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FULL PAPER

A study of lanthanide complexes formed with the terdentate nitrogen ligand 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine. Relevance to the separation of actinides and lanthanides by solvent extraction†

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The terdentate ligand 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine L^4 has been shown to have useful actinide(III)/lanthanide(III) separation properties relevant to nuclear reprocessing. The complexation of this ligand with the lanthanides has been investigated. Crystallographic analyses show the formation of five structural types. In the first part of the lanthanide series, (La–Sm), these structural types are (1) $[LnL^4(NO_3)_3(H_2O)_2]$, 11-coordinate, only for Ln = La; (2) $[LnL^4(NO_3)_3(H_2O)]$, 10-coordinate, for Ln = La, Pr, Nd, Sm; (3) $[LnL^4(NO_3)_2(H_2O)_3][NO_3]$ 10-coordinate for Ln = Nd, Sm. In the second part of the series from Eu to Lu the structures are all 9-coordinate but have two different stoichiometries; (4) $[LnL^4(NO_3)_2(H_2O)_2][NO_3]$ for Ln = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu; (5) $[LnL^4(NO_3)_3(H_2O)]$ unusually with one unidentate nitrate for Ln = Yb, and Y. With M = Sc the structure obtained is $[ScL^4(NO_3)_3]$ which is 8-coordinate with one unidentate nitrate. The structure types found for particular lanthanides can be correlated with the size of the ion, although several of the lanthanides form two structure types. Particularly noticeable is the alternative pairing of one bidentate nitrate ion or two water molecules in the coordination sphere with a concomitant free nitrate anion in the latter case. Type 5 includes the relatively rare sighting of a unidentate nitrate anion. Extensive intermolecular hydrogen bonding involving the free amine group is found in all the structures.

Introduction

The most likely scenario for successful 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, otherwise 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 of lanthanides and actinides from nuclear waste and their subsequent separation.[2–6] Various aza-aromatic bases have been shown to selectively extract actinides in preference to the lanthanides from nitric acid solutions into an organic phase. Nitric acid is used in the extraction experiments because it is envisaged that the An(III)/Ln(III) separation process will take place after the existing PUREX and DIAMEX processes. The PUREX process is already used to separate uranium and plutonium from a concentrated acid solution and the DIAMEX process will be used to coextract the lanthanides and actinides prior to their separation.[1] Particularly useful have been tridentate planar ligands such as 2,2′:6′,2″-terpyridine (L^1),[3,5,7] 2,4,6-tris(4-alkyl-2-pyridyl)-1,3,5-triazine (L^2),[8,9,10] 2,6-bis(5-alkyl-1,2,4-triazol-3-yl)pyridine (L^3),[4,11] 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine (L^4) and 2,6-bis(5,6-dialkyl-1,2,4-triazin-3-yl)pyridine (L^5) (Fig. 1).[11,12,13]

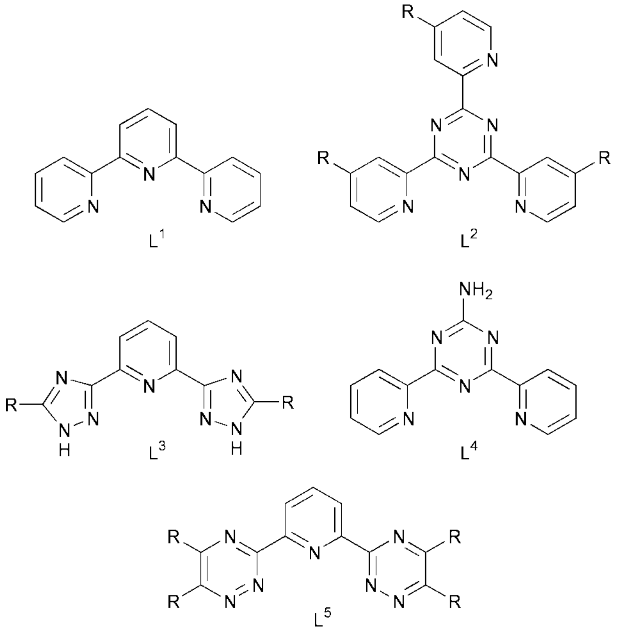

Fig. 1 The ligands L^1, L^2, L^3, L^4 and L^5.

These ligands give rise to a variety of different separation factors (SFs) for actinides over lanthanides. While L^1, L^2 and L^4 give SFs of 6–12, L^3 and L^5 gave much higher values. For L^3 it was necessary to provide synergistic combination with 2-bromohexanoic acid and at concentrations between 0.003 and 0.03 M,

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† Electronic supplementary information (ESI) available: thermogravimetric analysis data. See http://www.rsc.org/suppdata/dt/b0/b002529l/

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L^3 (R = methyl) was able to extract from an aqueous phase containing 0.05 M HNO_3 and 0.1 M NH_4NO_3 into hydrogenated tetrapropene (TPH), an industrial aliphatic diluent with highly branched chains, with separation factors between 41 and 68. With R = butyl, L^3 is an even better extractant and 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 SFs of up to 150 at low ligand concentrations between 0.014 and 0.055 M.[11] L^5 also gave remarkable SFs often over 100 from 1 to 2 M nitric acid solution and by contrast with L^3 did not require any synergic accompanying acid.[11,13]

While considerable progress has been made in our research program, the identity of the species extracted with these ligands has not yet been established for certain. It is probable that the species extracted at low levels of aqueous acidity are simple metal coordination complexes and the available evidence suggests that all the ligands L coordinate to the metal in a planar terdentate manner. We wished to establish the stoichiometries of the metal complexes extracted at low acid concentrations with a view to understanding the processes involved, to relate the structures obtained with the separation properties of the different ligands and hence to establish the optimum ligands for the An/Ln separations. To this purpose we have studied systematically by X-ray diffraction the complexes of the lanthanides with some of these ligands, namely 2,2′:6′,2″-terpyridine L^1,[5] the triazoles L^3,[4] and the triazines L^5.[12] However, for many of the 2,4,6-tris(4-alkyl-2-pyridyl)-1,3,5-triazine L^2 derivatives it proved very difficult to grow crystals and very few structures have been obtained. The few examples include for R = *t*-butyl, M = Ce,[8] and for R = H, M = Sm,[9] Eu, Pr.[10]

However with the related terdentate ligand 4-amino-bis(2,6-(2-pyridyl))-1,3,5-triazine (L^4) it did prove possible to prepare high quality crystals with the majority of the lanthanides probably owing to the stabilising effect in the crystal of intermolecular hydrogen bond formation through the 4-amino group and a series of crystal structures were obtained that showed a wide range of variations with coordination numbers and types of bonding. In this paper we describe the structures of complexes with the elements from La to Sm which proved to be 10 or 11 coordinate and elements (Eu to Lu) which proved to be 9-coordinate. Many complexes were isomorphous and in total five different stoichiometries were established with L^4.

