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# Separation of lanthanides and actinides(III) using tridentate benzimidazole, benzoxazole and benzothiazole ligands

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The ability of new hydrophobic tridentate ligands based on 2,6-bis(benzimidazol-2-yl)pyridine, 2,6-bis(benzoxazol-2-yl)pyridine and 2,6-bis(benzothiazol-2-yl)pyridine to selectively extract americium(III) from europium(III) was measured. The most promising ligand – 2,6-bis(benzoxazol-2-yl)-4-(2-decyl-1-tetradecyloxy)pyridine $L^9$ was found to give separation factors ($SF_{Am/Eu}$) of up to 70 when used to extract cations from 0.02–0.10 M $HNO_3$ into TPH in synergy with 2-bromodecanoic acid. Six structures of lanthanide complexes with 2,6-bis(benzoxazol-2-yl)pyridine $L^6$ were then determined to evaluate the types of species that are likely to be involved in the separation process. Three structural types were observed, namely $[LnL^6(NO_3)_3(H_2O)_2]$, 11-coordinate only for La, $[LnL^6(NO_3)_3(CH_3CN)]$, 10-coordinate for Pr, Nd and Eu and $[LnL^6(NO_3)_3(H_2O)]$, L 10-coordinate for Eu and Gd. Quantum Mechanics calculations were carried out on the tridentate ligands to elucidate the conformational preferences of the ligands in the free state and protonated and diprotonated forms and to assess the electronic properties of the ligands for comparison with other terdentate ligands used in lanthanide/actinide separation processes.

## Introduction

There is continued urgent interest in the partitioning of the minor actinides(III) and their subsequent transmutation as part of a strategy for a more efficient reprocessing of nuclear fuel.[1,2] Our work has focused on the partitioning of the most radiotoxic minor actinide, americium from lanthanide cations such as europium(III). The partitioning step is difficult because americium(III) has to be separated from the chemically similar lanthanide(III) ions by exploiting minor but significant differences between Am(III) and Eu(III). It has been shown that polydentate nitrogen ligands can separate Am(III) from the Ln(III) and the separation performance of many different polydentate nitrogen ligands has been assessed in recent years, mainly using europium as a representative of the lanthanide series.[3–6] The use of heterocycles such as pyridine, pyrazine, pyrimidine, 1,2,4-triazole, 1,2,4-triazine and 1,3,5-triazine, in various combinations has allowed us to begin to correlate extraction performance with the chemical and electronic properties of the heterocycles. It appears that the electron density on the donor N atoms and the basic character of these atoms are of great importance for controlling the interaction of the ligands with the metal cations. The best Am(III)/Eu(III) SF (SF = separation factors) have been obtained with either two weakly basic terminal 1,2,4-triazine or 1,2,4-triazole groups incorporated into a tridentate ligand.[7,8] Both types of ligand were found to give Am(III)/Eu(III) SF values of 50–150 depending on the conditions used for the extractions. Although the most promising results were obtained with the 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines, these ligands were found to be susceptible to hydrolysis and radiolysis which would greatly hinder their use in a future industrial process.[9] Work in our laboratory is now focused on the synthesis of weakly basic extracting agents with increased stability to hydrolysis and radiolysis which are also able to separate efficiently Am(III) from Eu(III).

The synthesis of tridentate ligands such as 2,6-bis(benzimidazol-2-yl)pyridine $L^1$ (Fig. 1) containing benzimidazole ligands caught our attention because the cyclisation reaction to form the benzimidazole rings occurs at 200–230 °C in polyphosphoric acid.[10] The stability of these ligands at high temperature in relatively strong acid conditions would be of great advantage in a future industrial partitioning process. We were particularly interested in similarly synthesised tridentate ligands containing either benzoxazoles or benzothiazoles

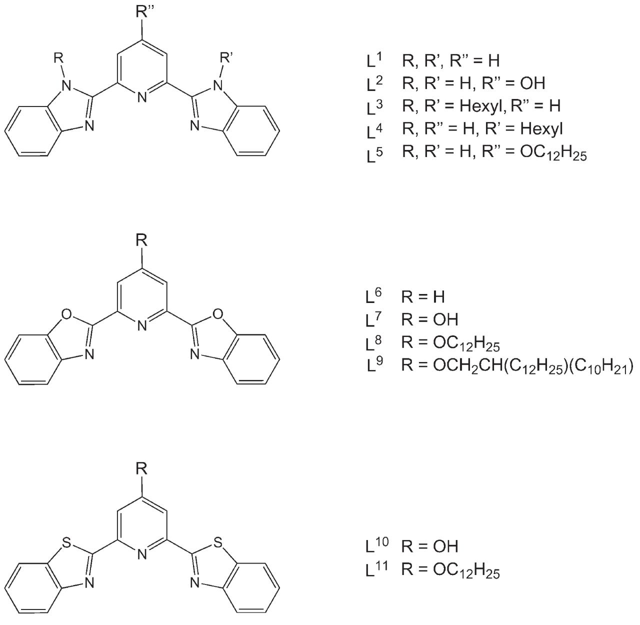

**Fig. 1** Ligands $L^1$ to $L^{11}$.

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in addition to benzimidazoles because benzoxazole (p$K_a$ −0.3) and benzothiazole (p$K_a$ 1.2) are more weakly basic than benzimidazole (p$K_a$ 5.53).[11] The weakly basic nature of the benzoxazole and benzothiazole ligands could be expected to improve the separation of Am(III) from Eu(III) since coordination could take precedence over protonation. In this study, hydrophobic derivatives of $L^1$ containing either benzimidazole, benzoxazole or benzothiazole groups were synthesised and tested for their ability to separate americium from europium. In addition, 2,6-bis(benzoxazol-2-yl) pyridine $L^6$ was synthesised in order to provide a suitable ligand for complexation studies with the lanthanides. No X-ray crystal structures of lanthanide complexes with a coordinating benzoxazole ligand have been published previously. Thus such studies were carried out in order to gain some insight into the species which may be involved in the separation.

## Results and discussion

### Synthesis

$L^6$ was synthesised using the literature method for ($L^1$).[10] A similar method was used to prepare 2,6-bis(benzimidazol-2-yl)-4-hydroxypyridine $L^2$, 2,6-bis(benzoxazol-2-yl)-4-hydroxypyridine $L^7$ and 2,6-bis(benzothiazol-2-yl)-4-hydroxypyridine ($L^{10}$),[12] the precursors required for the synthesis of the hydrophobic solvent extraction reagents. Subsequent deprotonation of the hydroxy groups with $K_2CO_3$ and alkylation with 1-bromododecane gave the corresponding hydrophobic derivatives – 2,6-bis(benzimidazol-2-yl)-4-dodecyloxypyridine $L^5$, 2,6-bis(benzoxazol-2-yl)-4-dodecyloxypyridine $L^8$ and 2,6-bis-(benzothiazol-2-yl)-4-dodecyloxypyridine $L^{11}$. *N*-Alkylated derivatives of $L^1$ were also prepared for comparison by deprotonation of the benzimidazole N atoms with either NaH or $K_2CO_3$ and subsequent alkylation with 1-bromohexane to give 2,6-bis(8-hexylbenzimidazol-2-yl)pyridine $L^3$ and 2-(hexylbenzimidazol-2-yl)-6-(benzimidazol-2-yl)pyridine $L^4$. Even with attached dodecyl chains, ligands $L^5$, $L^8$ and $L^{11}$ had poor solubility in the alkane based solvents favoured for solvent extraction processes and preliminary solvent extraction experiments had to be carried out using 1,1,2,2-tetrachloroethane. These experiments were sufficient to identify 2,6-bis(benzoxazol-2-yl)-4-dodecyloxy pyridine $L^8$ as the most promising extracting agent. As a result, $L^9$, a more hydrophobic version of $L^8$ was prepared with an attached 2-decyl-1-tetradecyl chain. $L^9$ was synthesised directly from the reaction of 2-decyl-1-tetradecyl tosylate with $L^7$. $L^9$ proved to have good solubility in the solvent of choice – TPH, (hydrogenated tetrapropene, an industrial aliphatic diluent with highly branched chains) and extraction results were obtained at ligand concentrations of 0.02 M in TPH when the ligand was used to extract from 0.021–0.10 M $HNO_3$.

