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FULL PAPER

Americium(III) and europium(III) solvent extraction studies of amide-substituted triazine ligands and complexes formed with ytterbium(III)

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4-Amino-bis(2,6-(2-pyridyl))-1,3,5-triazine L^4 and several, amide derivatives with hydrophobic alkyl substituents have been synthesised. Solvent extraction studies carried out on Am(III) and Eu(III) with L^4 and its amide derivatives in synergistic combination with α-bromodecanoic acid, show that these ligands can selectively extract actinides with respect to lanthanides. The structures of $[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$ and two amide derivatives have been determined and show respectively the *trans*, *trans*; *cis*, *cis*; and *cis*, *trans* conformations of the adjacent aromatic rings. These observed conformations are in agreement with the results of quantum mechanics calculations on L^4 and its protonated derivatives. The structures of two Yb complexes with amide derivatives are also reported with stoichiometry $[Yb(L)(NO_3)(H_2O)_4]\cdot 2NO_3\cdot 0.5H_2O$ and $[Yb(L)(NO_3)_3(H_2O)]\cdot 2MeCN$ and show the metal in 9 coordinate environments.

Introduction

One possible future scenario in nuclear reprocessing is the conversion or transmutation of the long-lived minor actinides, such as americium, into short-lived isotopes by irradiation with neutrons.[1] In order to achieve this transmutation it is necessary to separate the trivalent minor actinides from the trivalent lanthanides by solvent extraction, because the lanthanides absorb neutrons effectively and hence prevent neutron capture by the transmutable actinides.

For many years we have been designing and testing ligands for the co-extraction[2,3] of lanthanides and actinides from nuclear waste and their subsequent separation.[4,5] Oligoamines such as 2,2′:6′2″-terpyridine[4–6] (L^1) and 2,4,6-tris(2-pyridyl)-1,3,5-triazine[5] (L^2) have been shown to selectively extract actinides in preference to the lanthanides from nitric acid solutions into an organic phase. For extraction it proved necessary to use these ligands in synergistic combination with α-bromodecanoic acid. Separation factors for Am(III) relative to Eu(III) were found to be around 7 and 10 for L^1 and L^2 respectively.[5] Although a separation factor of around 12 can be obtained with a more hydrophobic derivative of L^2 (2,4,6-tris(4-*tert*-butyl-2-pyridyl)-1,3,5-triazine (L^3), the synthesis is difficult and the ligand can only be prepared on a small scale. The promising solvent extraction results obtained with L^2 and L^3 led us to the synthesis of 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine (L^4). This ligand contains the same major binding cavity as L^2 but is much more easily functionalised to prepare the appropriate hydrophobic derivatives. In this study, several new amide derivatives of L^4 have been prepared containing either 2,2,4-trimethyl-1-pentyl (L^5), 2,2-dimethyl-1-propyl (L^6), cyclohexyl (L^7), or heptyl (L^8) as the hydrophobic alkyl substituent (Fig. 1). The Am(III)/Eu(III) separation–extraction performance of L^4, L^5, L^7 and L^8 was measured in combination with α-bromodecanoic acid. The structures of a bis hydrochloride salt of L^4 and of the free ligands L^5 3,5,5-trimethylhexanoylamino-bis(2,6-(2-pyridyl)-1,3,5-triazine) and L^7 (4-cyclohexanoylamino-bis-(2,6-(2-pyridyl))-1,3,5-triazine) together with the corresponding Yb(III) complexes of L^6 and L^7 were also determined.

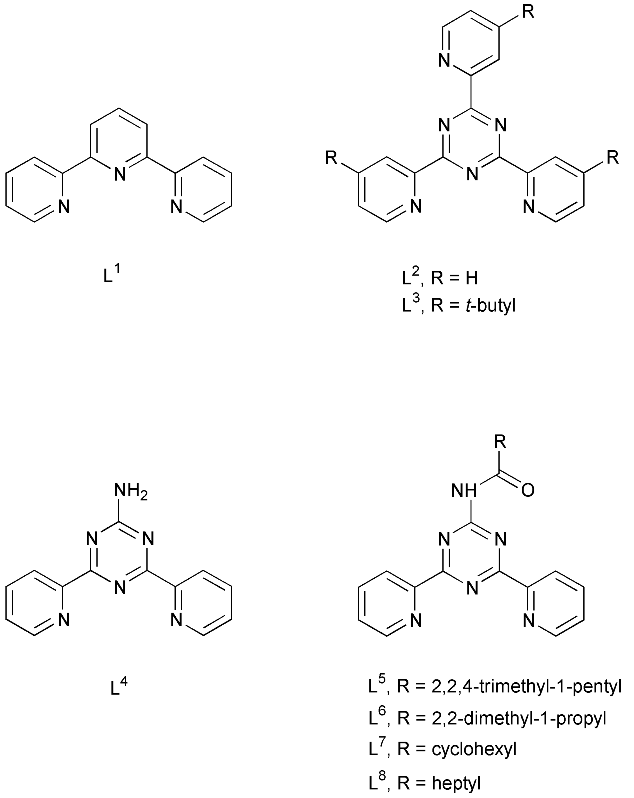

Fig. 1 Structures of ligands.

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Experimental

Synthesis

L^4 was prepared as described previously.[7] 3,5,5-Trimethylhexanoyl chloride, *tert*-butylacetyl chloride, cyclohexane carbonyl chloride, octanoyl chloride and ytterbium nitrate pentahydrate (99.9%) were used as received from Aldrich. Pyridine and acetonitrile were dried over 4 and 3 Å molecular sieves respectively.

Preparation of ligands

4-(3,5,5-Trimethylhexanoylamino)-bis(2,6-(2-pyridyl))-1,3,5-triazine (L^5). L^4 (31.78 g, 0.127 M) was stirred as a suspension in pyridine (500 cm^3) under a nitrogen atmosphere. The solution was heated to ≈115 °C and 3,5,5-trimethylhexanoyl chloride (66.40 g, 0.376 M) was added in one volume to the hot reaction mixture. The suspension of L^4 gradually disappeared on heating and the solution was allowed to cool after 2 h. After the volume of solvent was reduced to 100 cm^3 and 100 cm^3 of CH_2Cl_2 was added, the solution was extracted with a saturated $NaHCO_3$ solution (2 × 200 cm^3) and then twice with distilled water (2 × 200 cm^3). The organic phase was dried with sodium sulfate and the solvents were removed *in vacuo* to leave a dark brown oil which was then stirred vigorously with ethyl acetate (50 cm^3) and hexane (500 cm^3) for approximately 1 h. A white precipitate formed which was filtered, washed with cold hexane and recrystallised from ethyl acetate. (Yield 34 g, 70%), mp 148 °C. NMR measurements for this and all other compounds were carried out in $CDCl_3$. ^1H NMR: δ 0.89 (9H, s), 1.08 (3H, d), 1.24 (1H, dd), 1.42 (1H, dd), 2.31 (1H, m), 2.69 (1H, dd), 2.82 (1H, dd), 7.47 (2H, t), 7.91 (2H, t), 8.73 (2H, d), 8.91 (2H, d). Found: C, 67.64; H, 6.67; N, 21.19. $C_{22}H_{25}N_6O$ requires C, 67.67; H, 6.71; N, 21.52%.