The chemistry of the lanthanides is very wide-ranging, and large numbers of individual crystal structures have been determined. At the last count there were 3985 structures in the Cambridge Structural Database (CSD). However, there have been very few systematic surveys of crystal structures throughout the lanthanide series with a given ligand. One such survey was carried out with 2,2′:6′,2″-terpyridine (L^1) for which complexes of the type $LnCl_3(L^1)\cdot xH_2O$ (Ln = La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Y) were prepared and their structures determined.[14] For Ln = La–Nd, $x = 5$ and for Ln = Tb–Lu, $x = 4$ and for Ln = Sm, Gd there were between four and five water molecules in the coordination sphere. Also isolated was a dimeric species in which a samarium ion is coordinated to three nitrogen atoms from L^1, together with two bridging and two terminal chloride anions and one molecule of water. In discussing the (limited) differences between the structures, the authors made the point that systematic studies of lanthanide structures were not usually carried out for two reasons. Firstly, crystal structures were considered to be equivalent across the series and, therefore, such a study is often considered not to be worthwhile. Secondly, it was not always possible to obtain suitable crystals for a sufficient proportion of the lanthanides for a complete study. For example, other published studies of the lanthanides (*e.g.* with picrates[15] and with *p*-toluenesulfonates[16]) show only a limited number of structural differences. There have been more recent structural studies of L^1 with a range of anions such as acetate, trichloroacetate,[17] perchlorate[18] and nitrate.[19,20] It is most interesting that this work with nitrate is complementary to our own studies[5] as these authors found predominantly structures of the type $[Ln(NO_3)_2(L^1)(H_2O)_n]NO_3$ $n = 3$ for early and $n = 2$ for late lanthanides while we obtained $[Ln(NO_3)_3(L^1)(H_2O)_n]$ ($n = 1,0$) with $n = 1$ for early and $n = 0$ for late lanthanides. Our preparations were carried out under less hydrous conditions and this may account for the difference in structures observed although clearly the coordination numbers are the same for the elements. It has been noted previously[5,21,22] that the complexation properties of lanthanides with soft N donor ligands are very sensitive to the conditions under which the reaction takes place and in particular the nature of the solvent, the amount of solvent used, the temperature and solvent : water ratio. We have also carried out systematic structure determinations of L^3 and L^5 across the lanthanide series[4,12] and found a range of different stoichiometries. In this work we provide a systematic study of the structures found for L^4 which can be compared with those for L^1, L^3 and L^5 and can be used to postulate the reasons for the different extraction and separation properties of the ligands.

Experimental

Solvents and starting materials were used as supplied from Aldrich and used without further purification unless otherwise stated. Acetonitrile was dried and stored over 3 Å molecular sieves.

Preparation of L^4

The ligand L^4 was prepared according to the literature method[23] (Found: C, 62.36; H, 3.89; N, 33.70%. Calc. for $C_{13}H_{10}N_6$: C, 62.39; H, 4.03; N, 33.58%). δ_H (DMSO): 7.56–7.61 (t, 2H), 7.94 (s, 2H), 7.98–8.03 (t, 2H), 8.45–8.48 (d, 2H), 8.75–8.78 (d, 2H).

Preparation of metal complexes

Analyses of all complexes are provided in Table 1. 1-La and 2-La were obtained *via* similar preparations (the nomenclature *n*-M is used to describe the structure type *n* with metal M). Thus, 5 mg (0.02 mmol) of L^4 and 10 mg (0.023 mmol) of lanthanum nitrate hexahydrate were stirred in 30 cm^3 of acetonitrile and heated to approximately 50 °C. After 2 h the compounds had dissolved. Both heating and stirring were then stopped and the solvent was left to slowly evaporate. After approximately 3 days crystals, which were suitable for structure determination, were obtained.

2-Pr, 2-Nd and 3-Nd were prepared in an identical manner. 5 mg of L^4 (0.02 mmol) and 10 mg of the appropriate lanthanide nitrate hexahydrate were stirred in 20 cm^3 of acetonitrile and heated to approximately 40 °C. After 1 h the compounds had entered solution. Both heating and stirring were stopped and the solvent was again left to slowly evaporate. After 1 day crystals suitable for structure determination were obtained. 2-Sm and 3-Sm were prepared in an identical manner. Thus, 5 mg (0.02 mmol) of L^4 and 10 mg (0.022 mmol) of samarium nitrate hexahydrate were stirred in 15 cm^3 of acetonitrile. After 5 h the compounds had dissolved, the solvent was left to slowly evaporate. After approx. 3 days, crystals suitable for structure determination were obtained. The remaining crystals were prepared in an identical manner. 5 mg (0.02 mmol) of L^4 and approximately 10 mg (0.02 mmol) of lanthanide nitrate hexahydrate were stirred in 10 cm^3 of acetonitrile. After 2–3 h the compounds had dissolved, the solvent was left to slowly evaporate. After approx. 3 days, crystals suitable for structure determination were obtained.

Selected samples of the lanthanide-L^4 complexes were heated in a Stanton Redcroft TGA/DTA STA-1000. The samples were heated from room temperature up to 850 °C, at a ramp rate

Table 1 CHN Analysis of complexes

		Molecular formula					
		Theory (%)			Found (%)		
Formula	Complex	C	H	N	C	H	N
1-La	$\mathrm{LaL^4(NO_3)_3(H_2O)_2}$	25.55	2.31	20.62	25.87	2.39	20.41
2-La	$\mathrm{LaL^4(NO_3)_3(H_2O)C_2H_3N}$	28.41	2.38	22.08	28.35	2.34	22.21
2-Pr	$\mathrm{PrL^4(NO_3)_3(H_2O)C_2H_3N}$	28.32	2.38	22.01	28.02	2.37	22.29
2-Nd	$\mathrm{NdL^4(NO_3)_3{\cdot}H_2O(C_2H_3N)_2}$	30.00	2.78	22.64	30.12	2.54	22.60
3-Nd	$\mathrm{NdL^4(NO_3)_3(H_2O)_4}$	23.93	2.78	19.32	24.20	2.82	19.47
2-Sm	$\mathrm{SmL^4(NO_3)_3(H_2O)(C_2H_3N)}$	27.90	2.34	21.69	27.94	2.42	21.81
3-Sm	$\mathrm{SmL^4(NO_3)_3{\cdot}(H_2O)_3}$	24.37	2.52	19.68	24.06	2.91	19.77
3-Eu	$\mathrm{EuL^4(NO_3)_3{\cdot}(H_2O)_3}$	24.31	2.51	19.63	24.34	2.58	19.60
4-Eu	$\mathrm{EuL^4(NO_3)_3{\cdot}(H_2O)_4}$	23.65	2.75	19.09	23.98	2.81	19.08
4-Gd	$\mathrm{GdL^4(NO_3)_3{\cdot}(H_2O)_3{\cdot}C_2H_3N}$	26.16	2.78	20.34	23.07	2.62	18.84
4-Tb	$\mathrm{TbL^4(NO_3)_3{\cdot}(H_2O)_4}$	23.40	2.72	18.89	23.52	2.80	18.88
4-Dy	$\mathrm{DyL^4(NO_3)_3{\cdot}(H_2O)_4}$	23.28	2.70	18.79	23.47	2.78	18.71
4-Ho	$\mathrm{HoL^4(NO_3)_3(H_2O)_5}$	22.59	2.92	18.24	22.61	2.74	18.11
4-Er	$\mathrm{ErL^4(NO_3)_3(H_2O)_3{\cdot}C_2H_3N}$	25.79	2.74	20.05	26.98	3.01	20.07
4-Tm	$\mathrm{TmL^4(NO_3)_3(H_2O)_2}$	24.35	2.20	19.66	24.31	2.56	19.71
4-Yb	$\mathrm{YbL^4(NO_3)_3(H_2O)(C_2H_3N)_2}$	28.78	2.56	21.72	28.89	2.43	21.88
4-Lu	$\mathrm{LuL^4(NO_3)_3(H_2O)_4}$	22.85	2.66	18.45	22.99	2.71	18.56
5-Yb	$\mathrm{YbL^4(NO_3)_3(H_2O)_4}$	22.92	2.66	18.50	22.90	2.78	18.69

of 15 °C min^{-1}, under a static air atmosphere. Both the mass percent loss and the energy change *versus* temperature were recorded. The samples examined were: 2-Nd, 2-Sm, 4-Eu, 4-Gd, 4-Dy, 4-Ho, 4-Er and 5-Yb. Details of the mass loss and heat flow are given in the Supplementary Material.†

Crystallography

In the first part of the lanthanide series (La–Sm), seven crystal structures were determined, 1-La, 2-La, 2-Pr, 2-Nd, 2-Sm, 3-Nd and 3-Sm, in three different crystal structure types. In the second part of the series two different crystal types were found. Type 4 was found for 9 different cations and the structures are designated 4-Eu, 4-Gd, 4-Tb, 4-Dy, 4-Ho, 4-Er, 4-Tm, 4-Yb, 4-Lu while type 5 was only found for Yb among the lanthanides (5-Yb) but also for Y (5-Y). 6-Sc was also studied. Structure type 4 was twinned in some but not all of the metal complexes.