**Solvent extraction studies.** Solvent extraction studies to obtain the distribution coefficients $D_{Am}$, $D_{Eu}$, (defined as the ratio of concentrations of the metal in the organic and aqueous layers) and the separation factors ($SF_{Am/Eu}$) given by $D_{Am}/D_{Eu}$ were first carried out using $L^8$, $L^3$, $L^4$, $L^5$ and $L^{11}$ with our published methods.[13] Initially the organic solution contained the appropriate ligand at various concentrations together with α-bromodecanoic acid at 1 mol dm$^{-3}$ and the aqueous solution contained $Am^{241}$ and $Eu^{152}$ trace level in various concentrations of nitric acid. The presence of α-bromodecanoic acid (αBrDa), proved necessary for the extraction process. This reagent is thought to act both as a phase transfer reagent as well as being directly involved in the overall mechanism of the reaction, eqn. (1).

$$n(\mathrm{L}) + 3(\alpha\mathrm{BrDa}) + \mathrm{Am(III)} = [\mathrm{Am}(\alpha\mathrm{BrDa})_3(\mathrm{L})_n] + 3\mathrm{H}^+ \ldots\ldots \quad (1)$$

The extraction data using 0.021 M $HNO_3$ can be used to compare the extraction and separation performance of the ligands. Under these conditions, $L^8$ gave much the largest $SF_{Am/Eu}$ in comparison to the other ligands. Thus, $L^8$ gave a $SF_{Am/Eu}$of 36 while $L^5$, $L^3$, $L^4$ and $L^{11}$ gave SFs of 8, 7, 6 and 4 respectively. The good separation performance of $L^8$ might be expected as benzoxazole has the lowest p$K_a$ of the studied parent heterocycles. The poor performance of $L^{11}$ is more of a surprise because benzothiazole has a p$K_a$ (1.2) in between that of benzoxazole (−0.3) and benzimidazole (5.53). Obviously there are other factors which have an effect on the separation factors apart from the basicity of the extraction reagent. One further point of note is that there is very little difference between the $SF_{Am/Eu}$ values obtained for the *N*-alkylated benzimidazole ligands $L^3$ and $L^4$ and the *O*-alkylated benzimidazole ligand $L^5$ from 0.021 M $HNO_3$ (Table 1 and Fig. 2). The $D_{Am}$ values obtained for $L^3$, $L^4$ and $L^5$ are also quite similar at 0.0031, 0.0058 and 0.0025 respectively but very much less than the 9.0 observed for $L^9$. The direct attachment of electron donating alkyl groups to the benzimidazole N atoms would be expected to increase the basicity of the ligand which may lead to a reduction in $SF_{Am/Eu}$. The results obtained here show that direct *N*-alkylation of the benzimidazoles has very little effect on $SF_{Am/Eu}$ values.

As $L^8$ proved to be the most promising ligand, a comparable but more hydrophobic ligand $L^9$ was prepared and tested. Results for $L^8$ and $L^9$ are compared in Table 2 and Fig. 3. It is interesting that $SF_{Am/Eu}$ values obtained for both $L^8$ and $L^9$ were found to increase with increasing [$HNO_3$]. This is the first time such an increase in $SF_{Am/Eu}$ has been observed with increasing [$HNO_3$] for polydentate nitrogen ligands. Separation factors of 36–79 with $L^8$ and 43–70 with $L^9$ were subsequently obtained at 0.021 M $HNO_3$–0.1 M $HNO_3$. The $D_{Am}$ values are greater for the more hydrophobic ligand $L^9$ (9.0 to 0.08) than for $L^8$ (0.36 to 0.029) between 0.021 M $HNO_3$ and 0.1 M $HNO_3$.

Further solvent extraction experiments were then carried out with $L^9$ in TPH. The variation of $SF_{Am/Eu}$ with [$HNO_3$] for $L^9$ is also shown in Fig. 3. Values of $SF_{Am/Eu}$ for $L^9$ in TPH (19–26) are thus significantly lower than those previously obtained with $L^9$ in 1,1,2,2-tetrachloroethane (43–70) over the same $HNO_3$ concentration range. $D_{Am}$ values for $L^9$ in TPH (11.5–0.15) are slightly higher than those obtained with $L^9$ in 1,1,2,2-tetrachloroethane (9–0.08). Thus $L^9$ shows promise as a solvent extraction reagent for the separation of Am(III) from Ln(III). The $SF_{Am/Eu}$ obtained with $L^9$ in TPH are higher than those previously obtained with other studied hydrophobic tridentate nitrogen ligands based on 2,4,6-tris(2-pyridyl)-1,3,5-triazine,[3] 2,2′:6′,2″-terpyridine[5] and 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine.[6] These ligands gave $SF_{Am/Eu}$ from 6–14 when tested under similar conditions. The $D_M$ values obtained with $L^9$ are slightly lower when compared to the above ligands. This may reflect the fact that benzoxazole is a relatively weak ligand. The weakness of this type of ligand is shown by the fact that $L^6$ does not coordinate Cu(II) in acetonitrile solution.

Even so the $SF_{Am/Eu}$ values obtained with $L^9$ are still much lower than those obtained previously with 2,6-bis(5-alkyl-1,2,4-triazol-3-yl)pyridine ligands under similar conditions. Thus, for example, 2,6-bis(5-butyl-1,2,4-triazol-3-yl)pyridine was found to extract from an aqueous phase containing 0.1 M $HNO_3$ and 0.1 M $NH_4NO_3$ into TPH to give $SF_{Am/Eu}$ up to 150 at ligand concentrations between 0.014 and 0.055 M.[7] It was established that a synergist such as αBrDA was not required. The ligands of choice for An(III)/Ln(III) separations would still appear to be the 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines $L^{16}$, in spite of the documented stability problems. These ligands gave $D_{Am}$ values of *ca.* 22 and $SF_{Am/Eu}$ of 131–143 when 0.034 M of the ligand in modified TPH was used to extract from 0.9–0.3 M $HNO_3$ and varying amounts of $NH_4NO_3$.[7,8]

**Table 1** Extraction data for $L^3$, $L^4$, $L^5$. Organic layer contained the ligand L, and α-bromodecanoic acid at a concentration of 1.0 mol dm$^{-3}$ in tetrachloroethane . Aqueous layer, $Am^{241}$ and $Eu^{152}$, trace level in diluted nitric acid. $V_{org} = V_{aq} = 700$ μL, 298 K, mixing time = 60 minutes except for $L^{11}$ (90 minutes)

| Ligand concentration mol dm$^{-3}$ | $L^4$ 0.04 | $L^4$ 0.04 | $L^4$ 0.04 | $L^3$ 0.04 | $L^3$ 0.04 | $L^3$ 0.04 | $L^3$ 0.014 | $L^3$ 0.014 | $L^3$ 0.014 | $L^5$ 0.04 | $L^5$ 0.04 | $L^5$ 0.04 | $L^{11}$ 0.02 | $L^{11}$ 0.02 | $L^{11}$ 0.02 | $L^{11}$ 0.02 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $HNO_3$ concentration mol dm$^{-3}$ | 0.020 | 0.038 | 0.053 | 0.020 | 0.039 | 0.056 | 0.022 | 0.042 | 0.062 | 0.020 | 0.039 | 0.059 | 0.026 | 0.045 | 0.065 | 0.082 |
| $D_{Eu}$ | 0.001 | 0.0002 | 0.00012 | 0.0005 | 0.0002 | <0.0001 | 0.016 | 0.0015 | 0.0006 | 0.0003 | <0.0001 | <0.0001 | 0.004 | 0.002 | 0.0008 | 0.0005 |
| $D_{Am}$ | 0.0058 | 0.0018 | 0.00061 | 0.0037 | 0.0010 | 0.0006 | 0.031 | 0.007 | 0.0023 | 0.0025 | 0.001 | 0.0006 | 0.014 | 0.008 | 0.003 | 0.001 |
| $SF_{Am/Eu}$ | 6 | 9 | 5 | 7 | 5 | [a] | 2 | 4 | 4 | 8 | [a] | [a] | 4 | 4 | 4 | 3 |