4-*tert*-Butylacetanoylamino-bis(2,6-(2-pyridyl))-1,3,5-triazine (L^6). L^6 was prepared in a similar manner to L^5. ^1H NMR confirmed the presence of L^6 and the ligand was used without further purification for the preparation of the corresponding Yb complex. ^1H NMR: δ 1.11 (9H, s), 2.64 (2H, s), 7.58 (2H, t), 8.01 (2H, t), 8.61 (2H, d) 8.84 (2H, d), 9.11 (1H, br).

4-Cyclohexanoylamino-bis(2,6-(2-pyridyl))-1,3,5-triazine (L^7). L^7 was prepared in a similar manner to L^5. Yield 64%, mp 138 °C, ^1H NMR: δ 1.3 (3H, m), 1.6 (2H, m), 1.7 (1H, d), 1.9 (2H, m), 2.1 (2H, m), 2.8 (1H, t), 7.5 (2H, t), 7.9 (2H, t), 8.7 (2H, d), 8.9 (2H, d). Found: C, 66.61; H, 5.63; N, 23.54. $C_{20}H_{20}N_6O$ requires C, 66.65; H, 5.59; N, 23.32%. Crystals suitable for X-ray structural analysis were obtained after further recrystallisation from ethyl acetate.

4-Octanoylamino-bis(2,6-(2-pyridyl))-1,3,5-triazine (L^8). L^8 was prepared in a similar manner to L^5. Yield 62%, ^1H NMR: δ 0.88 (3H, t), 1.24–1.38 (6H, m), 1.44 (2H, q), 1.80 (2H, q), 2.90 (2H, t), 7.5 (2H, t), 7.9 (2H, t), 8.7 (2H, d), 8.9 (2H, d). Found: C, 67.02; H, 6.46; N, 22.33. $C_{21}H_{24}N_6O$ requires C, 67.00; H, 6.43; N, 22.32%.

$[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$. L^4 was dissolved in 2 M HCl and after complete evaporation of the solution, suitable crystals were obtained after a few weeks.

Preparation of metal complexes

$[Yb(L^7)(NO_3)(H_2O)_4]\cdot 2NO_3\cdot 0.5H_2O$. This complex was prepared by stirring $Yb(NO_3)_3\cdot 5H_2O$ (0.010 g, 0.02 mM) and L^7 (0.008 g, 0.02 mM) in 20 cm^3 CH_3CN until complete dissolution had occurred. The solution was allowed slowly to evaporate at room temperature. Suitable crystals were formed after 2 days.

$[Yb(L^6)(NO_3)_3]\cdot 2MeCN$. This complex was prepared by the dropwise addition of $Yb(NO_3)_3\cdot 5H_2O$ (0.0129 g, 0.03 mM) dissolved in 1 cm^3 CH_3CN to a stirred solution containing L^6 (0.01 g, 0.03 mM) also dissolved in 1cm^3 CH_3CN. Suitable crystals were obtained at room temperature after 2 days.

Solvent extraction studies

Aqueous solutions (800 μL) of diluted nitric acid (0.02 mol L^{-1} $\leq [HNO_3] \leq$ 0.13 mol L^{-1}), spiked with radioisotopes ^{241}Am and ^{152}Eu, were contacted for 30 minutes by means of an automatic vortex shaker with organic solutions (800 μL), containing either ligand L^4, L^5, L^7 or L^8 ($[L]_{initial}$ = 0.02 mol L^{-1}), diluted in a mixture of hydrogenated tetrapropene (TPH) and α-bromodecanoic acid ($[\alpha BrC_{10}]_{initial}$ = 1 mol L^{-1}). Aqueous and organic solutions were mixed in 2 mL Nalgene tubes thermostatted at 22 °C. After phase separation by centrifugation, 500 μL samples of both phases were analysed using a gamma counting spectrometer (HPGe detector, Eurisys Mesures). The peaks at 59.54 and 121.78 keV were used for ^{241}Am and ^{152}Eu activity measurements, respectively. The concentration of nitric acid in the aqueous phase at equilibrium ($[HNO_3]_{eq}$) was determined by automatic titration with NaOH.

The distribution ratio D_M for a metallic cation M is defined as the ratio of the concentration of the metallic species in the organic phase at equilibrium over its concentration in the aqueous phase at equilibrium. The error of the measure of D_M (M = Am(III) or Eu(III)) was estimated to be within 5%. The separation factor SF_{M^1/M^2} for two metallic cations M^1 and M^2 is defined as the ratio of their distribution ratios. The error of the determination of $SF_{Am/Eu}$ was estimated to be 7%.

Crystallography

The structures of the salt $[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$, the ligands $L^5\cdot 2H_2O$ and L^7, and the ytterbium complexes with L^6 and L^7 were determined. Crystal data and refinement details are provided in Table 1. Data for all 5 crystals were collected with Mo-Kα radiation using the MAR research Image Plate System. The crystals were positioned 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.[8] Default refinement details are described here while differences for specific structures are included below. Structures were solved using direct methods with the SHELX86 program.[9] All non-hydrogen atoms were refined anisotropically. 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 included when they could be located in a difference Fourier map and refined with distance constraints. The assignment of the positions of the nitrogen atoms in the pyridine rings was made straightforwardly on the basis of thermal parameters, dimensions, R values and hydrogen bond positions. An empirical absorption correction was made for the two metal complexes using the DIFABS program.[10]

In the structure of the salt $[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$, there are two formula units in the asymmetric unit. All the hydrogen atoms on the water molecules were located in a difference Fourier map and included in the refinement with distance constraints. The structure of L^7 contained no solvent. L^5 contained two water molecules in the asymmetric unit but the hydrogen atoms on these solvent molecules were not located. For $[Yb(L^7)(NO_3)(H_2O)_4]\cdot 2NO_3\cdot 0.5H_2O$ the hydrogen atoms on the water molecules were not located. The data were of poor quality and only the metal atom was refined anisotropically. For $[Yb(L^6)(NO_3)_3(H_2O)]\cdot 2MeCN$ the hydrogen atoms on the water molecules were located and refined with distance constraints. All structures were refined on F^2 till convergence using SHELXL.[11]

CCDC reference numbers 172878–172882.

