brown oil was chromatographed on aluminium oxide (elution with dichloromethane–ethanol 99 : 1) to afford *N,N,N′*-tris(2-pyridylmethyl)ethylenediamine (416 mg, 55%) as an orange oil. δ_H (400 MHz, $CDCl_3$, Me_4Si) 8.50 (3H, d, *J* 5.0, H^{Ar}), 7.62 (3H, t, *J* 7.8, H^{Ar}), 7.52 (2H, d, *J* 7.8, H^{Ar}), 7.29 (1H, d, *J* 1.6, H^{Ar}), 7.13 (3H, t, *J* 5.0, H^{Ar}), 3.85 (2H, s, H^8), 3.84 (4H, s, H^2), 2.81 (4H, s, H^1H^7); *m/z* 334.1 (MH^+, 100%).

***N,N,N′*-Tris(2-pyridylmethyl)-*N′*-(ethylacetate)ethylenediamine.** To a solution of *N,N,N′*-tris(2-pyridylmethyl)ethylenediamine (416 mg, 1.25 mmol) in 30 mL of dry acetonitrile under argon, were added ethylchloroacetate (160 μL, 1.5 mmol) and potassium carbonate (207 mg, 1.5 mmol). After stirring the mixture for 2 h at room temperature, the suspension was refluxed overnight, cooled at room temperature, filtered and evaporated. The resulting oil was chromatographed on aluminium oxide (elution with dichloromethane–methanol 99 : 1) to afford *N,N,N′*-tris(2-pyridylmethyl)-*N′*-(ethylacetate)-ethylenediamine (369 mg, 70%) as an orange powder. δ_H (400 MHz, $CDCl_3$, Me_4Si) 8.49 (3H, m, H^{Ar}), 7.61 (2H, td, *J* 7.8 and 1.6, H^{Ar}), 7.56 (1H, td, *J* 7.8 and 1.6, H^{Ar}), 7.49 (2H, d, *J* 7.8, H^{Ar}), 7.42 (1H, d, *J* 7.8, H^{Ar}), 7.13 (3H, m, H^{Ar}), 4.12 (2H, q, *J* 6.9, $COOCH_2CH_3$), 3.89 (2H, s, H^8), 3.81 (4H, s, H^2), 3.37 (2H, s, H^9), 2.89 (2H, t, *J* 7.8, H^1/H^7), 2.72 (2H, t, *J* 7.8, H^1/H^7), 1.22 (3H, t, *J* 6.9, $COOCH_2CH_3$).

L^{3py}H (*N,N,N′*-tris(2-pyridylmethyl)ethylenediamine-*N′*-acetic acid)·4HCl. A degassed 2 M HCl solution (75 mL) was added to *N,N,N′*-tris(2-pyridylmethyl)-*N′*-(ethylacetate)-ethylenediamine (369 mg, 0.88 mmol) and the resulting mixture was refluxed for 16 h under argon, cooled at room temperature and evaporated. The residue was washed with ethanol and diethyl ether and dried under vacuum for one day to afford L^{3py}·4HCl (270 mg, 50%) as a white solid (found: C, 46.09; H, 6.12; N, 11.38%. Calc. for $C_{22}H_{25}N_5O_2$·4HCl·2H_2O·1EtOH: C, 46.54; H, 6.35; N, 11.31%); δ_H (400 MHz, D_2O, DSS) 8.73 (2H, d, *J* 4.9, H^6), 8.62 (1H, d, *J* 5.9, $H^{6'}$), 8.53 (2H, t, *J* 7.8, H^4), 8.33 (1H, t, *J* 7.8, $H^{4'}$), 8.07 (2H, d, *J* 7.8, H^3), 7.98 (2H, t, *J* 6.8, H^5), 7.81 (2H, m, $H^{Ar'}$), 4.37 (2H, s, H^8), 4.30 (4H, s, H^2), 3.71 (2H, s, H^9), 3.26 (2H, t, *J* 6.8, H^7), 3.03 (2H, t, *J* 6.8, H^1); δ_C (100 MHz, D_2O, DSS) 172.80 (C11), 152.01 (C10), 151.28 (C10′), 147.28 (Cpyr), 144.28 (Cpyr), 143.77 (Cpyr), 141.58 (Cpyr), 127.19 (Cpyr), 126.48 (Cpyr), 126.12 (Cpyr), 125.84 (Cpyr), 56.18 (C9), 55.38 (C2), 55.19 (C8), 51.64 (C7), 50.82 (C1); *m/z* 392.2 (MH^+, 100%).