[a] not determined

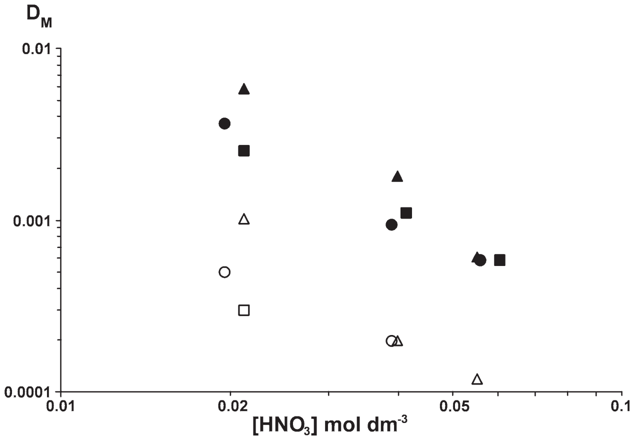


**Fig. 2** A plot of $D_M$ against nitric acid concentration (mol dm$^{-3}$) for $L^3$, $L^4$, $L^5$ and $L^{11}$ Closed symbols Am, Open symbols Eu. Triangles $L^4$, circles $L^3$, squares $L^5$.

## Structural studies

Prior to this study, there had been no studies concerning benzoxazole, oxazole or 4,5-dihydro-oxazole ligands. Thus the lanthanide structures with $L^6$ are the first lanthanide structures with this type of ligand. The structures containing Nd, Pr and Er are isomorphous as indeed are those containing Eu and Gd. The structures of the six complexes fall into a similar pattern to those observed with several other terdentate ligands shown in Fig. 4 such as 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine, $(L^{12})^{14}$ 2,2′:6′2″ terpyridine, $(L^{13})^5$ 2,4,6-tris(2-pyridyl)-1,3,5-triazine $(L^{14})^{15}$ and the 2,6-bis(5-alkyl-1,2,4-triazol-3-yl)pyridines $(L^{15})^6$ which have all been characterized by single-crystal X-ray diffraction.

In all structures containing $L^{12}$–$L^{15}$ inclusive and the present examples with $L^6$, the complexes contain one ligand per metal and three nitrates are bound to the metal in a bidentate manner. For the $L^6$ structures reported here in addition to these nine bonds, 1-La contains two water molecules to give a coordination number of 11 (Fig. 5), while 2-M (M = Nd, Pr, Er) contains 1 solvent acetonitrile molecule to give a coordination number of 10 (Fig. 6) and 3-M (M = Eu,Gd) contains one water molecule, also to give a coordination number of 10. (Fig. 7) In all cases the two nitrogen atoms of the five membered ring are bonded to the metal rather than the oxygen atoms. This is also found in a variety of complexes containing the oxazole and benzoxazole ligands with other metal ions such as those of transition metals.

The M–N bond lengths shown in Table 4 show interesting variations. The overall feature is a decrease in bond length with increase in atomic number as might be expected over the lanthanide contraction. However a particular interesting feature is the difference between the Ln–N(11) bond to the central pyridine and the Ln–N(21) and Ln–N(31) bonds to the oxazole ring. Only for La is the central bond the shortest of the three. Indeed for Nd, Pr and Er this Ln–N(11) bond is the longest. However in 3-Ln, the central bond is midway in length between the two outer bonds which themselves differ by significant amounts (0.075, 0.099 Å respectively). The reason for this difference is not clear but it could be due to the crowding within the coordination sphere to some extent engendered by the hydrogen bonding of the coordinated water molecule to the additional ligand in the unit cell. A comparison can be made with structures of europium nitrate complexes with substituted bis(benzimadazolyl)pyridines where the Eu–N(py) distances are invariably significantly longer than the Eu–N(bz) distances.[16]

In the six structures of $L^6$, the Ln(III) cations are also bonded to three nitrates in a bidentate fashion. As is often the case there

**Table 2** Extraction data for $L^8$ and $L^9$ organic layer contained the ligand L with α-bromodecanoic acid at a concentration of 1.0 mol dm$^{-3}$ in solvent. Aqueous layer, $Am^{241}$ and $Eu^{152}$, trace level in diluted nitric acid. $V_{org} = V_{aq}$ = 700 μL, 298 K, mixing time = 60 minutes

| Ligand in Solvent mol dm$^{-3}$ | $L^9$ in tetrachloroethane | | | | | $L^9$ in TPH | | | | | | $L^8$ in tetrachloroethane | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Concentration of ligand mol dm$^{-3}$ | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 0.02 | 0.02 | 0.02 | 0.1 | 0.1 | 0.1 | 0.04 | 0.04 | 0.04 | 0.04 |
| Concentration of $HNO_3$ mol dm$^{-3}$ | 0.021 | 0.042 | 0.061 | 0.081 | 0.100 | 0.020 | 0.059 | 0.090 | 0.059 | 0.083 | 0.117 | 0.022 | 0.042 | 0.062 | 0.082 |
| $D_{Eu}$ | 0.16 | 0.017 | 0.0054 | 0.0031 | 0.0012 | 0.0059 | 0.014 | 0.59 | 0.017 | 0.007 | 0.002 | 0.009 | 0.003 | 0.0008 | 0.0004 |
| $D_{Am}$ | 9.0 | 0.7 | 0.3 | 0.2 | 0.08 | 11.5 | 0.36 | 0.15 | 0.51 | 0.20 | 0.07 | 0.36 | 0.12 | 0.052 | 0.029 |
| $SF_{Am/Eu}$ | 55 | 40 | 50 | 60 | 70 | 25 | 30 | 30 | 30 | 30 | 35 | 45 | 50 | 60 | 80 |

is a considerable range of Ln–O distances but all are less than the Ln–N distances. In addition all coordination spheres contain at least 1 solvent molecule (one water for 3-Eu, 3-Gd and two waters for 1-La) and 1 solvent acetonitrile for 2-Nd, 2-Pr, 2-Er. In the 3-Ln structures, this water molecule is hydrogen bonded to the additional ligand. The hydrogen atoms on this water molecule were not locatable and it seems likely that they are disordered over different sites as the distance from O(100) to the three nitrogen atoms are similar. It is possible for two hydrogen atoms bonded to O(100) to form hydrogen bonds to N(81) and N(91) simultaneously (see Fig. 7), but an alternative scenario is for only one hydrogen bond to be formed and that to N(71). In 1-La, while the hydrogen atoms around the water molecules were not located, it is apparent from the O···O distances that both O(100) and O(200) form two intermolecular hydrogen bonds to nitrate oxygen atoms in different complexes.

The fact that $L^6$ forms 1:1 complexes with lanthanides gives a clear indication that the ligand acts similarly in the extraction process to ligands $L^{12}$–$L^{15}$ inclusive. All these ligands give relatively low *SF* values at any rate by comparison with $L^{16}$, 2,6-bis(5,6-dialkyl-1,2,4-triazine-3-yl)pyridine, (Fig. 8) and are dependent also on the use of the synergist α-bromodecanoic acid while $L^{16}$ gives good performance without the synergist.

Unlike $L^6$ and $L^{12}$–$L^{15}$ inclusive, $L^{16}$, uniquely among the terdentate ligands forms the $[LnL_3]^{3+}$ cation in the presence of nitric acid and this, we believe is responsible for its excellent performance in the extraction process. One possible explanation is that the $[LnL_3]^{3+}$ cation contains a hydrophobic exterior and can therefore readily pass into the organic layer. This occurs despite the fact that the cation is tripositive because the charge is masked by the surrounding ligands. By contrast the other ligands cannot readily pass into the organic layer despite the fact that they are neutral species because the bound nitrate anions are too hydrophilic. However with the α-bromodecanoic acid synergist, the acid anions can replace the nitrates to form a hydrophobic complex that can pass into the organic layer. However the decanoic acid does not surround the metal completely as do the three terdentate ligands of $L^{12}$ and therefore the performance is not so good.