Table 1 Crystal data and structure refinement details

Compound		$[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$	L^7	$L^5\cdot 2H_2O$	$[Yb(L^7)(NO_3)(H_2O)_4]\cdot 2NO_3\cdot 0.5H_2O$	$[Yb(L^6)(NO_3)_3(H_2O)]\cdot 2MeCN$
Empirical formula		$C_{13}H_{17}Cl_2N_6O_{2.5}$	$C_{20}H_{20}N_6O$	$C_{22}H_{29}N_6O_3$	$C_{20}H_{29}N_9O_{14.5}Yb$	$C_{24}H_{28}N_{11}O_{10}Yb$
Formula weight		368.23	360.42	425.51	800.56	803.61
Temperature/K		293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system, space group		Triclinic, $P\bar{1}$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/a$	Monoclinic, $C2/c$	Monoclinic, $C2/c$
a/Å		10.158(12)	9.946(12)	12.458(14)	24.35(3)	8.935(14)
b/Å		13.890(15)	17.15(2)	14.997(17)	16.760(18)	12.887(14)
c/Å		14.249(15)	11.849(14)	12.515(14)	14.812(17)	15.004(17)
α/°		69.20(1)	(90)	(90)	(90)	71.69(1)
β/°		67.61(1)	109.12(1)	93.54(1)	103.49(1)	87.14(1)
γ/°		71.60(1)	(90)	(90)	(90)	78.96(1)
Volume/Å^3		1699	1910	2334	5878	1610
Z, Calculated density/Mg m^{-3}		2, 1.439	4, 1.254	4, 1.211	4, 1.809	2, 1.658
Absorption coefficient/mm^{-1}		0.404	0.082	0.083	3.266	2.974
F(000)		764	760	908	3184	798
Reflections collected		5890	6387	7430	6980	5198
Unique reflections/R_{int}		5890	3383/0.0310	4416/0.0761	4420/0.0762	5198
Data/restraints/parameters		5890/15/457	3383/0/245	4416/4/297	4420/0/190	4198/2/428
Final R indices [$I > 2\sigma(I)$]	$R1$	0.0479	0.0844	0.0920	0.1119	0.0296
	$wR2$	0.1284	0.2336	0.2439	0.2809	0.0712
R indices (all data)	$R1$	0.0722	0.1544	0.2214	0.2547	0.0367
	$wR2$	0.1419	0.2846	0.3061	0.3363	0.0755
Largest diff. peak and hole/e Å^{-3}		0.260, −0.272	0.360, −0.233	0.697, −0.277	3.540, −1.922	0.997, −1.596

See http://www.rsc.org/suppdata/dt/b1/b104181a/ for crystallographic data in CIF or other electronic format.

Theoretical calculations

There are three possible conformations for L^4 which can be characterised by the N–C–C–N torsion angles as *tt* (*trans*, *trans*), *ct* (*cis*, *trans*) and *cc*(*cis*, *cis*). We have analysed these conformations for L^4, $[HL^4]^+$ and $[H_2L^4]^{2+}$ using the Gaussian94 program.[12] Starting models were built using the CERIUS2 software[13] and the three rings were made approximately coplanar but no symmetry was imposed. Structures were then optimised using the 6-31G** basis set.

Results and discussion

Synthesis

Hydrophobic amide derivatives of 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine L^4 were synthesised by reaction of L^4 with the appropriate acid chloride in refluxing pyridine. This method has been used previously for the acylation of 2,4-diamino-s-triazines.[14] There is a wide choice of hydrophobic substituents because of the large number of commercially available acid chlorides. The two ligands containing 2,2-dimethyl-1-propyl and cyclohexyl alkyl groups (L^6 and L^7), were prepared in order to facilitate crystallisation of the corresponding lanthanide complexes. The more organo-soluble L^5 and L^8 were prepared for the solvent extraction experiments. The 2,2,4-trimethyl-1-pentyl alkyl chain in L^5 was chosen because it bears a closer resemblance to the TPH solvent used as the organic phase in the extraction experiments. TPH (hydrogenated tetrapropene) is an industrial aliphatic diluent containing highly branched alkanes.

Extraction studies

The synergistic extraction of trivalent actinides and lanthanides observed when combining tridentate planar ligands such as L^2 with α-bromodecanoic acid (αBrC_{10}) in TPH can be described by the following equilibrium:[5]

$$M^{3+} + 3\alpha BrC_{10} + L \rightleftharpoons ML(\alpha BrC_{10})_3 + 3H^+$$

We have studied the synergistic extraction of Am(III) and Eu(III) by combining ligands L^4, L^5, L^7 or L^8 with α-bromodecanoic acid, used here as a cationic exchanger. The replacement of nitrate anions by α-bromodecanoate anions enhances the extraction of $[ML]^{3+}$ complexes in TPH. The results of these experiments are summarised in Table 2 together with the results related to ligands L^2 and L^3 and are also shown in Fig. 2 for ligands L^4 and L^5, and Fig. 3 for ligands L^7 and L^8, respectively.

Table 2 Extraction of Am(III) and Eu(III) by different synergistic systems[a]

Ligand	$[HNO_3]_{eq}$	$D_{Eu(III)}$	$D_{Am(III)}$	$SF_{Am/Eu}$
L^1	0.03	2.8	27	9.5
	0.05	0.3	3.5	10
	0.08	0.09	0.8	9
	0.11	0.03	0.3	9
L^2	0.03	8.7	124	14
	0.05	0.9	12	14
	0.08	0.2	2.1	11
	0.11	0.08	0.8	9
L^4	0.03	4.6	45	9.5
	0.05	0.5	5.5	10
	0.08	0.08	0.7	9.5
	0.11	0.02	0.2	11.5
L^5	0.02	2.2	14	6.5
	0.04	0.5	4.8	9.5
	0.06	0.12	1.1	9
	0.09	0.04	0.39	9
	0.13	0.02	0.21	9
L^7	0.03	2.2	24	11
	0.05	0.24	2.8	12
	0.10	0.04	0.4	10
L^8	0.03	2.4	19	8
	0.06	0.3	3.5	12
	0.10	0.03	0.4	12

[a] Organic solution: $[\alpha BrC_{10}]_{initial}$ = 1 M, $[L]_{initial}$ = 0.02 mol L^{-1}, TPH. Aqueous solution: $[HNO_3]_{initial}$ = variable, T = 22 °C.