***N,N,N′*-Tris(2-pyrazinylmethyl)ethylenediamine.** *N,N*-Bis(2-pyrazinylmethyl)ethylenediamine was first obtained from *N,N*-bis(2-pyrazinylmethyl)-*N′*-acetyl ethylenediamine (1.39 g, 4.84 mmol) according to published procedures.[12] The crude product was used for the reductive amination: a solution of 2-pyrazinecarbaldehyde (732 mg, 6.77 mmol) in dry methanol (50 mL) was added dropwise to a solution of *N,N*-bis(2-pyrazinylmethyl)ethylenediamine (1.397 g) in dry methanol (200 mL), and the mixture was refluxed for 2 h under argon. Sodium borohydride (649 mg, 17.16 mmol) was added and the mixture was stirred at room temperature overnight, and evaporated. The crude product was chromatographed on aluminium oxide (elution with dichloromethane–ethanol 99 : 1) to afford *N,N,N′*-tris(2-pyrazinylmethyl)ethylenediamine (443 mg, 27%) as an orange oil. δ_H (400 MHz, $CDCl_3$, Me_4Si) 8.70–8.46 (9H, m, H^{Ar}), 3.93 (6H, m, H^2/H^8), 2.89 (4H, s, H^1H^7).

***N,N,N′*-Tris(2-pyrazinylmethyl)-*N′*-(ethylacetate)ethylenediamine.** To a solution of *N,N,N′*-tris(2-pyrazinylmethyl)ethylenediamine (443 mg, 1.32 mmol) in dry acetonitrile (60 mL) under argon, ethylchloroacetate (267 μL, 1.58 mmol) and potassium carbonate (218 mg, 1.58 mmol) were added. After stirring the mixture for 2 h at room temperature, the suspension was refluxed overnight, cooled at room temperature, filtered and evaporated. The resulting oil was chromatographed on aluminium oxide (elution with ethylacetate–methanol 98 : 2) to afford *N,N,N′*-tris(2-pyrazinylmethyl)-*N′*-(ethylacetate)ethylenediamine (271 mg, 49%) as an orange powder. δ_H (400 MHz, CD_3CN, Me_4Si) 8.65 (2H, s, H^{Ar}), 8.62 (1H, s, H^{Ar}), 8.41 (6H, m, H^{Ar}), 4.07 (2H, q, *J* 7.0, $COOCH_2CH_3$,), 3.88 (2H, s, H^8), 3.82 (4H, s, H^2), 3.37 (2H, s, H^9), 2.84 (2H, t, *J* 6.3, H^1/H^7), 2.69 (2H, t, *J* 6.3, H^1/H^7), 1.85 (3H, t, *J* 7.0, $COOCH_2CH_3$).

L^{3pz}K (*N,N,N′*-tris(2-pyrazinylmethyl)ethylenediamine-*N′*-acetic acid). *N,N,N′*-Tris(2-pyrazinylmethyl)-*N′*-(ethylacetate)-ethylenediamine (271 mg, 0.641 mmol) was dissolved in a solution containing degassed 1 M KOH solution (770 μL, 0.77 mmol), H_2O (22.5 mL) and ethanol (7.5 mL). The

resulting mixture was stirred for 16 h under argon at room temperature. Then the resulting solution was evaporated, dissolved in acetonitrile and filtrated. The filtrate was concentrated under pressure to afford $L^{3pz}K$ (267 mg, 81%) as an orange oil (found: C, 44.57; H, 5.58; N, 21.35%. Calc. for $C_{19}H_{21}N_8O_2K$, 4.5 H_2O: C, 44.43; H, 5.89; N, 21.82%.), δ_H (400 MHz, D_2O, Me_4Si) 8.56 (1H, s, $H^{6'}$), 8.48 (1H, d, *J* 2.9, $H^{3'}$), 8.42 (1H, d, *J* 2.9, $H^{5'}$), 8.36 (2H, s, H^6), 8.33 (2H, s, H^3), 8.29 (2H, d, *J* 2.9, H^5), 4.51 (2H, s, H^8), 3.87 (4H, s, H^2), 3.67 (2H, s, H^9), 3.57 (2H, t, *J* 5.8, H^7), 3.17 (2H, t, *J* 5.8, H^1); δ_C (100 MHz, D_2O, DSS) 169.96 (COOH), 153.27 (C10), 146.24 (C10′), 144.69 (CAr), 144.62 (CAr), 144.58 (CAr), 143.92 (CAr), 142.95 (CAr), 57.01 (C2), 55.51 (C8), 55.02 (C9), 51.71 (C7), 48.76 (C1); *m*/*z* 433.1 (MK^+, 100%).

Potentiometry

Carbonate-free 0.1 mol L^{-1} KOH and 0.1 mol L^{-1} HNO_3 were prepared from Fisher Chemicals concentrates. Potentiometric titrations were performed in 0.1 mol L^{-1} aqueous KNO_3 under an argon atmosphere; the temperature was controlled to ±0.1 °C with a circulating water bath. The p[H] (p[H] = −log [H^+], concentration in molarity) was measured in each titration with a combined pH glass electrode (Metrohm) filled with 3 mol L^{-1} KCl and the titrant addition was automated by use of a 751 GPD titrino (Metrohm). The electrode was calibrated in hydrogen ion concentration by titration of HNO_3 with KOH in 0.1 mol L^{-1} KNO_3.[23] A plot of meter reading *versus* p[H] allows the determination of the electrode standard potential (E°) and the slope factor (*f*).