That hypothesis leads to the question as to why $L^6$ and $L^{12}$–$L^{15}$ inclusive do not form the $[ML_3]^{3+}$ cation. Two explanations can be considered possible, one structural and the other electronic. For the structural explanation, it is noticeable that in metal complexes with all ligands other than $L^{16}$ the 1:1 complex can be stabilised by the formation of intramolecular hydrogen bonds between the hydrogen atoms bonded to atoms *ortho* to the donor nitrogen atoms in the two outer rings and either nitrate or water molecules in the coordination sphere. For the present compounds, for example, in 1-La, H···O distances from H(28) to O(200) and from H(38) to O(61) are 2.79, 2.71 Å, in 2-Nd, H(28) to O(42) and from H(38) to O(51) are 2.82, 2.76 Å and in 3-Gd H(28)–O(100), H(38)–O(64) and H(38)–O(62) are 2.62, 2.77 and 2.79 Å, respectively. Of course this is not possible with $L^{16}$ because there is no such hydrogen atom, the *ortho* atom being nitrogen. The electronic explanation is discussed in the next section.

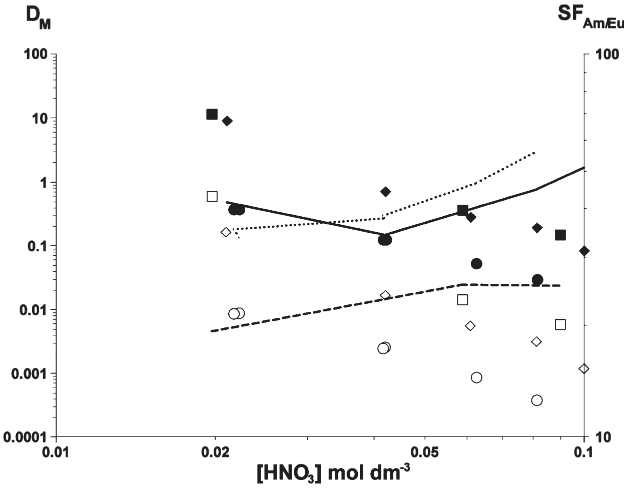


**Fig. 3** A plot of $D_M$ (left side *y* axis) against nitric acid concentration (mol dm$^{-3}$) for $L^8$ and $L^9$. Closed symbols Am, Open symbols Eu. Diamonds $L^9$ at 0.04 mol dm$^{-3}$ in tetrachloroethane, squares $L^9$ at 0.02 mol dm$^{-3}$ in TPH, circles $L^8$ at 0.04 mol dm$^{-3}$ in tetrachlorethane. The lines represent the SF values (right side *y* axis) calculated from the $D_M$ values for Am and Eu with the continuous line obtained from a concentration of 0.04 mol dm$^{-3}$ of $L^9$ in tetrachloroethane; the dashed line a concentration of 0.02 mol dm$^{-3}$ of $L^9$ in TPH and the dotted line a concentration of 0.04 mol dm$^{-3}$ of $L^8$ in tetrachlorethane.

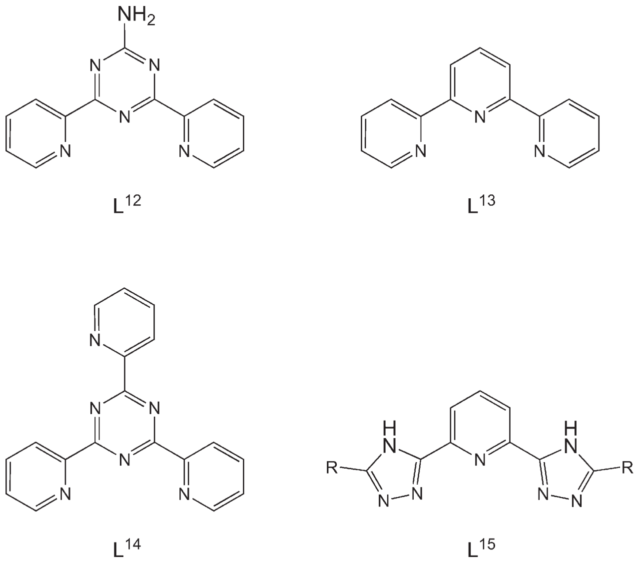


**Fig. 4** Further tridentate ligands used in lanthanide and actinide separation.

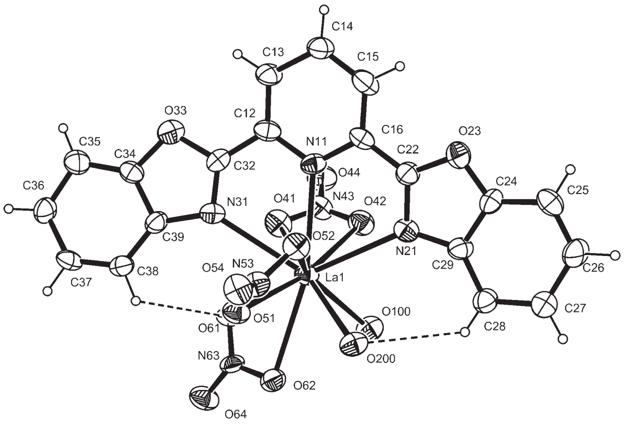


**Fig. 5** The structure of 1-La with ellipsoids at 25% probability. Intramolecular hydrogen bonds are shown as dotted lines.

## Quantum mechanics calculations

Quantum mechanics calculations were carried out on the free ligand $L^6$ and its monoprotonated and diprotonated cations to establish their electronic properties, in particular to establish the low energy conformation of the various species and to relate these to the performance of the ligand in the extraction process.

**Free ligand.** The three conformers of benzoxazole (Fig. 9) were constructed using CERIUS2 and minimised using Gaussian98[17] at the HF/6-31G* level. The conformations are described *via* the N($n$1)–C–C–N(11) torsion angles, $n = 2,3$ for the two oxazole rings with values of 0° described as *cis*(*c*) and 180° as *trans*(*t*). The resulting energy order was $tt < ct < cc$, with relative energies of 0.00, 9.33, 20.25 kJmol$^{-1}$ respectively. This order is the same as that found for the terpyridine ligand but in that molecule the energy differences were far greater due to the presence of steric interactions from *ortho*-hydrogen atoms in adjacent rings. It is interesting that the *tt* conformation has the lowest energy despite the fact that in the *cc* conformation the oxygen atoms of the lateral rings are closer to the *ortho*-hydrogens H(13) and H(15) of the central pyridine ring: (O(n3)···H 2.435 Å) than are the nitrogen atoms (N($n$1)···H 2.597 Å) in the *tt* conformation. However for the oxygen atoms electron density is found to be out of the ring plane by contrast to the nitrogen atoms where it is concentrated in the ring plane. This suggests that these O···H interactions may be less attractive than the N···H interactions despite the closer distance.

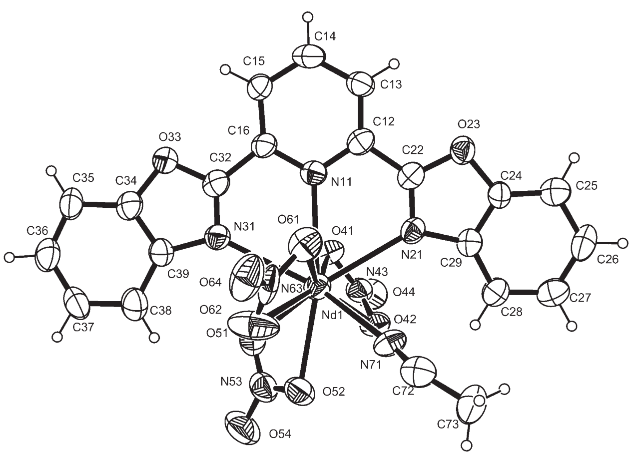


**Fig. 6** The structure of 2-Nd with ellipsoids at 25% probability. Intramolecular hydrogen bonds are shown as dotted lines.