Although not as efficient as ligand L^2, ligands L^4, L^5, L^7 and L^8 appeared to be as efficient as ligand L^1 when used in a synergistic mixture with α-bromodecanoic acid for the extraction of Am(III) and its separation from Eu(III). For the three rather hydrophobic substituted ligands L^5, L^7 and L^8, the log–log plots of the experimental D_M values *vs.* $[HNO_3]_{eq}$ fitted well with a linear regression. The slope of which was close to −3, in agreement with the above proposed extraction equilibrium. However, for the non-substituted ligand L^4, the log–log plots of the

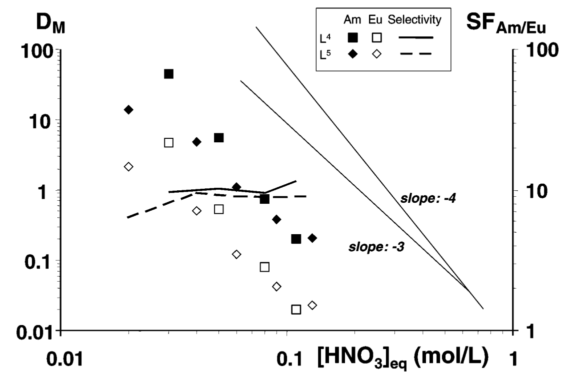

Fig. 2 Am(III) and Eu(III) extraction by L^4 and L^5 in a synergistic mixture with α-bromodecanoic acid. Organic solution: $[\alpha BrC_{10}]_{initial}$ = 1 M, $[L]_{initial}$ = 0.02 mol L^{-1}, TPH. Aqueous solution: $[HNO_3]_{initial}$ = variable, T = 22 °C. The symbols denote each measurement of D_M. The approximately horizontal lines represent calculated SF values.

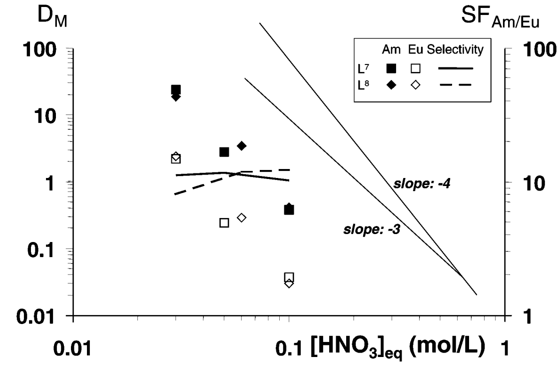

Fig. 3 Am(III) and Eu(III) extraction by L^7 and L^8 in a synergistic mixture with α-bromodecanoic acid. Organic solution: $[\alpha BrC_{10}]_{initial}$ = 1 M, $[L]_{initial}$ = 0.02 mol L^{-1}, TPH. Aqueous solution: $[HNO_3]_{initial}$ = variable, T = 22 °C. The symbols denote each measurement of D_M. The approximately horizontal lines represent calculated SF values.

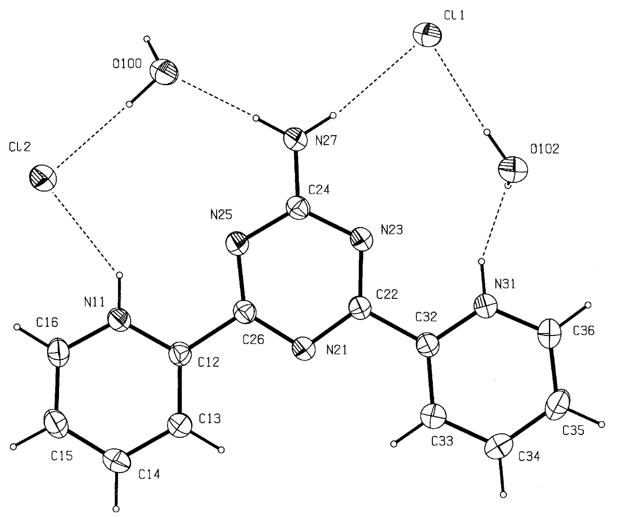

Fig. 4 The structure of the $[H_2L^4]^{2+}$ cation A showing the hydrogen bond pattern (dotted lines). Ellipsoids at 30% probability.

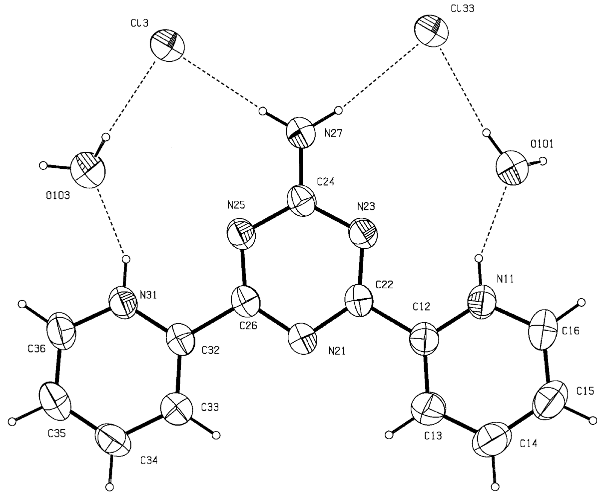

Fig. 5 The structure of the $[H_2L^4]^{2+}$ cation B showing the hydrogen bond pattern (dotted lines). Ellipsoids at 30% probability.

experimental D_M values *vs.* $[HNO_3]_{eq}$ were better fitted with a linear regression, the slope of which is close to −4, possibly because of the redistribution of this rather hydrophilic ligand in the aqueous acidic phase after protonation (*i.e.*: $[HNO_3]_{eq} \geq$ 0.08 M).

Structural studies

Ligands. L^4 is sparingly soluble in most solvents and we were unable to prepare suitable crystals of the free ligand. We did, however, manage to crystallise the corresponding dihydrochloride salt on evaporation of a 2 M HCl solution containing the ligand. The structure of $[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$ shows two discrete cations, together with anions and solvent water molecules in the asymmetric unit. Both independent cations are protonated in the same way with the hydrogen atoms situated on the nitrogen atoms in the pyridine rings. The three nitrogen atoms N(11), N(21), N(31) are arranged in a *trans*, *trans* (*tt*) formation. It is possible that this conformation and protonation pattern is facilitated by the presence of the water molecules and chloride anions and this is considered in the theoretical section below. The protonated cations A and B are shown in Figs. 4 and 5 together with their hydrogen bond patterns, details of which are listed in Table 3. Surprisingly, the patterns are different for A and B. Thus the intramolecular hydrogen bonds show that, in cation A, the amine nitrogen atom N(27) is hydrogen bonded to a water molecule and a chloride anion, whilst in B it is bonded to two chloride anions. Similarly N(11A) is bound to a chloride anion and N(31A) to a water molecule, while both N(11B) and N(31B) are bonded to water molecules. In addition, there are hydrogen bonds between the water molecules and the chloride anions. It is likely that the short intramolecular contacts in the ligands between N(11) and N(25), and between N(31) and N(23) of *ca.* 2.70 Å represent weak hydrogen bonds.