Details of data collection and refinement are given in Table 2. All crystals were positioned on a Marresearch Image Plate system. The crystal to plate distance was 70 mm and data were collected over 95 frames using 2° scans and 2 minutes per scan. The standard refinement technique is detailed here. Variations are reported below for specific structures. Data were processed using the XDS program.[24]

The structures were determined from general heavy atom methods using the SHELX86 program[25] although isomorphous structures were refined from established coordinates. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms bonded to carbon were included in calculated positions. The hydrogen atoms on water molecules could not be located and were not included. Empirical absorption corrections were applied using the DIFABS program.[26] The structures were then refined on F^2 using SHELXL.[27]

1-La was treated *via* the default methodology. 2-La, 2-Pr and 2-Sm are isomorphous and all contain one molecule of solvent acetonitrile. 2-Nd contains two molecules of solvent acetonitrile. 3-Nd and 3-Sm had no special features. The monoclinic crystals of structure type 4 showed a propensity for merohedral twinning (*hkl*, *hk*−*l*) to give a reciprocal lattice that appeared orthorhombic. This tendency varied significantly over the 9 isomorphous compounds that were studied. Thus 4-Eu, 4-Tb were twinned 55:45, 4-Ho was twinned 53:47 and 4-Er 86:14. All these compounds had β angles close to 90°. However for 4-Gd, 4-Dy, 4-Tm, 4-Yb and 4-Lu where the β angle was between 90.4 and 91.1° no twinning was observed. For the twinned structures the treatment of 4-Eu was typical. The structure was first refined in space group $P2_1/n$ isotropically to an $R1$ of 0.125. Twin refinement was then introduced and the factor refined to close to 50% with an $R1$ of 0.065. Then anisotropic refinement was introduced on all non-hydrogen atoms in the structure including the two water molecules. For the twinned structures no absorption correction was carried out. For the untwinned structures, the default refinement methodology was applied. 5-Yb and 5-Y were isomorphous and both structures were treated in the default manner as indeed was 6-Sc.

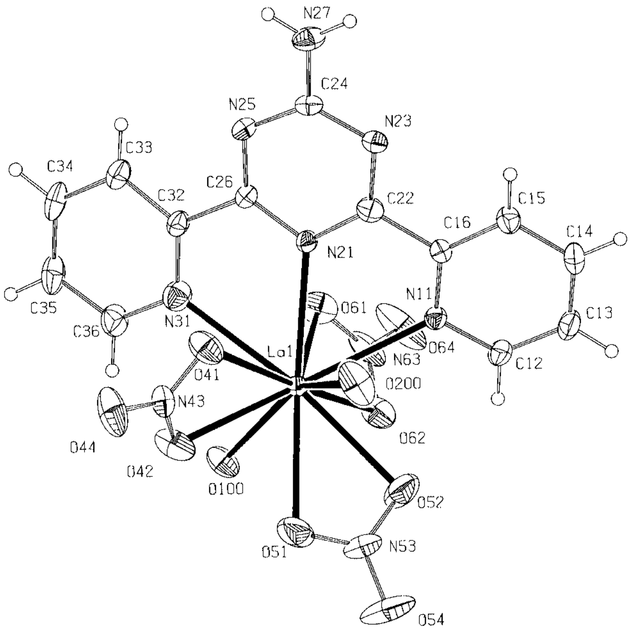

Fig. 2 Structure type 1. The structure of 1-La with the atomic numbering scheme. Ellipsoids at 30% probability.

CCDC reference number 186/2062.

See http://www.rsc.org/suppdata/dt/b0/b002529l/ for crystallographic files in .cif format.

Discussion

The structure of 1-La, $\mathrm{[LaL^4(NO_3)_3(H_2O)_2]}$ is shown in Fig. 2 together with the atomic numbering scheme, which is common to all structures. The metal atom is 11-coordinate, being bonded

Table 2 Crystal data and structure refinement for the crystal structures

Code	1-La	2-La	2-Pr	2-Sm	2-Nd	3-Nd
Empirical formula	$C_{13}H_{14}N_9LaO_{11}$	$C_{15}H_{15}N_{10}LaO_{10}$	$C_{15}H_{15}N_{10}PrO_{10}$	$C_{15}H_{15}N_{10}SmO_{10}$	$C_{17}H_{18}N_{11}NdO_{10}$	$C_{13}H_{18}N_9NdO_{13}$
Formula weight	611.24	634.28	636.28	647.74	680.66	652.60
Crystal system, space group	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a/Å	7.846(8)	9.943(9)	9.943(9)	9.936(9)	9.191(9)	9.332(9)
b/Å	11.552(12)	11.172(12)	11.101(12)	11.106(12)	11.710(12)	9.521(9)
c/Å	12.041(9)	11.871(12)	11.836(12)	11.831(12)	13.339(13)	13.622(12)
α/°	89.47(1)	117.19(1)	117.28(1)	117.35(1)	109.89(1)	79.38(1)
β/°	77.16(1)	91.44(1)	91.32(1)	91.33(1)	103.99(1)	81.90(1)
γ/°	73.67(1)	100.28(1)	100.62(1)	100.54(1)	90.78(1)	73.88(1)
Volume/Å^3	1022	1145	1133	1131	1303	1138
Z, Calculated density/Mg m^{-3}	2, 2.004	2, 1.839	2, 1.866	2, 1.901	2, 1.735	2, 1.911
Absorption coefficient/mm^{-1}	2.180	1.939	2.226	2.670	2.065	2.368
Reflections collected	3562	3977	3992	3960	4142	3610
Unique reflections/R(int)	3562	3977	3992	3960	4142	3610
Data/restraints/parameters	3562/0/308	3977/0/326	3992/0/326	3960/0/327	4142/0/363	3610/0/325
Final R indices [$I > 2\sigma(I)$] R1	0.0267	0.0394	0.0469	0.0224	0.0328	0.0438
wR2	0.0753	0.1077	0.1274	0.0617	0.0814	0.1315
R indices (all data) R1	0.0299	0.0478	0.0541	0.0263	0.0387	0.0498
wR2	0.0800	0.1194	0.1399	0.0370	0.0858	0.1382

Code	3-Sm	4-Eu	4-Gd	4-Tb	4-Dy	4-Ho
Empirical formula	$C_{13}H_{18}N_9SmO_{13}$	$C_{13}H_{18}N_9EuO_{13}$	$C_{13}H_{18}N_9GdO_{13}$	$C_{13}H_{18}N_9TbO_{13}$	$C_{13}H_{18}DyN_9O_{13}$	$C_{13}H_{18}HoN_9O_{13}$
Formula weight	658.71	660.32	665.61	647.74	670.86	673.29
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a/Å	9.361(9)	8.789(9)	8.767(9)	8.777(9)	8.780(9)	8.763(9)
b/Å	9.454(9)	11.256(13)	11.205(13)	11.223(3)	11.219(13)	11.195(13)
c/Å	13.611(12)	23.39(3)	23.29(3)	23.34(3)	23.33(3)	23.234(27)
α/°	79.72(1)	(90)	(90)	(90)	90	90
β/°	81.84(1)	90.00(1)	90.46(1)	90.00(1)	90.31(1)	90.14(1)
γ/°	74.11(1)	(90)	(90)	(90)	90	90
Volume/Å^3	1134	2314	2288	2299	2298	2279
Z, Calculated density/Mg m^{-3}	2, 1.931	4, 1.895	4, 1.932	4, 1.928	4, 1.939	4, 1.962
Absorption coefficient/mm^{-1}	2.674	2.793	2.982	3.160	3.335	3.555
Reflections collected	3355	3650	6376	7614	5336	5417
Unique reflections/R(int)	3355	2901/0.0252	3710/0.0318	4019/0.0234	3257/0.0377	3097/0.0275
Data/restraints/parameters	3355/0/325	2901/0/326	3710/0/326	2645/0/326	3257/0/327	3097/0/327
Final R indices [$I > 2\sigma(I)$] R1	0.0591	0.0444	0.0601	0.0469	0.0518	0.0563
wR2	0.1669	0.1280	0.1937	0.1798	0.0757	0.1765
R indices (all data) R1	0.0631	0.0586	0.0902	0.0566	0.1483	0.0769
wR2	0.1724	0.1424	0.2326	0.1926	0.1624	0.1957