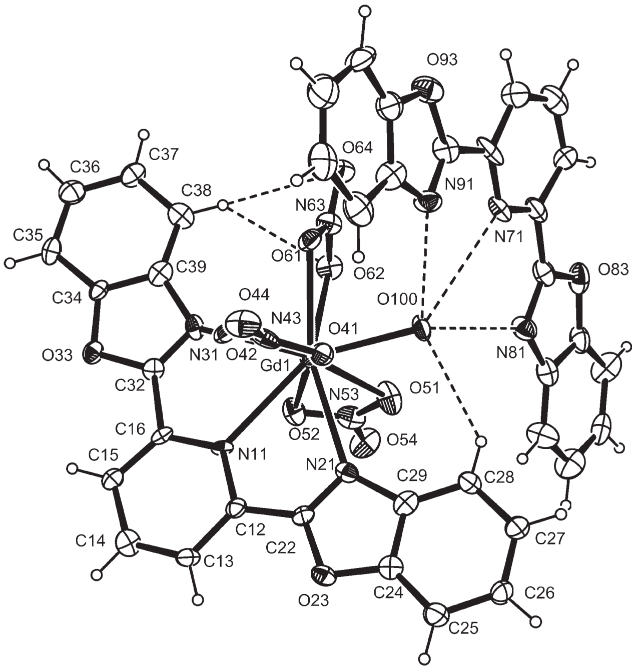


**Fig. 7** The structure of 3-Gd with ellipsoids at 25% probability. Intramolecular hydrogen bonds are shown as dotted lines.

It is interesting that in the *cc* conformation the C(py)–C(ox)–N angles are 128.4° compared to C(py)–C(ox)–O angles of 116.0°. In the *tt* conformation only minor changes to these angles are observed 125.8, 118.4° respectively. However the Mulliken charges do show some variation with O, N being −0.678, −0.546 e in the *cc* conformation and −0.639, −0.597 e in the *tt* conformation. This could suggest that in the *tt* conformation, electron density is withdrawn from the oxygen atom to the nitrogen atom to facilitate hydrogen bonding to the *ortho* hydrogen atoms. The charge on the pyridine nitrogen atom remains unchanged in the 3 conformations at −0.550 e.

As in the other terdentate ligands $L^{12}$–$L^{15}$, and indeed in the best ligand for separation $L^{16}$, the lowest energy conformation of $L^6$ is therefore one which is not suitable for metal complexation and the ligand must change from *tt* to *cc*. However there is a relatively small energy barrier to rotation which is 17.35 kJ mol$^{-1}$ per ring so 34.70 kJ mol$^{-1}$ overall. This compares to 17.09 kJ mol$^{-1}$ per ring for $L^{16}$ and 28.92 kJ mol$^{-1}$ per ring for terpyridine, the higher value in the latter ligand being due to the interactions between *ortho* hydrogen atoms.

There have been several attempts to consider whether there are any special electronic properties of $L^{16}$ which may lead to its unique separation properties. Recently,[18] the electronic properties of $L^{16}$ have been compared at the HF/6-31G* level to those of six other terdentate ligands including $L^{12}$ to $L^{15}$, for which extraction properties have also been measured and found to be far less efficient. It was found that $L^{16}$ had some unique electronic properties compared to these other six ligands including the fact that the total Mulliken charge for the atoms in the central ring is positive (0.070 e) while that for the outer rings is negative (−0.035 e). By comparison, the reverse is true for all the other six terdentate ligands investigated. For $L^6$ this is not so clear cut as in the *cc* conformation the central ring has a charge of −0.004 e and in the *tt* conformation 0.001 e, values which indicate that the ring charge distribution is not unique for $L^{16}$ although clearly the size of the charges in $L^6$ are very small. A further difference established in $L^{16}$ is that the partial charge on the donor nitrogen atoms in the outer ring (−0.306 e in the *cc* conformation) are far less than those found for example in terpyridine (−0.524 e) although values for the nitrogen in the central ring are similar (−0.544 e for $L^{16}$, −0.541 e for terpy). For $L^6$ we found that

**Table 3** Cell data for the structures

| | 1-La | 2-Nd | 2-Pr | 2-Er | 3-Eu | 3-Gd |
|---|---|---|---|---|---|---|
| Formula | C19 H17 La N6O14.5 | C21H14N7NdO11 | C21H14N7O11Pr | C21 H14 Er N7O11 | C38 Eu H24 N9 O14 | C38 H24 Gd N9 O14 |
| *M* | 700.28 | 684.63 | 681.30 | 701.64 | 982.62 | 987.92 |
| Space group | monoclinic, $C2/c$ | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ | triclinic, $P\bar{1}$ |
| Cell dimensions (Å,°) | $a$ 33.77(4) | 9.094(13) | 8.769(12) | 8.618(9) | 10.533(14) | 10.527(14) |
| | $b$ 8.900(14) | 9.561(13) | 9.483(12) | 9.458(12) | 10.680(14) | 10.643(14) |
| | $c$ 21.83(3) | 15.038(17) | 15.525(17) | 15.445(17) | 17.12(2) | 17.09(2) |
| | $\alpha$ (90) | 98.74(1) | 99.73(1) | 100.46(1) | 86.07(1) | 86.19(1) |
| | $\beta$ 128.81(1) | 100.34(1) | 98.24(1) | 97.73(1) | 79.22(1) | 79.14(1) |
| | $\gamma$ (90) | 93.34(1) | 93.80(1) | 94.18(1) | 82.23(1) | 82.19(1) |
| $U$ (Å$^3$) | 5113 | 1266 | 1254 | 1221 | 1873 | 1861 |
| $Z$, dm (gm cm$^{-3}$) | 8, 1.810 | 2, 1.795 | 2, 1.805 | 2, 1.909 | 2, 1.760 | 2, 1.752 |
| $\mu$ (mm$^{-1}$) | 1.754 | 2.124 | 2.018 | 3.515 | 1.742 | 1.865 |
| No of reflections/ $R$(int) | 6052/0.093 | 4581 | 4377 | 3936 | 5521 | 6246 |
| Reflections/constraints/ parameters | 3612/0/358 | 4581/0/362 | 4377/0/363 | 3936/0/362 | 5521/0/560 | 6246/0/559 |
| $R1$, $wR2$ ($I > 2\sigma(I)$) | 0.0784, 0.2119 | 0.0851, 0.2113 | 0.0458, 0.1487 | 0.0454, 0.1281 | 0.1059, 0.3030 | 0.0691, 0.1918 |
| $R1$,$wR2$ (all data) | 0.1242, 0.2361 | 0.1796, 0.2579 | 0.0531, 0.1644 | 0.0577, 0.1392 | 0.1668, 0.3313 | 0.0954, 0.2175 |
| Largest peak/hole e Å$^{-3}$ | 1.544, −0.545 | 1.586, −1.165 | 1.601, −1.929 | 1.913, −1.680 | 2.968, −1.888 | 2.939, −2.040 |

the charges on the atoms in the outer rings were −0.546 e for N and −0.679 e for O, thus the values for nitrogen are very similar to those found in terpyridine.

Thus while there are significant differences in the electronic properties of L$^{16}$ compared to L$^6$ and similar ligands, it would seem likely that the lack of potential for hydrogen-bond formation discussed above is of equal importance in the characterization of L$^{16}$ as a unique ligand.

**Mono-protonated ligand.** There is a likelihood of protonation of the ligand during the extraction process due to the low pH found in the nuclear waste solution and it is therefore of interest to investigate the protonation patterns in the ligands.