The structure of L^7 is shown in Fig. 6. There is one strong hydrogen bond between N(41) and N(11) (x, 0.5 − y, 0.5 + z) with an N ··· N distance of 3.00 Å. The arrangement of the three nitrogen atoms is *cis*, *cis* (*cc*). On the other hand, the structure of $L^5\cdot 2H_2O$ exhibits the ligand in the *ct* conformation as shown in Fig. 7. A water molecule O(200) forms donor hydrogen bonds to both N(31) at 2.84(1) and O(43) at 2.79(1) Å. The second water molecule in the asymmetric unit (not shown in the Figure) forms two hydrogen bonds to O(200) but not to L^5. In addition N(11) forms an intermolecular hydrogen bond to N(41) (5 + x, 0.5 − y, z) at 2.94 Å.

The fact that L^5 is in the *ct* conformation and L^7 is in the *cc* conformation (and indeed that $[H_2L^4]^{2+}$ is in the *tt* conformation) is particularly interesting. Our theoretical calculations on the parent amine (see below) show that there are only small energy differences between these three conformations, much lower than is found for ligands (*e.g.* 2,2′:6′2″-terpyridine (L^1))[6] with a central pyridine ring. The energy barrier between conformations is also likely to be much lower in these ligands containing a central triazine ring than in those containing a central pyridine ring where the *ortho*-hydrogen atoms on adjacent rings restrict rotation.

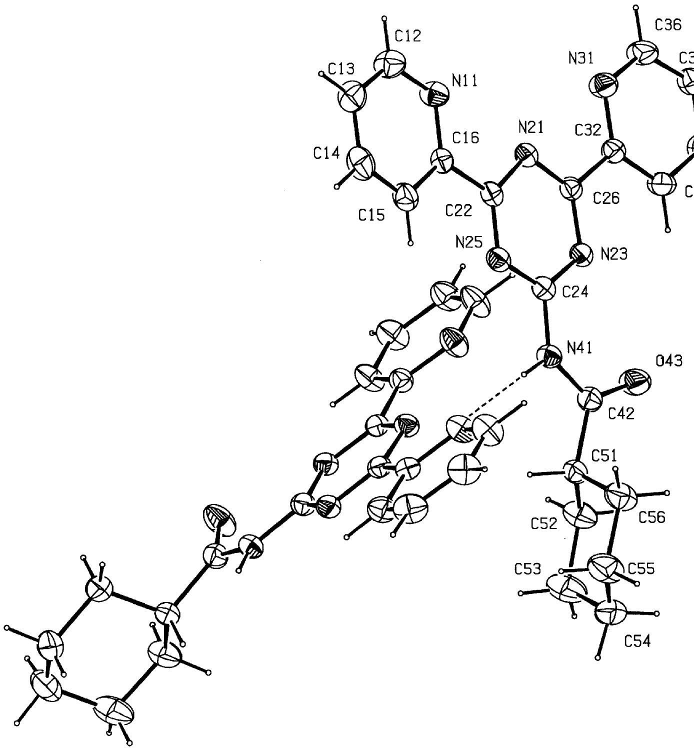

Fig. 6 The structure of L^7 with ellipsoids at 30% probability.

Table 3 Hydrogen bond distances (Å) in the structures

$[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$			
O(100) ··· Cl(1)	3.15	N(11B) ··· O(101)$3	2.69
O(100) ··· Cl(2)$2	3.11	N(11B) ··· N(25B)	2.70
O(101) ··· Cl(3)	3.17	N(27A) ··· O(100)$2	2.84
O(101) ··· Cl(4)$4	3.14	N(27A) ··· Cl(1)	3.26
O(102) ··· Cl(1)	3.07	N(27B) ··· Cl(3)$3	3.33
O(103) ··· Cl(3)	3.21	N(27B) ··· Cl(3)	3.34
O(103) ··· Cl(4)	3.21	N(31A) ··· O(102)	2.68
O(104) ··· Cl(4)	3.13	N(31A) ··· N(23A)	2.72
O(104) ··· Cl(2)$1	3.11	N(31B) ··· O(103)	2.69
N(11A) ··· N(25A)	2.71	N(31B) ··· N(23B)	2.69
N(11A) ··· Cl(2)	3.09		
L^7			
N(41) ··· N(11)$1	3.00		
$L^5\cdot 2H_2O$			
N(11) ··· N(41)$3	2.94	O(100) ··· O(200)$7	2.91
O(43) ··· O(200)	2.79	O(100) ··· O(200)$6	2.96
O(200) ··· N(31)	2.84		
$[Yb(L^7)(NO_3)(H_2O)_4]\cdot 2NO_3\cdot 0.5H_2O$			
O(100) ··· O(61)$4	2.79	O(102) ··· O(64)$5	2.67
O(100) ··· O(62)$4	2.96	O(102) ··· O(51)$1	2.86
O(101) ··· O(44)$6	2.97	N(41) ··· O(54)$2	2.82
O(101) ··· O(61)$5	3.07		
$[Yb(L^6)(NO_3)_3]\cdot 2MeCN$			
O(100) ··· N(500)$5	2.76	N(41) ··· N(400)$4	3.14

Symmetry elements. For $[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$: \$1 $x, y, 1 + z$; \$2 $1 - x, 1 - y, -z$; \$3 $-x - 1, 2 - y, -z$; \$4 $-x - 1, 2 - y, 1 - z$. For L^7: \$1 $x, 0.5 - y, 0.5 + z$. For $L^5\cdot 2H_2O$: \$3 $0.5 + x, 0.5 - y, z$; \$6 $2.5 - x, 0.5 + y, 1 - z$; \$7 $x + 0.5, 0.5 - y, z - 1$. For $[Yb(L^7)(NO_3)(H_2O)_4]\cdot 2NO_3\cdot 0.5H_2O$: \$1 $x, 1 - y, z - .5$; \$2 $0.5 - x, 0.5 - y, 1 - z$; \$4 $1 - x, y, 0.5 - z$; \$5 $1 - x, 1 - y, 1 - z$; \$6 $x, 1 - y, 0.5 + z$. For $[Yb(L^6)(NO_3)_3]\cdot 2MeCN$: \$4 $1 - x, 1 - y, -z$; \$5 $x + 1, y, z$.