Code	4-Er	4-Tm	4-Yb	4-Lu	5-Yb	5-Y	6-Sc
Empirical formula	$C_{13}H_{18}ErN_9O_{13}$	$C_{13}H_{18}TmN_9O_{13}$	$C_{13}H_{18}YbN_9O_{13}$	$C_{13}H_{18}LuN_9O_{13}$	$C_{17}H_{18}N_{11}O_{10}Yb$	$C_{17}H_{18}N_{11}O_{10}Y$	$C_{15}H_{16}N_9O_{10}Sc$
Formula weight	675.62	677.29	681.40	683.33	709.46	625.34	527.33
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$	Triclinic, $P\bar{1}$
a/Å	8.759(9)	8.745(9)	8.745(9)	8.733(9)	9.034(9)	9.047(9)	8.891(11)
b/Å	11.176(13)	11.172(13)	11.183(13)	11.162(13)	11.667(14)	11.668(12)	10.784(12)
c/Å	23.25(3)	23.22(3)	23.233(27)	23.191(27)	13.156(18)	13.209(12)	11.785(14)
α/°	90	90	90	90	107.50(1)	107.48(1)	100.66(1)
β/°	90.49(1)	90.62(1)	91.01(1)	90.73(1)	103.28(1)	103.47(1)	92.60(1)
γ/°	90	90	90	90	90.96(1)	90.45(1)	93.97(1)
Volume/Å^3	2276	2268	2272	2260	1282	1289	1106
Z, Calculated density/Mg m^{-3}	4, 1.972	4, 1.983	4, 1.992	4, 2.008	2, 1.838	2, 1.611	2, 1.584
Absorption coefficient/mm^{-1}	3.772	3.948	4.201	4.452	3.721	2.348	0.406
Reflections collected	6884	5533	4584	7271	4353	4225	3944
Unique reflections/R(int)	3968/0.040	3129/0.050	2658/0.090	3996/0.029	4353	4225	3944
Data/restraints/parameters	3968/0/327	3129/0/326	2658/0/326	3996/0/326	4353/0/355	4225/0/355	3944/0/318
Final R indices [$I > 2\sigma(I)$] R1	0.0738	0.0650	0.0517	0.0621	0.0613	0.0849	0.0585
wR2	0.2147	0.1836	0.1326	0.1125	0.1531	0.1134	0.1399
R indices (all data) R1	0.1140	0.1178	0.1079	0.0900	0.0967	0.2310	0.0883
wR2	0.2457	0.2156	0.1515	0.1209	0.1691	0.2574	0.1523

to a single tridentate L^4 ligand, three bidentate nitrates and two water molecules. This coordination number is often found for lanthanum but very rarely for the later and smaller metals in the series and so it is not surprising that this structure type is unique to La. It is noteworthy that in this structure the terdentate L^4 ligand shows signs of steric strain in complexing to the metal. In many of the lower coordinate structures, *e.g.* type 4, the three rings of the ligand are coplanar and the metal atom is within 0.05 Å of the composite plane. However, in 1-La, the angles between adjacent planes are 9.7(1) and 13.1(1)° and the metal is 1.09 Å from the plane of the 18 atoms in the chelating L^4 ligand.

Table 3 Hydrogen bonds (Å) in the crystal structure of 1-La

N(27)···O(64)#1	2.943(6)
N(27)···O(54)#2	2.977(7)
O(100)···O(42)#3	2.872(6)
O(100)···O(44)#1	2.921(6)
O(200)···O(64)#4	2.923(9)

#1 1 + *x*, −*y*, *z*; #2 *x* − 1, *y*, *z* + 1; #3 −*x*, 1 − *y*, −*z*; #4 *x* − 1, *y*, *z*.

Table 4 Hydrogen bonds (Å) in the crystal structures of 2-M

	2-La	2-Pr	2-Sm
N(27)···O(61)#1	3.098(8)	3.093(9)	3.092(6)
N(27)···O(44)#3	3.271(10)	3.221(12)	3.223(8)
O(100)···O(51)#2	2.811(7)	2.818(7)	2.812(5)
O(100)···O(54)#2	3.183(9)	3.169(9)	3.175(6)
N(100)···O(100)	2.818(8)	2.822(10)	2.816(7)

#1 *x*, 1 + *y*, *z*; #2 −*x*, −*y*, −*z*; #3 1 − *x*, 1 − *y*, −*z*.

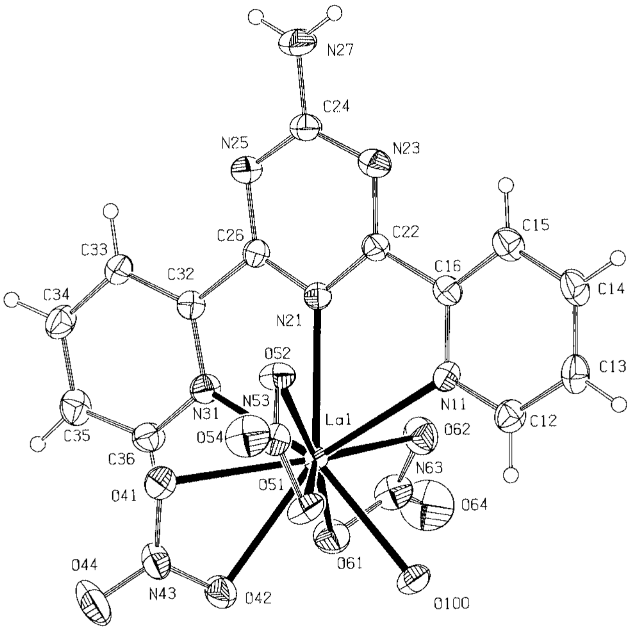

Fig. 3 Structure type 2. The structure of 2-La with the atomic numbering scheme. Ellipsoids at 30% probability. 2-Pr and 2-Sm are isostructural.

By contrast 2-La (Fig. 3) $[ML^4(NO_3)_3(H_2O)]$ has one coordinated water less than 1-La and as a consequence is only 10-coordinate. The deviation from planarity is reduced to 0.54 Å, and the ligand becomes almost planar (rms of atoms in the plane 0.05 Å). So it would seem that the deviation in the 11-coordinate 1-La structure, is partly due to the metal being too big for the cavity and also due to the higher coordination number which leads to steric crowding. However, in the 10-coordinate 2-La, the deviation is due to the metal being too big for the cavity and not steric crowding. In 1-La the two N–H bonds of the N(27) amine group are hydrogen bonded to two adjacent molecules through the nitrate oxygen atoms O(54) and O(64) ‡ that are not themselves, bonded to the metal atoms.