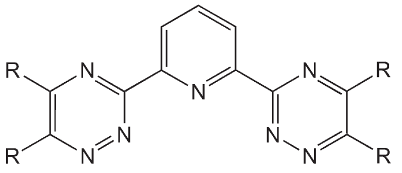
For benzoxazole, L$^6$ and similar ligands there are 3 different protonation sites N(11), N($n$1) and O($n$3) ($n$ = 2 or 3) and 3 possible conformations of the ligand, giving 11 unique structures for the monoprotonated ligand. The 4 structures with oxygen O($n$3) protonated can however be ignored as they all have much higher energy (> 150 kJ mol$^{-1}$) than the minimum energy structure. In these oxygen-protonated structures the hydrogen atom is located in a tetrahedral position out of the ring plane, thus confirming the direction of the excess electron density. The five low energy conformations are *cc*-1, *ct*-*n*, *cc*-*n*, *ct*-1 and *tt*-1 where the number refers to the nitrogen atom that is protonated (1 for the pyridine nitrogen, $n(=2{,}3)$ for the oxazole nitrogen), so there seem little energy difference between the protonation of N(11) in the pyridine ring and N($n$1) in the oxazole rings. The lowest energy structure is *cc*-1 where the pyridine nitrogen is protonated. This is the only configuration which allows two intramolecular hydrogen bond interactions to occur (N(1)–H···N($n$1) 2.368 Å). The importance of these interactions is indicated by the fact that the other two configurations with N(1) protonated *e.g.* *ct*-1 and *tt*-1 have higher energies (by 5.83, 14.04 kJmol$^{-1}$) no doubt because they contain one or no intramolecular hydrogen bond respectively. This is despite the fact that the *tt* and *ct* conformations being more stable for the free ligand. Clearly the formation of the hydrogen bond from N(1)–H to O($n$3) is less favourable than that to N($n$1), probably because the excess electron density around O($n$3) is out of the plane of the ligand. In fact, configurations *ct*-2 and *cc*-2 are the next lowest in energy (at 2.54, 5.33 kJ mol$^{-1}$) after *cc*-1, rather than *ct*-1

**Table 4** Dimensions in the metal coordination spheres (Å)

| | 1-La | 2-Nd | 2-Pr | 2-Er | 3-Eu | 3-Gd |
|---|---|---|---|---|---|---|
| M–N(11) | 2.744(11) | 2.720(10) | 2.715(5) | 2.617(7) | 2.657(14) | 2.640(7) |
| M–N(21) | 2.781(11) | 2.654(11) | 2.669(5) | 2.564(7) | 2.625(16) | 2.588(8) |
| M–N(31) | 2.770(11) | 2.667(11) | 2.664(7) | 2.545(7) | 2.699(15) | 2.679(8) |
| M–O(41) | 2.670(11) | 2.542(10) | 2.537(6) | 2.407(7) | 2.433(17) | 2.524(8) |
| M–O(42) | 2.771(11) | 2.544(9) | 2.552(5) | 2.425(6) | 2.541(14) | 2.530(7) |
| M–O(51) | 2.658(11) | 2.553(12) | 2.568(5) | 2.488(7) | 2.543(17) | 2.548(7) |
| M–O(52) | 2.587(10) | 2.549(12) | 2.558(6) | 2.470(6) | 2.482(17) | 2.480(7) |
| M–O(61) | 2.585(9) | 2.512(10) | 2.519(5) | 2.403(7) | 2.457(14) | 2.454(7) |
| M–O(62) | 2.775(15) | 2.604(14) | 2.545(6) | 2.463(7) | 2.494(15) | 2.462(7) |
| M–N(71) | — | 2.545(11) | 2.664(6) | 2.526(8) | — | — |
| M–O(100) | 2.581(10) | — | — | — | 2.455(13) | 2.413(6) |
| M–O(200) | 2.532(10) | — | — | — | — | — |

Hydrogen bonds distances (Å) in 3-M

| | Eu | Gd |
|---|---|---|
| O(100)···N(81) | 2.92 | 2.94 |
| O(100)···N(91) | 3.05 | 3.06 |
| O(100)···N(71) | 3.06 | 3.08 |



$L^{16}$

**Fig. 8** $L^{16}$ which provides high separation factors for actinides over lanthanides.

and *tt*-1. In *ct*-2 and *cc*-2, a single H-bond interaction occurs between the protonated N(*n*1) and N(1) with N(*n*1)–H···N(1) distances of 2.455 and 2.433 Å respectively. The difference in energy between *ct*-2 and *cc*-2 is a consequence of the change in conformation of the unprotonated oxazole ring – a rotation from the trans to the *cis* form increases the energy of the structure. This difference is in agreement with the energy ordering of the unprotonated conformers, where a similar change in the conformation of a single ring from *cis* to *trans* lowers the energy of the free ligand.

From the difference between the energies of the pyridine-protonated structures and the neutral conformers, it is clear that the energy gained from H-bonding interactions of the proton is highest in the *cc* conformation (−0.3918 a.u.). For *ct* this figure falls to −0.3854 a.u. and for *tt* −0.3788 a.u. This provides some evidence that the interactions with oxygen atoms are less favourable than those with nitrogen.

The remaining two configurations with protonated nitrogen atoms *tt*-2 and *ct*-3 have relatively high energies (40.05, 47.14 kJ mol$^{-1}$) because of *ortho* interactions with hydrogen atoms on the central pyridine ring which is somewhat alleviated by a rotation of the oxazole rings by *ca.* 15° from the pyridine ring plane, although this reduces the stabilising conjugation in the ligand.

From these data, it can be argued that protonation will lead to the conformation of the ligands changing from *tt*, which is unsuitable for metal complexation and found in the free ligand to *cc* where the metal can replace the proton to form the complex. The proton affinities (defined as E(L)–E(LH$^+$)) of $L^6$, $L^{12}$, $L^{13}$ and $L^{16}$ have been calculated at the 6-31G* level taking into account the zero point energies, using the *cc* conformations for both the free and protonated ligands, as 993.64, 1068.78, 1070.33 and 1018.18 kJ mol$^{-1}$ respectively, values which show that the benzoxazole ligands are less likely to be protonated than the other ligands considered here. These results are consistent with the experimental p$K_a$ values for $L^6$ and $L^{13}$ which are −0.3 and 4.9 respectively.

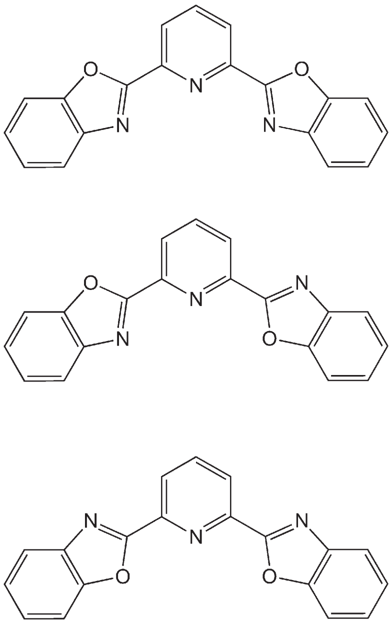


**Fig. 9** The three conformations of benzoxazole, top *cc*, middle *ct*, bottom *tt*. Relative energies at the HF/6-31G* level are 20.25, 9.33, 0.00 kJ mol$^{-1}$.

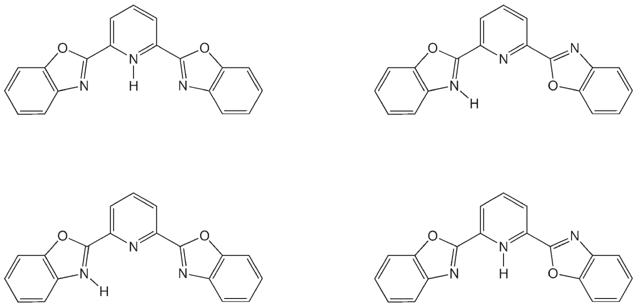


**Fig. 10** The four lowest energy structures of the monoprotonated benzoxazole [HL$^6$]$^+$. Relative energies are *cc* (top left) 0.00, *ct*2 (top right), 2.54, *cc*2 (bottom left) 5.33, *ct*1 (bottom right) 5.83 kJ mol$^{-1}$.

**Di-protonated ligand.** There are only 3 low energy configurations for the di-protonated ligand since all the others have energies more than 100 kJ mol$^{-1}$ above the lowest energy. The three low energy configurations (Fig. 11) show protonation at the two nitrogen atoms in the oxazole rings.