Ligand concentration was determined by potentiometric titrations and was in accordance with the elemental analysis of the molecules. Lanthanide salt solutions were prepared by dissolving the appropriate amount of lanthanide nitrate in water. The exact metal ion concentration was determined by colorimetric titration using standardized EDTA solutions (Fisher Chemicals) and xylenol orange as indicator. Continuous potentiometric titrations with KOH 0.1 mol L^{-1} were conducted on 20 mL of aqueous solutions containing 10^{-3} mol L^{-1} of the ligand and 0, 0.5, 1 and 2 equiv. of the desired metallic cation. Back titrations with HNO_3 0.1 mol L^{-1} were systematically performed after each experiment to check whether equilibration had been achieved. In a typical experiment, 100 points were measured with a 2 min delay between the measurements for the free ligand, and a 5 min delay for metallic complexes.

Experimental data were refined using the computer program Hyperquad 2000.[24] All equilibrium apparent constants are expressed as concentration ratios and not activities. The ionic product of water at 25 °C and 0.1 mol L^{-1} ionic strength is pK_w = 13.78.[13] The initial concentrations of ligand, metal and proton were fixed, as well as the ligand p*K* values for the metallic complex stability constant determination. All values and errors (one standard deviation) reported represent the average of at least three independent experiments.

NMR spectroscopy

Samples for NMR spectroscopy were prepared by mixing appropriate volumes of stock solutions of the ligand (~0.005 mol L^{-1}) and the lanthanide triflate salt in deuterium oxide. Ligand concentrations were determined by potentiometric titration, and the metal concentrations by EDTA titrations using xylenol orange indicator. The pD of the samples were adjusted to the desired value by adding stock solutions of DCl or NaOD in D_2O. The pD were measured according to pD = pH_{read} + 0.41.[25]

Luminescence

Terbium and europium luminescence lifetimes were measured on a Perkin-Elmer LS50B spectrofluorimeter by recording the decay of the emission intensity at 545 nm for Tb and 616 nm for Eu (excitation at 274 nm). The decays of luminescence intensities followed systematically monoexponential laws and were analyzed as single-exponential decays. The instrument settings were as follows: a gate time of 1 ms, a flash count of 1, excitation and emission slit widths of 10 nm, and a varied delay time. The complexes were prepared *in situ* by mixing 0.9 equivalents of the metal solution with one equivalent of ligand. The concentration selected was 1 mM for europium complexes and 0.5 mM for terbium complexes either in H_2O or D_2O. The pH (or pD) was then adjusted to 7 with a NaOH (or NaOD) solution. Reported lifetimes, τ, are average of three separate measurements calculated by monitoring the emission intensity after at least 20 different delay times covering two or more lifetimes.

Back-extraction experiments

Abbreviations: HDEHP: bis(2-ethylhexyl)phosphoric acid, DMDOHEMA: *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexylethoxy malonamide, TPH (hydrogenated tetrapropylene) is a mixture of highly branched alkanes containing 11 to 13 carbon atoms, HEDTA: *N*-hydroxyethylethylenediaminetriacetic acid.

All extraction experiments were performed at 25 °C. First, to prepare the organic phase containing the metallic ions, 4 mL of an organic solution (0.3 M HDEHP, 0.6 M DMDOHEMA, TPH) and 4 mL of an aqueous solution (HNO_3 3 M, $[Ln]_{tot}$ = 25 mM spiked with ^{241}Am(III) and ^{152}Eu(III)) were equilibrated by vortexing for 10 min. Preliminary experiments showed that a 10 min vortexing time is adequate to reach equilibrium. The organic and aqueous phases were separated by centrifugation. The organic phase was scrubbed by an aqueous solution (citric acid 0.5 M, pH 3) and used in the following for the back-extraction experiments.

The aqueous solutions used in the back-extraction experiments were prepared with a ligand concentration of 0.5 M (or 0.05 M), citric acid 0.4 M, and pH adjusted to 3 with sodium hydroxide (L^{py} and L^{3py}) or nitric acid (L^{pz} and L^{3pz}). For the back-extraction experiment performed at pH 2, the pH of the aqueous phase was adjusted to 2 with HNO_3. 0.5 mL of the aqueous solution of ligand and 0.5 mL of the organic phase containing the metal ions were equilibrated by vortexing for 60 min at 25 °C. After separation by centrifugation aliquots of both phases were analyzed using a gamma counting spectrometer (Hyper pure Ge detector, CANBERRA). ^{152}Eu and ^{241}Am tracers were used for the measurement of the Eu–Am distribution. In the range of 0.1–10 the error in *D* values is about 5%, while in the ranges of 0.01–0.1 and 10–100 the error is greater, about 10%.

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