In addition, there are hydrogen bonds between the water molecules, which are bonded to the metal and adjacent coordinated nitrate groups. All hydrogen bonds are listed in Tables 3–9. It is noteworthy that in 1-La each metal complex forms hydrogen bonds with 8 surrounding molecules. The pyridyl nitrogen–metal bond lengths in 2-La are as expected significantly shorter than those in 1-La. One of the features of structures with these types of terdentate ligands[19] is the prevalence of oxygen atoms adjacent to the ligands in the ML^4 plane and this has been interpreted as indicating stabilizing aromatic CH···O hydrogen bonds. This is noticeable in both 1-La and 2-La structures with H···O distances of 2.59 Å (H(36)···O(100) see Fig. 3) and 2.52 Å respectively (H(12)···O(100) see Fig. 4). The metal bond dimensions in the isostructural 2-La, 2-Pr, 2-Sm and in 2-Nd show variations consistent with the differences in metal size (*e.g.* La–Nd > Pr–Sm). In these structures the amine group N(27) is hydrogen bonded to two oxygen atoms of the nitrate groups in adjacent molecules, one of which O(61) is a metal-bonded oxygen and the other O(44) is a free nitrate oxygen atom. In addition the coordinated water molecule O(100) is hydrogen bonded to a metal bound oxygen O(51), a free nitrate oxygen O(54) and N(100) from the solvent acetonitrile. By contrast in 2-Nd N(27) is bonded to a metal bonded nitrate oxygen O(62) and a solvent acetonitrile nitrogen N(300), while the coordinated water molecule O(100) is hydrogen bonded to O(44) and the other solvent acetonitrile nitrogen N(400). In the series 2-La, 2-Pr, 2-Nd, 2-Sm, the deviations of the metal atoms from the ligand planes are greater for the first two 0.56, 0.38 Å than for the second 0.02, 0.38 Å. The discontinuity at 2-Nd compared to the

Table 5 Hydrogen bonds (Å) in the crystal structure of 2-Nd

N(27)···O(62)#1	3.051(6)
N(27)···N(300)#2	3.131(6)
O(100)···O(44)#3	2.815(6)
O(100)···N(400)	2.875(6)

#1 −*x*, −1 − *y*, 1 − *z*; #2 −*x*, 1 − *y*, −*z*; #3 −*x*, −*y*, −*z*.

Table 6 Hydrogen bonds (Å) in the crystal structures of 3-M

	3-Nd	3-Sm
N(27)···O(51)#1	2.997(9)	2.995(12)
N(27)···O(41)#2	3.057(9)	3.081(12)
O(100)···O(61)#5	2.869(8)	2.875(14)
O(200)···O(62)#3	2.726(8)	2.716(10)
O(300)···O(400)#4	2.777(9)	2.787(11)
O(300)···O(400)	2.839(9)	2.831(10)
O(400)···O(54)#5	2.797(8)	2.790(12)
O(400)···O(61)#6	2.868(14)	2.865(17)

#1 −*x*, 1 − *y*, 1 − *z*; #2 −*x*, −*y*, 1 − *z*; #3 −*x*, −*y*, − *z*; #4 1 − *x*, −*y*, −*z*.

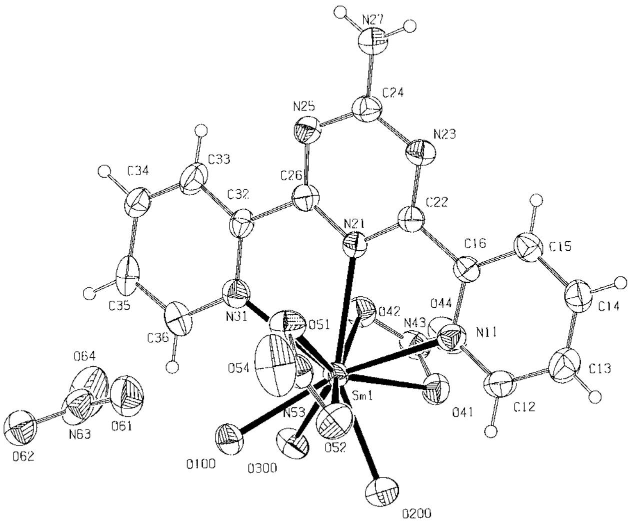

Fig. 4 Structure type 3. The structure of 3-Sm with the atomic numbering scheme. Ellipsoids at 30% probability. 3-Nd is isostructural.

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‡ In our numbering scheme nitrate oxygen atoms are numbered O(*nm*), where *n* = 4,5,6 and *m* = 1,2 for coordinated oxygen atoms and 4 for non-coordinated oxygen atoms.

Table 7 Hydrogen bonds (Å) in the crystal structures of 4-M

	4-Eu	4-Gd	4-Tb	4-Ho	4-Er	4-Tm	4-Yb	4-Lu
O(100) · · · O(61)#6	2.81(1)	2.81(1)	2.79(2)	2.88(2)	2.82(1)	2.78(2)	2.80(1)	2.81(1)
O(100) · · · O(502)	2.64(2)	2.65(1)	2.66(1)	2.66(2)	2.66(2)	2.68(2)	2.60(2)	2.66(1)
O(100) · · · O(64)#6	3.16(2)	3.17(1)	3.15(2)	3.18(2)	3.14(2)	3.16(2)	3.27(2)	3.08(2)
O(200) · · · O(64)#2	2.76(1)	2.76(1)	2.78(1)	2.78(1)	2.77(2)	2.77(2)	2.78(1)	2.80(1)
O(200) · · · O(503)#4	2.67(1)	2.69(1)	2.66(1)	2.70(1)	2.69(2)	2.73(2)	2.66(1)	2.66(1)
O(41) · · · O(503)	2.90(1)	2.90(1)	2.90(1)	2.90(1)	2.91(2)	2.89(2)	2.84(1)	2.90(1)
O(44) · · · O(502)#3	3.00(1)	2.99(1)	2.99(1)	3.04(2)	3.00(2)	3.04(2)	3.04(1)	3.02(1)
O(54) · · · O(502)#4	3.16(1)	3.13(1)	3.16(1)	3.10(2)	3.15(2)	3.14(2)	3.14(1)	3.20(1)
N(27) · · · O(502)#1	3.09(3)	3.15(2)	3.14(3)	3.27(3)	3.16(3)	3.15(3)	3.17(3)	3.11(3)
N(27) · · · O(503)#7	3.16(2)	3.17(2)	3.11(2)	3.09(2)	3.13(2)	3.13(2)	3.15(2)	3.21(2)
O(61) · · · O(503)#7	2.98(2)	3.01(2)	3.06(2)	2.99(2)	3.00(2)	3.02(2)	3.13(2)	3.05(2)
O(62) · · · O(503)#7	3.06(2)	3.03(2)	3.07(2)	3.06(2)	3.03(3)	3.08(2)	3.13(2)	3.16(2)
O(502) · · · O(52)#3	2.92(1)	2.93(1)	2.94(1)	2.92(1)	2.96(2)	2.91(1)	2.89(1)	3.00(1)

#1 $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; #2 $-x + 1, -y + 2, -z + 1$; #3 $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; #4 $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; #6 $x + \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$; #7 $-x + 2, -y + 2, -z + 1$.

Table 8 Hydrogen bonds (Å) in the crystal structures of 5-M

	5-Yb	5-Y
O(64) · · · O(100)#1	2.74(1)	2.71(1)
O(100) · · · N(400)	2.73(1)	2.76(1)
N(27) · · · N(300)#2	3.03(1)	3.06(1)
N(27) · · · O(52)#3	3.17(1)	3.17(1)

#1 $1 - x, 1 - y, 1 - z$; #2 $x, y, z - 1$; #3 $-x, -y, -z$.

Table 9 Hydrogen bonds in the crystal structure of 6-Sc

N(27) · · · O(100)#7	2.92(1)
N(27) · · · O(42)#4	3.13(1)
O(100) · · · O(52)#5	3.06(1)

#4 $x, y - 1, z$; #5 $2 - x, 2 - y, 2 - z$; #7 $x - 1, y - 1, z$.

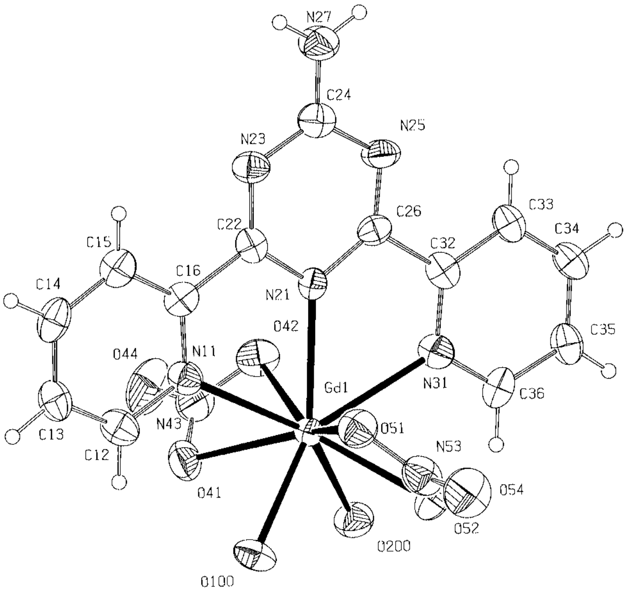

Fig. 5 Structure type 4. The structure of 4-Gd with the atomic numbering scheme. Ellipsoids at 30% probability. Structures containing Eu, Tb, Dy, Ho, Er, Tm, Yb and Lu are isostructural.

other structures may be due to the fact that 2-Nd is the only non-isomorphous compound and has a different packing arrangement.