Ytterbium complexes. We were able to prepare suitable crystals of two Yb(III) complexes formed with L^6 and L^7 but were unable to crystallise the corresponding complexes formed with the larger lanthanides. This is in direct contrast to our study on the lanthanide complexes formed with L^4 in which we obtained suitable crystals with the majority of the lanthanides.[15] The ease of crystallisation using L^4 was probably due to the stabilising effect in the crystal of intermolecular hydrogen bond formation through the 4-amino group.

Table 4 Dimensions in $[Yb(L^7)(NO_3)(H_2O)_4]\cdot 2NO_3\cdot 0.5H_2O$ and $[Yb(L^6)(NO_3)_3(H_2O)]\cdot 2MeCN$

$[Yb(L^7)(NO_3)(H_2O)_4]\cdot 2NO_3\cdot 0.5H_2O$			
Yb(1)–O(102)	2.290(16)	Yb(1)–O(42)	2.437(19)
Yb(1)–O(101)	2.313(15)	Yb(1)–N(31)	2.52(2)
Yb(1)–O(103)	2.385(18)	Yb(1)–O(41)	2.548(18)
Yb(1)–N(21)	2.39(2)	Yb(1)–N(11)	2.57(2)
Yb(1)–O(100)	2.398(16)		
$[Yb(L^6)(NO_3)_3(H_2O)]\cdot 2MeCN$			
Yb(1)–O(41)	2.277(4)	Yb(1)–N(21)	2.419(4)
Yb(1)–O(100)	2.298(4)	Yb(1)–O(52)	2.470(4)
Yb(1)–O(51)	2.362(4)	Yb(1)–N(11)	2.489(5)
Yb(1)–O(61)	2.400(4)	Yb(1)–N(31)	2.519(5)
Yb(1)–O(62)	2.404(4)		

The structure of the $[Yb(L^7)(NO_3)(H_2O)_4]^{2+}$ cation is shown in Fig. 8. There are two nitrate anions together with a disordered water molecule in the asymmetric unit. The structure of the cation shows the Yb to be in a 9-coordinate environment with the metal bond lengths shown in Table 4, together with the atomic numbering scheme. The water molecules show the shortest bonds although there is significant variation [2.29(2)–2.39(2) Å] but in addition, each of them forms two strong hydrogen bonds with adjacent non-coordinated nitrate anions. This formation of a doubly charged ionic complex containing a lanthanide with only one nitrate ion is unique and is not found in any of the 100 or so structures that we have determined of lanthanide nitrate complexes with terdentate nitrogen ligands.[4,6,15] The bond to the central triazine nitrogen atom Yb(1)–N(21) is at 2.39(2) Å much shorter than the bonds to the outer pyridine nitrogen atoms (Yb(1)–N(31) 2.52(2), Yb(1)–N(11) 2.57(2) Å). The amide N–H group is hydrogen bonded to a nitrate oxygen atom (which is not bonded to the metal) from an adjacent molecule, *viz* (N(41) ··· O(54) $(0.5 - x, 0.5 - y, 1 - z)$, 2.84 Å. There are many hydrogen bonds (Table 3)

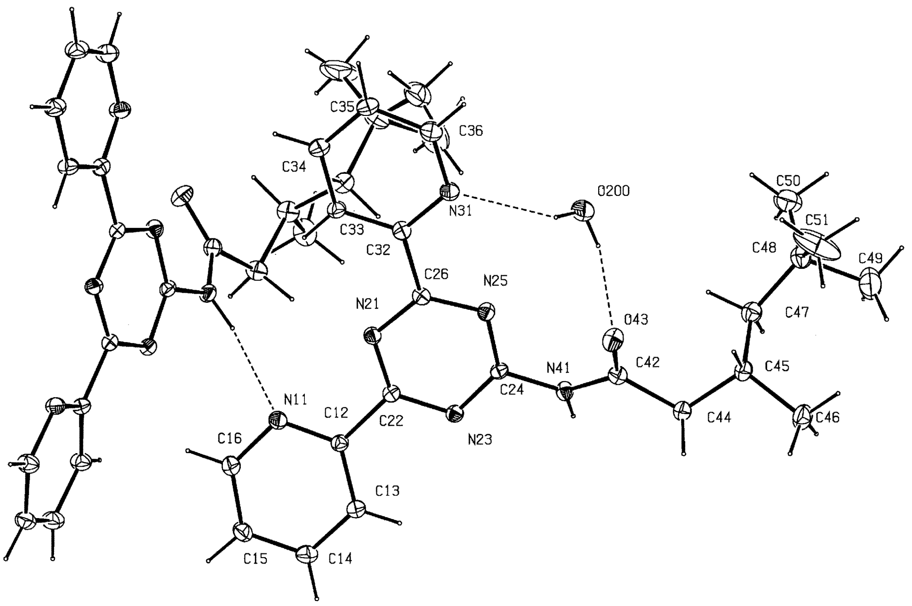

Fig. 7 The structure of $L^5{\cdot}2H_2O$ with ellipsoids at 30% probability. One water molecule, present in the asymmetric unit, is not shown.

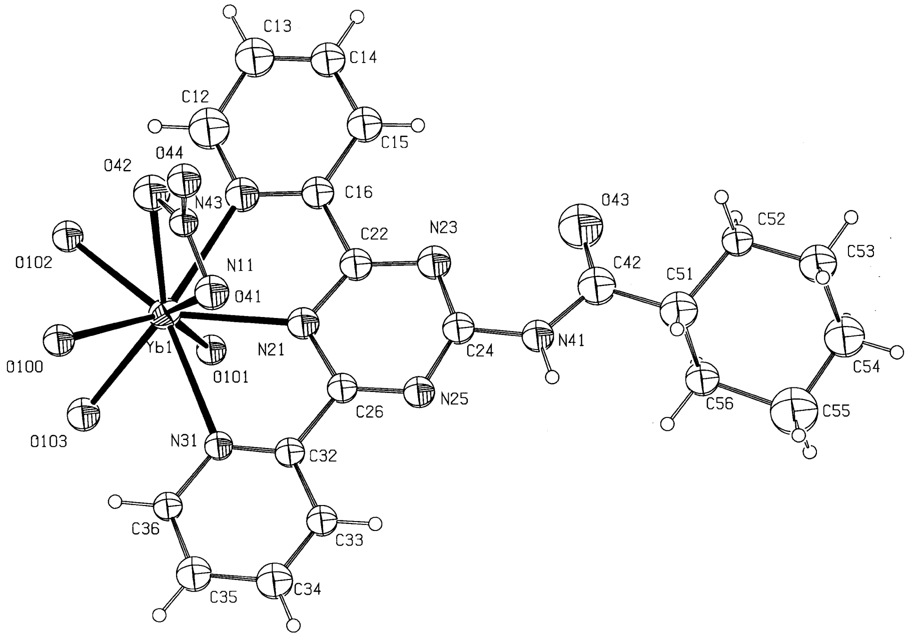

Fig. 8 The structure of the $[Yb(L^7)(NO_3)(H_2O)_4]^{2+}$ cation with the atomic numbering scheme. Ellipsoids at 30% probability. Hydrogen atoms on the water molecules could not be located and are not shown.

between the coordinated water molecules and nitrates in adjacent molecules.