The lowest energy conformation *cc*2,3 shows hydrogen bonding interactions from both protons with N(11). This is the only possible configuration which provides two N–H···N interactions without protonating an oxygen which, as has already been observed, is highly unfavourable. Configurations *ct*2,3 and *tt*2,3 are next highest in energy, but the *trans* conformation gives rise to *ortho* hydrogen interactions which are alleviated by rotation of the rings by *ca.* 20° which reduces the stabilising conjugation. The next four structures (*ct*1,3, *tt*1,*n*, *cc*1,*n* and *ct*1,2) show protonation of the pyridine N(11) and oxazole N(*n*1) nitrogen atoms For conformations *ct*1,3 and *tt*1,2 the protonated oxazole ring is *trans* to the pyridine ring, but the structures are stabilised in planar conformations from the interaction of the N(11)–H with the oxygen of the *trans* ring. Conformations *cc*1,2 and *ct*1,2 show the oxazole N(*n*1) nitrogen atom to be protonated in the *cis* conformation w.r.t the protonated pyridine ring. This leads to adjacent protonated nitrogen atoms and the distance between them is increased by a ring rotation of *ca.* 24°.

The minimum energy structures of the protonated and di-protonated ligands show different nitrogen atoms to be protonated, thus N(11) in the former and N(21) and N(31) in the latter. However it can be readily imagined that the

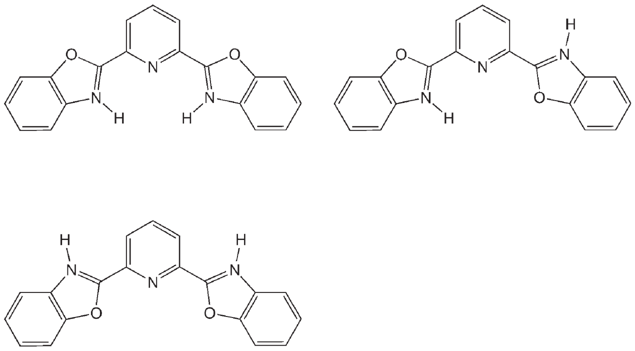


**Fig. 11** The lowest energy structures of di-protonated benzoxazole [H$_2$L$^6$]$^{2+}$ with relative energies, *cc*2,3 (top left) 0.00, *ct*2,3 (top right) 10.74, *tt*2,3 (bottom left) 34.46 kJ mol$^{-1}$.

second protonation step will involve migration of the hydrogen atom from N(11) to N(21) and addition of the second hydrogen atom at N(31).

## Conclusions

Several hydrophobic terdentate ligands have been investigated in order to assess their suitability for extracting americium(III) from europium(III), an important part of the reprocessing of nuclear fuel. Extraction experiments show that $L^9$ 2,6-bis-(benzoxazol-2-yl)dodecycloxypyridine is the most effective reagent for the separation of Am(III) and Ln(III). The reagent is a rather weak Brønsted base and such protonation that does take place occurs at the nitrogen atoms in preference to the oxygen atoms. The most probably extracted species involves only one ligand and probably up to three α-bromodecanoate synergist anions together with one or more water molecules dependent upon the size of the metal ions. The performance of the terdentate ligands in separation is promising but not as good as that of the 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridines $L^{16}$. The superiority of $L^{16}$ relative to $L^6$ and its derivatives is likely to be connected with the ability of the former to form $[ML_3]^{3+}$ cations, which can be used for phase transfer. The inability of $L^6$ and its derivatives to form this cation may be due to the stabilizing factor of intramolecular hydrogen bonds between the ligand and nitrates in the coordination sphere in 1:1 complexes and also the unique electronic properties of $L^{16}$ in regard of the charges on the nitrogen atoms in the outer rings.

## Experimental

All starting materials were purchased from Aldrich. DMF was dried over and distilled from $CaH_2$ . Pyridine was dried over 4 Å molecular sieves. *p*-toluenesulfonyl chloride was purified by standard methods before use.[19] Column chromatography was performed using Kieselgel silica (40–63 μm) from Merck. All glassware used in the alkylation reactions was dried overnight in an oven at 100 °C before use. NMR spectra were run on a JEOL JNM-EX 400 spectrometer. Microanalyses were carried out by Medac Ltd., Brunel Science Centre.

$L^1$ and $L^2$ were prepared according to the literature methods.[10,13]

$L^3$ was prepared as follows: NaH (0.231 g, 5.78 mM, 60% dispersion in mineral oil) was washed with hexane in order to remove the mineral oil and added in small portions to a solution of $L^1$ (0.75 g, 2.4 mM) in 10 $cm^3$ DMF under a nitrogen atmosphere. The mixture was heated to 80 °C for 3 h, cooled to room temperature, stirred for a further 1 h and then 1-bromohexane (0.68 $cm^3$, 4.8 mM) was added dropwise in a stream of nitrogen gas. The solution was heated to 100 °C for 2 h, cooled to room temperature, $NH_4Cl$ (100 $cm^3$) was added and then the aqueous solution was extracted with DCM (100 ml). The extract was washed with distilled water then sodium chloride solution, dried over sodium sulfate and the DCM was removed to give a yellow/green oil. This was purified by column chromatography using petroleum ether (60–80 °C)/ethyl acetate (1:1). $L^3$ eluted as the first band to give a yellow oil after evaporation of the solvents. (Yield 0.74 g, 64%), $^1H$ NMR, $CDCl_3$ $\delta_H$ 0.64 (6H, t), 0.92–1.20 (12H, m), 1.76 (4H, q), 4.70 (4H, t), 7.31–7.43 (2H, m), 7.43–7.53 (2H, m), 7.80–7.95 (2H, m), 8.06 (1H, dd), 8.32 (2H, d). Found: C, 76.66; H, 7.81; N, 14.27. $C_{31}H_{37}N_5{\cdot}0.5H_2O$ O requires C, 76.19; H, 7.84; N, 14.33%.

$L^4$. A small amount of $L^4$ was prepared after reaction of $L^2$ (1 g, 0.003 M) with $K_2CO_3$ (0.44 g, 0.03 M) in DMF at 90 °C followed by alkylation with 1-bromohexane (0.9 $cm^3$, 0.0064 M) at 90 °C overnight. Work-up was as described previously for $L^3$. Deprotonation of $L^2$ with $K_2CO_3$ is not as efficient as with NaH and both the di-alkylated $L^3$ and the mono-alkylated $L^4$ were formed in the reaction. Column chromatography using petroleum ether (60–80 °C)/ethyl acetate (1:1) eluted $L^3$ first followed by a small amount of $L^4$. $^1H$ NMR of $L^2$, $CDCl_3$ 0.60 (3H, t), 0.75–1.13 (6H, m), 1.20–1.38 (2H, m), 3.70 (2H, t), 7.09–7.18 (1H, m), 7.31–7.52 (4H, m), 7.52–7.61 (1H, m), 7.73–7.83 (1H,m), 7.84–7.98 (2H, m), 7.98–8.08 (1H, m), 8.08–8.17(1H,m).

$L^5$. 1 g ($L^2$) (3.06 mM) was stirred with $K_2CO_3$ (0.21 g, 1.53 mM) in DMF (20 ml) for 2 h at 80 °C and then for 15 min at 90 °C. After cooling to RT, 1-bromododecane (0.73 ml, 3.06 mM) was added dropwise by means of a pipette in a stream of nitrogen gas. The solution was stirred at RT for 5 min, at 90 °C for 3 h and then finally at 70 °C overnight. After cooling to RT, approx. 150 ml aqueous NaCl was added and the aqueous layer was extracted with DCM (3 × 100 ml). The organic layer was dried with $Na_2SO_4$ and the solvents were removed on an evaporator. The crude product was recrystallised from ethyl acetate/ethanol and washed with cold ethyl acetate to give a pink solid. (Yield 0.68 g, 45%), $^1H$ NMR, $CDCl_3$ $\delta_H$ 0.83 (3H, t), 1.17–1.41 (16H, m), 1.47 (2H, br), 1.80 (2H, q), 4.29 (2H, t), m.p. 252–254 °C. Found: C, 74.12; H, 7.44; N, 13.98. $C_{31}H_{37}N_5O{\cdot}0.5H_2O$ requires C, 73.78; H, 7.59; N, 13.88%