Structure type 3, $[ML^4(NO_3)_2(H_2O)_3]NO_3{\cdot}H_2O$ is also 10-coordinate like type 2 but two additional water molecules occupy the coordination sphere instead of one nitrate anion which was located unbound in the asymmetric unit. The three water molecules are mutually *cis* with all O–M–O angles less than 80° (Fig. 4 for M = Sm) with one of the oxygen atoms in the plane of the ML^4 moiety thus allowing the formation of the C–H · · · O stabilizing hydrogen bond. In the isostructural 3-Nd and 3-Sm, the bond lengths, for the most part, are slightly greater in the former structure reflecting the difference in ionic radii. However, in both structures there is a tendency for one nitrate to become unidentate and the M(1)–O(52) bond length is 0.12 Å in 3-Nd and 0.26 Å in 3-Sm longer than the bond to O(51). It is likely that this distortion from a bidentate nitrate is introduced by steric crowding, the two unidentate water molecules taking up more room than the compact bidentate nitrate ion in structure type 2. Not surprisingly this effect is greater for the smaller Sm ion.

In this structure type there is extensive hydrogen bonding from the water molecules in the coordination sphere (Tables 3–9), while N(27) is hydrogen bonded to two metal-bonded nitrate oxygen atoms O(41) and O(51) from different cations. In structure types 1, 2 and 3, it is found that the bonds from the metal atom to the two outer nitrogen atoms N_o N(11) and N(31) in the terdentate ligand are significantly longer than those to the central nitrogen atom N_c N(21). We have analysed L^1 structures in the Cambridge Structural Database[28] as implemented at the Daresbury Laboratory[29] and have found an approximately linear relationship between M–N and the difference in bond length {(M–N_c)–(M–N_o)} such that when the M–N_c distances are greater than 2.58 Å, M–N_c < M–N_o, and for distances less than 2.58 Å, M–N_o > M–N_c. This is consistent with the results reported here for L^4 with the larger lanthanides, though the value at which the bond lengths are equivalent may be slightly lower.

This formulation $[ML(NO_3)_2(H_2O)_3](NO_3)$ was also observed for a series of L^1 complexes[19] and the geometry of the coordination spheres was very similar to that found in this structure type 3 with the three water molecules mutually *cis*.

Structure type 4, by contrast with structure type 3 is $[ML^4(NO_3)_2(H_2O)_2]NO_3{\cdot}2H_2O$ in which the cation (Fig. 5 for M = Gd) contains one less water molecule so that the metal atoms are nine-coordinate being bonded to L^4, two bidentate nitrate anions and two water molecules. The two water molecules in the coordination sphere are alternatively slightly above and below the ML^4 plane such that the C–H · · · O interactions are found H(12) · · · O(100) 2.54, H(36) · · · O(200) 2.60 Å (see Fig. 5). In addition to the unbonded nitrate anion, there are two water molecules in the asymmetric unit. The variations in dimensions in the 9 structures can be related to the known decrease in the ionic radii. The two uncoordinated water molecules in the asymmetric unit O(502) and O(503) form hydrogen bonds to the two hydrogen atoms of the -NH_2 group. In 4-Eu these distances are N(27) · · · O(502) 3.09(3) and N(27) · · · O(503) 3.16(2) Å. In addition, these water molecules form stronger hydrogen bonds to the two water molecules bonded

Table 10 Dimensions in the metal coordination spheres. Bond lengths (Å) and angles (°) for structure type 1

	1-La
La(1)–O(100)	2.589(4)
La(1)–O(200)	2.610(4)
La(1)–O(61)	2.628(4)
La(1)–O(21)	2.637(4)
La(1)–O(42)	2.659(5)
La(1)–O(51)	2.672(5)
La(1)–O(52)	2.646(5)
La(1)–O(62)	2.702(5)
La(1)–N(31)	2.739(4)
La(1)–N(11)	2.755(5)
La(1)–O(41)	2.805(6)

Table 11 Bond lengths (Å) and angles (°) for structure type 2: 2-La, 2-Pr, 2-Sm and 2-Nd

	La	Pr	Sm	Nd
M(1)–O(100)	2.483(5)	2.439(5)	2.440(4)	2.470(4)
M(1)–O(62)	2.525(5)	2.475(6)	2.476(4)	2.597(4)
M(1)–O(42)	2.573(5)	2.519(6)	2.525(4)	2.546(4)
M(1)–O(61)	2.573(5)	2.523(5)	2.547(4)	2.566(4)
M(1)–N(21)	2.576(5)	2.541(5)	2.523(4)	2.552(4)
M(1)–O(51)	2.607(5)	2.554(5)	2.558(3)	2.548(4)
M(1)–O(41)	2.620(5)	2.580(6)	2.594(4)	2.592(4)
M(1)–O(52)	2.620(5)	2.593(6)	2.592(4)	2.557(4)
M(1)–N(31)	2.625(5)	2.597(5)	2.578(4)	2.618(5)
M(1)–N(11)	2.641(5)	2.600(6)	2.602(4)	2.645(4)

Table 12 Bond lengths (Å) and angles (°) for structure type 3: 3-Nd, 3-Sm

	M = Nd	M = Sm
M(1)–O(200)	2.464(5)	2.417(6)
M(1)–O(300)	2.488(5)	2.464(7)
M(1)–O(100)	2.504(5)	2.465(6)
M(1)–N(21)	2.575(5)	2.542(7)
M(1)–O(41)	2.588(6)	2.547(7)
M(1)–O(42)	2.602(5)	2.569(7)
M(1)–N(31)	2.605(5)	2.561(7)
M(1)–O(51)	2.608(5)	2.591(7)
M(1)–N(11)	2.630(6)	2.590(8)
M(1)–O(52)	2.728(7)	2.849(14)

to the metal. In 4-Eu these distances are (Table 7) O(100)···O(502) 2.64(2), and O(200)···O(503) 2.67(1) Å. In addition O(502) forms hydrogen bonds to the two bonded nitrates {O(502)···O(52) 2.92(1) Å, O(502)···O(44) 3.00(1) Å} and O(503) to the unbonded nitrate {O(503)···O(61) 2.98(2), O(503)···O(62) 3.06(2) Å}. While these distances are not exactly the same in all the other isomorphous structures, values are comparable and within 0.05 Å of these values (Table 7). The range in bond lengths covers *ca.* 0.10 Å from 4-Eu to 4-Lu with the other structures containing intermediate values. In all the structures the two shortest bonds from the metal are to the water molecules, then follow the four bonds to the nitrate and the three bonds to L^4. In the structures of some of the smaller ions, *e.g.* 4-Yb, 4-Lu there is some indication of steric strain in the coordination sphere as there is a significant difference between the metal to nitrate oxygen bond lengths. However, in all the structures it is found that the metal fits well into the planar terdentate ligand and the distance of the metal from the least squares plane of the 18 atoms in the ligand is less than 0.05 Å in all cases.