This structural type, $[Yb(L^7)(NO_3)(H_2O)_4]^{2+}$, is different from the two types obtained previously for Yb(III) and L^4 as in $[Yb(L^4)(NO_3)_2(H_2O)_2]$, $[NO_3]$, Yb is coordinated to one tridentate L^4 ligand, two bidentate nitrates and two water molecules and in $[Yb(L^4)(NO_3)_3(H_2O)]$, Yb is coordinated to one L^4, two bidentate nitrates, one monodentate nitrate and one water molecule.[15] The latter structure is similar to that of $[Yb(L^6)(NO_3)_3(H_2O)]$ which is shown in Fig. 9. This structure also contains two solvent acetonitrile groups in the asymmetric unit. This structure is also 9-coordinate as one of the nitrate anions is monodentate. As is usually the case, the shortest Yb–O bond is to the monodentate nitrate Yb(1)–O(41) 2.277(4) Å, followed by the bond to the water molecule Yb(1)–O(100) 2.298(4) Å. The next shortest bonds are those to the bidentate nitrate although the bond to O(52) at 2.470(4) Å is significantly longer than the other three (2.362(4), 2.400(4), 2.404(4) Å). As was found for $[Yb(L^7)(NO_3)(H_2O)_4]{\cdot}2NO_3{\cdot}0.5H_2O$, the bond to the triazine nitrogen atom is, at 2.419(4) Å, significantly shorter than the bonds to the other nitrogen atoms (2.489(5), 2.519(5) Å). The amide nitrogen atom in this case is hydrogen bonded to a solvent acetonitrile molecule (N(41) ··· N(400) $(1 - x, 1 - y, -z)$ 3.14 Å).

We ascribe no particular significance to the difference in stoichiometry between the two metal complexes of Yb with L^6 and L^7. In previous work we have shown that there can be very different coordination geometries for specific metals with these planar terdentate ligands and it seems likely that the replacement of one bidentate and one monodentate nitrate by three water molecules is not unusual and that both structures together with others are likely to co-exist in solution. The only thing in common is that in both cases the metal cations are 9-coordinate as is usually found for ytterbium. It is likely that with these ligands the smaller lanthanides are 9-coordinate and have the form $[ML(NO_3)_n(H_2O)_m]^{p+}$ with $n = 1$, 2 or 3; $m = 6 - 2n + x$, where x is the number of monodentate nitrates. General structural trends show that the number of monodentate nitrates will be either 1 or 0, and that at least one bidentate nitrate will be coordinated so that the charge p on the complex is 0, 1 or 2.

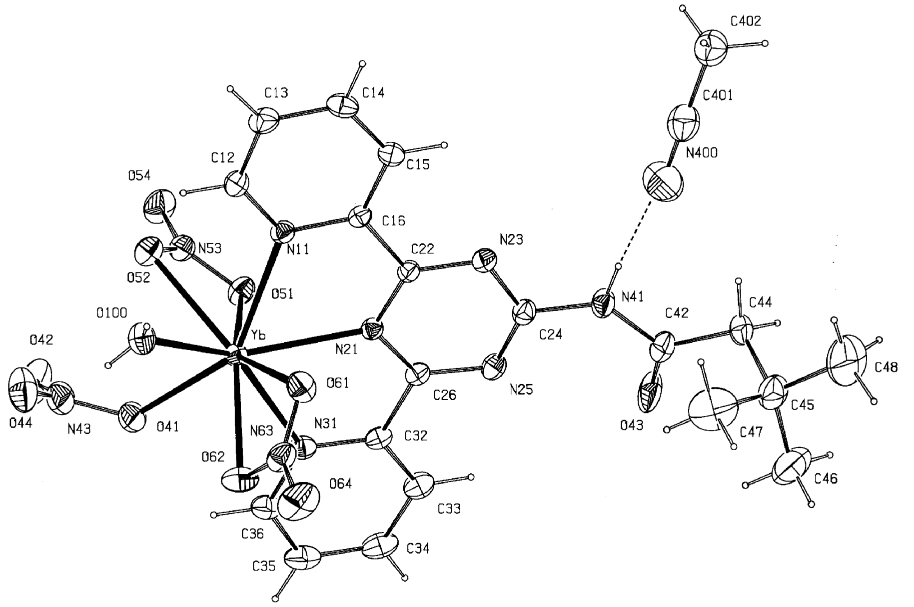

Fig. 9 The structure of the [Yb(L^6)(NO_3)$_3$(H_2O)] complex with ellipsoids at 30% probability. One of the two solvent acetonitrile molecules is shown.

It can also be considered that there are several different entities for the complexes in solution.

It is interesting to note that 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine which provides a separation ratio for An/Ln of greater than 100,[16] when used without a synergist, forms the 1 : 3 complex in the presence of nitrate with the smaller lanthanides (Sm–Lu) [17] but not for the larger lanthanides (La–Sm).[18] This suggests that ligands that always form 1 : 1 complexes are not likely to give high separation ratios in the absence of a synergist. While we have only determined crystal structures with Yb and not the other lanthanides, all indications from previously obtained structural information [2,4,15] is that when Yb forms 1 : 1 complexes with particular ligands then so do the other lanthanides and therefore we conclude that these ligands do not form 1 : 3 complexes with any lanthanide. Another factor that may lessen the usefulness of L^4 and derivatives is that they always form hydrogen bonds with either solvent molecules or other metal complexes, a feature not present in the ML_3^{3+} complex of 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine, which has a hydrophobic exterior. The propensity for hydrogen bond formation as indicated by Table 3 is widespread in all the crystal structures for ligands and metal complexes alike and the aggregation of molecules may occur in solution to prevent efficient extraction.