$L^6$. $L^6$ was prepared according to the method described for $L^2$ using 2,6-pyridine-dicarboxylic acid and 2-aminophenol as starting materials. (Yield 83%) $^1H$ NMR, DMSO-$d_6$ $\delta_H$7.44 (4H, m), 7.76 (2H, d), 7.88 (2H, d), 813 (1H, t), 8.55 (2H, d). Found: C, 70.72; H, 3.50; N, 12.91. $C_{19}H_{11}N_3O_2{\cdot}0.5H_2O$ requires C, 70.80; H, 3.75; N, 13.04%

$L^7$. $L^7$ was prepared according to the method described for $L^2$ using 2-aminophenol and chelidamic acid as starting materials. (Yield 72%), $^1H$ NMR, DMSO-$d_6$ $\delta_H$ 7.51 (4H, m), 7.88 (2H, s), 7.92 (4H, m). Found: C, 62.34; H, 3.53; N, 11.49. $C_{19}H_{11}N_3O_3{\cdot}2H_2O$ requires C, 62.46; H, 4.14; N, 11.50%

$L^8$. $L^7$ (0.99 g, 3 mM) and $K_2CO_3$ (0.24 g, 1.7 mM) were stirred in refluxing ethanol (50 ml) and DMF (30 ml) for 1 h until a brown solution formed. This was cooled to approx. 70 °C and 1-bromododecane 0.72 ml (3 mM) was added. The resulting solution was heated for 24 hours at 80 °C before being evaporated under vacuum. The residue was crystallised from hot ethyl acetate to give $L^8$ (Yield 0.69 g, 46%), m.p. 120–122 °C, $^1H$ NMR, $CDCl_3$ $\delta_H$ 1.27 (s, 20H), 1.91 (q, 3H), 4.26 (t, 2H), 7.43 (m, 4H), 7.73 (d, 2H), 7.86 (d, 2H), 8.04 (s, 2H). Found: C, 74.04; H, 7.08; N, 8.34. $C_{31}H_{35}N_3O_3{\cdot}0.5H_2O$ requires C, 73.49; H, 7.16; N, 8.29%

### 2-Decyl-1-tetradecyl tosylate

*p*-toluenesulfonyl chloride (4.98 g, 0.0261 M) was added in small portions to a stirred solution of 2-decyl-1-tetradecanol (10 $cm^3$, 0.0237 M) in 10 $cm^3$ pyridine at −10 °C. The temperature of the solution was maintained below −5 °C for 1 h, during which time a solid white mass was formed. The temperature was maintained at 0 °C for a further 3 h and then the solid was added to ice (1:l) and concentrated HCl (250 $cm^3$). The product was then extracted with DCM (3 × 150 $cm^3$) and the organic layer was washed with 0.1 M HCl (3 × 150 $cm^3$), saturated brine (3 × 150 $cm^3$) and distilled water (3 × 150 $cm^3$). The organic extracts were dried with sodium sulfate and reduced in volume to give a white solid. (Yield 9.96 g, 82.6%) $^1H$ NMR, $CDCl_3$ $\delta_H$ 0.85–0.91 (6H, m), 1.05–1.77 (41H, m), 2.45 (3H, t), 3.91 (2H, d), 7.32–7.36 (2H, d), 7.77–7.81 (2H, d). 2-decyl-1-tetradecyl tosylate was used without further purification for the preparation of $L^9$.

$L^9$. $L^7$ (3.14 g, 9.54 mM) was stirred with $K_2CO_3$ (0.65 g, 4.77 mM) in DMF (50 $cm^3$) for 3.5 h at 90 °C. A beige solid precipitated during this time. After cooling to 50 °C, 2-decyl-1-tetradecyl tosylate (4.84 g, 9.54 mM) was added in small portions in a stream of nitrogen gas. The solution was stirred at 50 °C for 5 min, and then at 90 °C for 24 h. After cooling to

RT, approx. 200 ml aqueous NaCl was added and the aqueous layer was extracted with DCM (3 × 150 ml). The organic layer was washed with distilled water (3 × 150 $cm^3$), dried with sodium sulfate and the solvents were removed on an evaporator. The crude product was purified by column chromatography using petroleum ether (60–80 °C)/ethyl acetate (9:1) to give a white solid. (Yield 30%) $^1H$ NMR, $CDCl_3$ $\delta_H$ 0.84–0.90 (6H, m), 1.12–1.67 (40H, m), 1.88 (1H, q), 4.14 (2H, d), 7.37–7.58 (4H, m), 7.69–7.81 (2H, m), 7.81–7.96 (2H, m), 8.05 (2H, s), m.p. 55–57 °C. Found: C, 77.51; H, 8.99; N, 6.31. $C_{43}H_{59}N_3O_3$ requires C, 77.55; H, 8.99; N, 6.27%

$L^{10}$. $L^{10}$ was prepared according to the method described for $L^2$ using chelidamic acid and 2-aminothiophenol as starting materials. (Yield 80%), $^1H$ NMR DMSO-$d_6$ $\delta_H$ 7.59 (4H, m), 7.81 (2H, s), 8.12 (2H, d), 8.23 (2H, d). Found: C, 57.43; H, 2.97; N, 10.59. $C_{19}H_{11}N_3S_2O–2H_2O$ requires C, 57.42; H, 3.80; N, 10.57%

$L^{11}$. 1 g of $L^6$ (2.8 mM) and 0.19 g of $K_2CO_3$ (1.45 mM) were stirred at 120 °C in DMF (20 ml) under nitrogen to 1-bromododecane (0.67 ml, 2.8 mM) was added, the mixture was cooled to 80 °C and after 24 h, the solvent was removed under vacuum. The black, crude material was crystallised from the minimum amount of hot ethyl acetate to give $L^{11}$ (Yield 1.1 g, 78%), $^1H$ NMR, $CDCl_3$ $\delta_H$1.27 (s, 20H), 1.91 (q, 3H), 4.26 (t, 2H), 7.43 (m, 4H), 7.73 (d, 2H), 7.86 (d, 2H), 8.04 (s, 2H), m.p. 110–112 °C.

Metal complexes of $L^6$. The La complex was prepared by refluxing (27.5 mg, 0.064 mM) $La(NO_3)_3{\cdot}6H_2O$ with 20 mg (0.064 mM) ligand in 29 $cm^3$ MeCN for 2 hours. The Nd complex was prepared by refluxing 28 mg, 0.06 mM $Nd(NO_3)_3{\cdot}6H_2O$ with 20 mg (0.064 mM) ligand in 29 $cm^3$ MeCN for 2 hours. The isomorphous Pr and Er complexes were prepared similarly. The Gd complex was prepared by refluxing 28.7 mg (0.064 mM) $Gd(NO_3)_3{\cdot}5H_2O$ and 20 mg (0.064 mM) ligand) in 32.5 $cm^3$ MeCN for 2 hours. The isomorphous Eu compound was prepared similarly. All solutions were left to cool slowly and crystals appeared after several weeks.

### X-ray crystallography

The structures of six lanthanide complexes with $L^6$ have been determined. Crystal data and refinement details are provided in Table 3. Data for all 6 crystals were collected with MoKα radiation using the MARresearch Image Plate System. The crystals were positioned at 70 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program.[20] Structure solution and refinement were carried out similarly. Structures were solved using direct methods with the Shelx86 program.[21] All non-hydrogen atoms were refined anisotropically, apart from the disordered water molecules in 1-La which were refined isotropically. Hydrogen atoms on the carbon atoms and nitrogen atoms were included in calculated positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Hydrogen atoms on water molecules were not located. An empirical absorption correction was made for the two metal complexes using the DIFABS program.[22] All structures were refined on $F^2$ till convergence using Shelxl.[23] Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre reference number CCDC 193084–193089. See http://www.rsc.org/suppdata/nj/b3/b314321j/ for crystallographic data in .cif or other electronic format.

### Theoretical calculations

Starting models were built using the CERIUS2 software[24] and the three rings were made approximately coplanar but no symmetry was imposed. All possible structures of $L^6$, $[HL^6]^+$ and $[H_2L^6]^{2+}$ were then optimised with the Gaussian98 program[17] using the 6-31G* basis set.

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