The hydrogen bonds in these structures are shown in Tables 3–9. The amino group N(27) forms hydrogen bonds to two uncoordinated water molecules while there is an extensive hydrogen bond pattern involving interactions between all water molecules and the nitrates. It is interesting that the M–N_c distances are shorter than the M–N_o distances in all these compounds despite the M–N_c distances being as low as 2.42 Å. This result contrasts with that found in the CSD from the structures of L^1 where for these relatively short M–N_c distances, M–N_o < M–N_c and must be due to the increased strength of the bond to the central nitrogen atom when N is contained within a triazine ring compared to a pyridine ring. Thus in $[ML^1(NO_3)_3(H_2O)]$, for M = Ho, M–N_o are 2.503(11), 2.510(9) and M–N_c 2.545(8) Å and for M = Tm 2.494(19), 2.475(16) and 2.463(17) Å while in $[YbL^1(NO_3)_3]$, M–N_o are 2.417(7), 2.419(8) and M–N_c 2.395(8) Å. So in every case with L^1, M–N_o < M–N_c while as is apparent from Tables 10–14, the reverse is true for L^4. This formulation $[ML(NO_3)_2(H_2O)_2](NO_3)$ was also observed for a series of L^1 complexes[19] and the geometry of the coordination spheres was very similar to that found in this structure type 4. Structure type 5, $[ML^4(NO_3)_3(H_2O)]$, 2MeCN, is only found for Yb (Fig. 6) and Y and one of the nitrate anions is unidentate so that the metal atoms are 9-coordinate. Unidentate coordination of a nitrate to the metal is relatively rare although it was found quite frequently in the recent studies of terpyridine structures.[5,19] As is often found, the bond from the metal to the oxygen of the unidentate nitrate M–O(61) is significantly shorter than the other nitrate bonds and indeed is shorter than the bond to the water molecule M–O(100) for both structures (2.275(8) *vs.* 2.326(8) Å for Yb and 2.281(7) *vs.* 2.352(7) Å for Y). The difference between M–N_o and M–N_c bond lengths is approximately 0.09 Å in the two structures with M–N_o the shorter, again showing a major difference from the structures of L^1 and L^3 where M–N_c is the longer. In this structure type the amino group is hydrogen bonded to a coordinated nitrate oxygen O(52) and an acetonitrile nitrogen atom N(300). For comparison we also carried out a structure determination on a scandium complex 6-Sc, $ScL^4(NO_3)_3$ (Fig. 7).

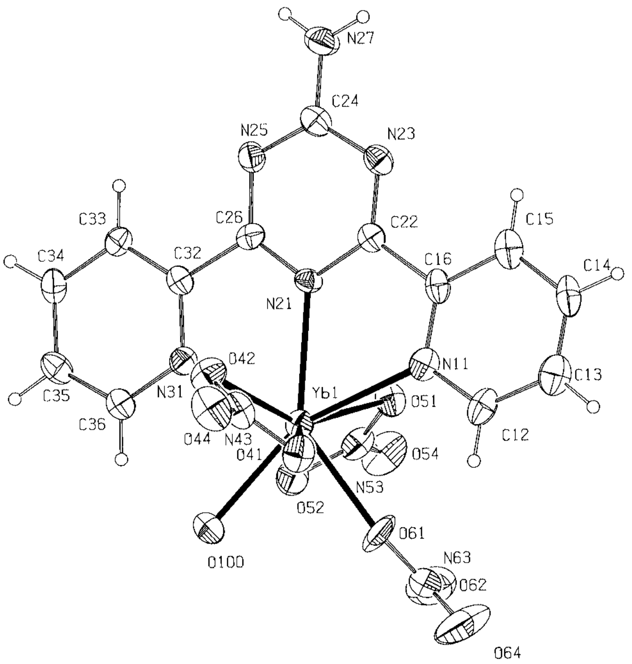

Fig. 6 Structure type 5. The structure of 5-Yb with the atomic numbering scheme. Ellipsoids at 30% probability. 5-Y is isostructural.

Here the metal atom is 8-coordinate being bonded to the terdentate ligand and three nitrates, with one unidentate or perhaps more precisely intermediate between bidentate and unidentate as the bond length is 2.617(4) Å. As to be expected the Sc–N and Sc–O bond lengths are much shorter than in the lanthanide structures with the former at 2.349(3), 2.242(3), 2.392(3) Å and the latter ranging from 2.213(3)–2.304(3) Å.

Table 13 Bond lengths (Å) and angles (°) for structure type 4: 4-Eu, 4-Gd, 4-Tb, 4-Ho, 4-Er, 4-Tm, 4-Yb, 4-Lu

	4-Eu	4-Gd	4-Tb	4-Ho	4-Er	4-Tm	4-Yb	4-Lu
M(1)–O(100)	2.378(8)	2.326(8)	2.354(11)	2.280(11)	2.298(11)	2.292(10)	2.286(10)	2.286(7)
M(1)–O(200)	2.363(7)	2.328(9)	2.336(8)	2.324(8)	2.331(12)	2.306(9)	2.338(10)	2.298(8)
M(1)–O(51)	2.478(7)	2.438(8)	2.432(7)	2.444(11)	2.392(12)	2.392(12)	2.398(11)	2.373(8)
M(1)–O(42)	2.480(7)	2.433(8)	2.463(7)	2.427(11)	2.420(11)	2.418(13)	2.362(11)	2.385(9)
M(1)–O(52)	2.517(7)	2.480(8)	2.492(7)	2.486(11)	2.457(13)	2.460(12)	2.538(13)	2.420(9)
M(1)–O(41)	2.506(7)	2.486(9)	2.475(7)	2.471(12)	2.453(12)	2.495(15)	2.466(12)	2.478(8)
M(1)–N(11)	2.580(7)	2.541(8)	2.575(7)	2.561(11)	2.519(13)	2.512(14)	2.522(12)	2.530(10)
M(1)–N(21)	2.532(7)	2.460(9)	2.515(9)	2.463(9)	2.460(13)	2.434(11)	2.423(10)	2.435(8)
M(1)–N(31)	2.590(7)	2.549(9)	2.569(9)	2.499(12)	2.553(16)	2.539(15)	2.484(11)	2.493(10)

Table 14 Bond lengths (Å) and angles (°) for structure types 5 and 6: 5-Yb, 5-Y, 6-Sc

	Yb	Y	Sc
M(1)–O(100)	2.326(8)	2.352(7)	—
M(1)–O(61)	2.275(8)	2.281(7)	2.213(3)
M(1)–O(42)	2.413(8)	2.427(6)	2.259(4)
M(1)–O(51)	2.414(8)	2.441(7)	2.283(3)
M(1)–O(41)	2.420(8)	2.452(7)	2.222(3)
M(1)–O(52)	2.470(9)	2.473(6)	2.304(3)
M(1)–N(11)	2.517(10)	2.552(7)	2.392(3)
M(1)–N(21)	2.425(8)	2.452(6)	2.242(3)
M(1)–N(31)	2.506(9)	2.539(7)	2.349(3)

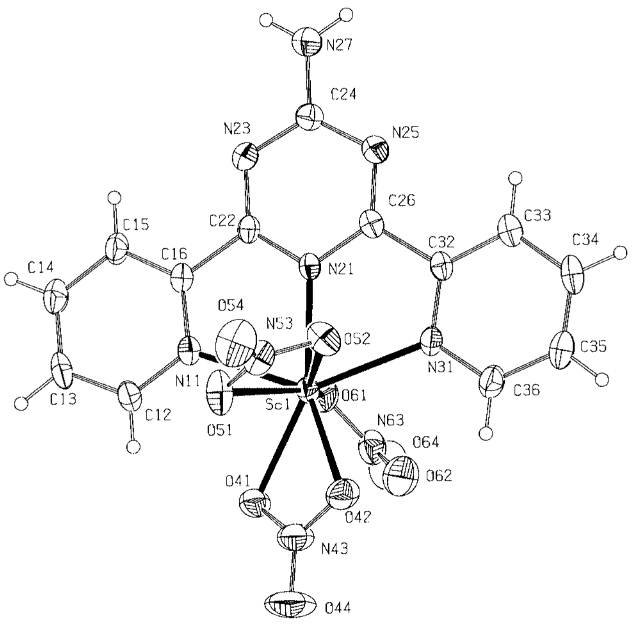

Fig. 7 Structure type 6. The structure of 6-Sc with the atomic numbering scheme. Ellipsoids at 30% probability.