Theoretical analysis of L^4, $[HL^4]^+$ and $[H_2L^4]^{2+}$

Results are summarised in Table 5 for L^4, $[HL^4]^+$ and $[H_2L^4]^{2+}$. For the neutral ligand L^4, the relative energies of the *cc*, *ct* and *tt* form were 2.36, 0.00, and 0.49 kcal mol^{-1} respectively. This result contrasts with that found for terpyridine where the relative energies of the three forms were 12.55, 6.90, and 0.00 kcal mol^{-1} respectively.[6] There is a much smaller difference in energy in L^4 for the three conformers compared to terpyridine because there is no possible clash of *ortho* hydrogen atoms as the central ring is a triazine rather than a pyridine. It can be argued that the differences between the energies of the three conformers in L^4 are less than packing effects, which may account for the occurrence of the *ct* and *tt* forms in the crystal structures of L^5 and L^7 respectively (Figs. 7 and 6). It is likely that these conformational preferences in L^5 and L^7 will be comparable to those of L^4. This is in contrast to terpyridine where the energy differences between conformers are much more significant such that only the *tt* form is likely to be observed. In general it can be noted from the Cambridge Crystallographic Database that all polypyridine structures exhibit the *trans* conformation in the absence of a metal or another coordinating species. While our calculations have been carried out in the gas phase, it seems likely that the similar qualitative results will pertain in solution, that it will be more favourable for terdentate ligands with central triazine rings to form the *cc* conformation necessary for metal complexation than those with a central pyridine ring.

We then investigated the possible structures of $[HL^4]^+$ cations. Given that N(11) and N(31) are equivalent as indeed are N(25) and N(23) in *cc* and *tt* conformations we constructed 14 different structures, combinations of the nitrogen to be protonated and the three possible conformations. The *cc* conformation with N(21) protonated was *ca.* 10 kcal mol^{-1} lower in energy than all the others. The relative stability of this configuration is probably due to a combination of factors, N(21) is the preferred nitrogen to be protonated, and also it can form weak hydrogen bonds to the *ortho* nitrogen atoms in the terminal pyridine rings. In addition, there are no steric repulsions owing to adjacent *ortho* hydrogen atoms. The next most favourable configuration is the *cc* conformation with N(11) protonated but this only forms one weak intramolecular hydrogen bond. The *ct* conformation with N(21) protonated is disfavoured owing to repulsion between *ortho* hydrogen atoms on N(21) and C(33). It is interesting that in this case (and in others) the presence of two mutually *ortho*-hydrogen atoms leads to a twist in the rings of *ca.* 33–46° leading to a loss of conjugation. The highest energies (>44 kcal mol^{-1}) occur with N(27) protonated even though this does not lead to increased steric repulsions so that these energies must be due to the unfavourable nature of protonation at that atom.

Results for $[H_2L^4]^{2+}$ are less clear cut and show three configurations with comparable low energies within 5.4 kcal mol^{-1}, all with N(11) and N(31) protonated. The lowest energy configuration has the *tt* conformation in which there are two weak hydrogen bonds formed between N(11)–H ··· N(25) and N(31)–H ··· N(23) and no *ortho* ··· *ortho* interactions. This is the structure found in the crystal structure of $[H_2L^4]\cdot 2Cl\cdot 2.5H_2O$ (Figs. 4 and 5) where the configuration is further stabilized by intermolecular hydrogen bonds. The other conformations *ct* and *cc* also have low energies. With a *cis* conformation the pyridine nitrogen atom N(11) and/or N(31) can form hydrogen bonds to the central nitrogen atom N(21) but again there are no undesirable *ortho* ··· *ortho* interactions. All other configurations have an energy of 13.8 kcal mol^{-1} greater than the minimum. There are several features that can be discerned from the energy distribution. Unlike in $[HL^4]^+$ protonation of N(21) is not favourable, because the second proton, wherever

Table 5 Results from quantum mechanics calculations on L^4, L^2, $[HL^4]^+$ and $[H_2L^4]^{2+}$. Energies are given in kcal mol^{-1} relative to the lowest energy configuration for each type

Conformation	Protonated nitrogen	*cc*	*ct*	*tt*
L^4		2.36	0.00	0.49
L^2		12.55	6.90	0.00
$[HL^4]^+$	N(11)	9.77	14.67	14.55
	N(31)	=N(11)	12.22	=N(11)
	N(21)	0.00	10.13	22.19
	N(25)	28.98	27.07	14.55
	N(23)	=N(25)	14.05	=N(25)
	N(27)	51.10	46.15	44.38
$[H_2L^4]^{2+}$	N(11), N(21)	24.35	40.53	34.20
	N(11), N(31)	5.37	1.79	0.00
	N(11), N(25)	33.99	39.75	45.83
	N(11), N(23)	24.55	14.18	13.82
	N(11), N(27)	41.70	44.15	45.70
	N(21), N(23)	=N(21), N(25)	34.00	=N(21), N(25)
	N(21), N(25)	37.82	50.57	49.71
	N(21), N(27)	50.98	60.49	73.44
	N(21), N(31)	=N(11), N(21)	18.52	=N(11), N(21)
	N(25), N(31)	=N(11), N(23)	26.33	=N(11), N(23)
	N(23), N(25)	69.04	51.03	35.82
	N(23), N(27)	=N(25), N(27)	91.29	=N(25), N(27)

placed, always leads to *ortho* ··· *ortho* intramolecular interactions unless it is situated on N(27) which is an unfavourable site. Protonation on N(25) {or N(23)} is favourable in the *trans* conformation because it gives rise to N(25)–H ··· N(11) or {N(23)–H ··· N(31)} interactions but not in the *cis* conformation because of *ortho* ··· *ortho* interactions which lead to rotation of the rings. An intermediate situation arises in configurations such as the *cis* conformation with N(11) protonated where there is a weak hydrogen bond between N(11)–H and N(21). However, a repulsion between N(25)–H and C(13)–H, which is resolved *via* an intermediate rotation of 20° compared to the *ca.* 40°, found where there is no such hydrogen bond formation. We can draw the overall conclusion that the order of preference for protonation is N(11) > N(21) > N(25) > N(27) but that this order can be varied according to which other nitrogen atoms are protonated and the presence of solvent which can lead to intramolecular hydrogen bonds. The energy barrier to rotation between *cis* and *trans* in L^4 with a central triazine ring is far less than that observed with a central pyridine ring as in terpy where *ortho* ··· *ortho* hydrogen interactions provide a high energy barrier.

Conclusion

The experimental extraction studies indicate that these new amide ligands have selectivities towards Am(III) that are comparable to that of ligand L^2. Furthermore, since they can be synthesised on a large scale much more easily than ligand L^2, they are promising reagents in industrial solvent extraction for the separation of An(III) and Ln(III). The solid state studies show that these ligands form 1 : 1 complexes with the lanthanides of a similar type to those formed with the parent L^4. These ligands however show a propensity to form intermolecular hydrogen bonds through the amide groups which may prevent more efficient extraction. These ligands do not form the 1 : 3 complexes found with 2,6-bis(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine. The formation of this stoichiometry in a lanthanide complex might well be indicative of high separation factors as this ligand has a value for An/Ln of greater than 100.

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