The Sc atom is 0.29 Å from the plane of the tridentate ligand showing that the metal is too small to fit neatly into the ligand cavity. The structure of $ScL^4(NO_3)_3$ is similar to the previously published structure of $ScL^1(NO_3)_3$ except that in the latter, the longest Sc–O bond length is 2.482 Å and the Sc was described as being 9-coordinate.[30]

The exact geometry of all these complexes is irregular and does not conform to any of the ideal geometries that can be found for the higher coordination complexes.[31,32] This is unsurprising not only because of the different types of ligand, L^4, nitrate and water with different stereochemical requirements but also because the presence of stabilising aromatic C–H · · · O hydrogen bonds between the L^4 and nitrate and/or water molecules leads to an equatorial plane of five atoms (the three donor nitrogen atoms in L^4 and the two hydrogen bonded oxygen atoms) with the remaining atoms in the coordination sphere above and below this plane.

Structural comparisons

One of the major problems in studying the extraction and separation properties of the terdentate nitrogen ligands (or indeed any ligands) is to establish the extracting species. This solid state survey has shown that a significant range of stoichiometries are possible though for any particular lanthanide the maximum different number of complexes found was only 2. Of course this number might be greater in solution where extraction occurs and it can be debated whether the complexes found in the solid state are also prevalent in solution.

It will be noted that we used acetonitrile for crystallisation of all the crystals whose structures are reported here. It can be argued that the use of this solvent may lead to compounds that are not formed during the solvent extraction process where acetonitrile is not used. However, none of the compounds reported here shows acetonitrile in the primary coordination sphere and therefore we are confident that the compounds are representative of those found in the solvent extraction process. However, we have noted previously in our terpyridine studies[5] that use of acetonitrile rather than water as a crystallising medium can favour inclusion of nitrate over water molecules in the coordination sphere. Acetonitrile is located in the lattice, primarily as a source of acceptor hydrogen bonds for the free amine in L^4. It is necessary to include a synergist such as 2-bromodecanoic acid to obtain useful extraction with L^4 but its exact role is unclear though it seems unlikely to participate in binding to the metal.

In order to compare the structures of lanthanide complexes in solution with those in the solid state, the EXAFS technique is particularly valuable although clearly difficult to apply to high coordinate complexes. However from our EXAFS studies of lanthanide complexes[33] we have shown that while it is not always possible to interpret spectra in terms of the exact arrangement of donor atoms, it is possible to obtain coordination numbers and range of metal–ligand distances. Indeed in our recent study we have clearly identified the presence of observed monodentate nitrate ligands. It is also possible to compare the EXAFS from both solid and solution samples and in this previous work we have found little discernible difference between the radial distribution factors obtained in solution and in the solid state[33] and we conclude that crystal structures can be used as good indications of the species present in solution.

The structures obtained across the lanthanide series for L^4 described here can be compared to the patterns obtained for L^1 and L^3 in previous work and this is done in Table 15. In all these studies the nitrate anion was used because the nuclear waste that we are investigating has a high nitric acid content and the extraction process occurs in such a solution. We first consider the common structural features of these complexes and relate them to the differences between the lanthanides, and second consider the differences between the structures found for the different ligands and relate these to the extraction and separation properties of the ligands.

First it is clear that for all the ligands there is a range of different structures which can be related to the size of the individual ions. Lanthanum often has a unique structure compared

Table 15 Crystal structures of the 1 : 1 LnL complexes with nitrates

Lanthanide	L^1	L^3	L^4	Coordination number
Reference	5, 19, 20	4	This work	
La	[c]		[a,b]	11,10
Ce				
Pr			[b]	10
Nd	[b]	[b]	[b,c]	10
(Pm)				
Sm		[b]	[b,c]	10
Eu	[c]		[f]	9,10
Gd	[c]		[f]	9,10
Tb	[f]	[b]	[f]	9,10
Dy		[d]	[f]	9
Ho	[d]		[f]	9
Er	[d]	[e]	[f]	9
Tm	[d]		[f]	9
Yb	[e,f]	[e]	[d]	9
Lu	[f]		[d]	9

[a] $[ML(NO_3)_3(H_2O)_2]$, 11-coordinate. [b] $[ML(NO_3)_3(H_2O)]$, 10-coordinate. [c] $[ML(NO_3)_2(H_2O)_3]^+$, 10-coordinate. [d] $[ML(NO_3)_3(H_2O)]$, 9-coordinate, unidentate nitrate. [e] $[ML(NO_3)_3]$, 9-coordinate. [f] $[ML(NO_3)_2(H_2O)_2]^+$, 9-coordinate.

to the other lanthanides and has coordination numbers of 10 or 11. Of course 12-coordination can be found for La *e.g.* in $[La(NO_3)_6]^{3-}$ but not in structures containing a terdentate ligand. The early lanthanides Pr–Sm have coordination numbers of 10 which is achieved either *via* $[ML(NO_3)_3(H_2O)]$ or with $[ML(NO_3)_2(H_2O)]^+$. Middle lanthanides Eu–Tb can have coordination numbers of 9 and 10 and show the greatest variety of complex. Thus for these elements 10-coordinate $[ML(NO_3)_3(H_2O)]$ and $[ML(NO_3)_2(H_2O)_3]^+$ are known but 9-coordination can be achieved by one of the nitrates becoming unidentate in the former as well as by losing a water molecule in the latter. The smaller lanthanides are predominantly 9-coordinate with formulations $[ML(NO_3)_3(H_2O)]$ (with a unidentate nitrate), $[ML(NO_3)_2(H_2O)_2]^+$ and $[ML(NO_3)_3]$. It is particularly relevant that structural analyses of lanthanide nitrates with L^1 have been carried out by two different groups[5,19] and one group obtained $[ML(NO_3)_2(H_2O)_2]^+$ and the other $[ML(NO_3)_3(H_2O]$ despite similar preparations.

Clearly it is possible to extrapolate from the results presented in Table 15 to the likely structures of uncharacterised complexes. We can conclude that each metal is known to achieve its preferred coordination number in two or three different ways with nitrates bidentate, unidentate or purely ionic and it can be imagined that, in solution, different stoichiometries can coexist owing to the facile replacement of NO_3^- and $2H_2O$. The metal containing complexing species is most likely to be neutral although cations can occur with less than three nitrates attached. NMR studies on solutions of lanthanides with L^1 have shown the existence of several different species.[34]

We now consider the differences in these structural patterns with ligand type. The most striking fact is that all complexes of L^3 and L^4 contain metal : ligand ratios of 1 : 1 as indeed do many complexes of L^1. But for L^1 ratios of 1 : 2§ and for L^5 ratios of 1 : 2 and 1 : 3 are well established though for clarity we have not included them in Table 15.

In our work with L^1 we found that the ratio obtained depended on the ratio of starting material. Thus with metal nitrate ligand ratios of 1 : 1, complexes of 1 : 1 stoichiometry were obtained, while with ratios of 1 : 4, complexes of 1 : 2 could be prepared for the larger lanthanides. By contrast with the smaller lanthanides a starting 1 : 4 ratio led to a 1 : 1 complex but with an extra L^1 molecule in the crystal lattice.[5] On the other hand with L^5 the $[Ln(L^5)_3]^{3+}$ cation was the predominant species found independent of the ratio of starting material particularly with the smaller lanthanides and this presumably accounts for this ligand's remarkable separation properties.

We did not obtain any solid state complexes of L^3 or L^4 with Ln : L ratios other than 1 : 1. Attempts were made to increase the amount of L^4 used, but the ligand was so insoluble that it would not fully dissolve and the maximum usable ratio was 1 : 2 which resulted in the 1 : 1 complex being formed. Even so, a contributing factor to the lack of formation of 1 : 2 complexes might be the fact that L^3 and L^4 contain NH and NH_2 groups respectively that can form intermolecular hydrogen bonds to acceptor groups available in solvent molecules or in symmetry related complexes, while L^1 and L^5 provide hydrophobic exteriors. It is significant that all structures that contain L^3 contain a strong NH hydrogen bond[4] and all structures (in this work) that contain L^4 contain two strong NH hydrogen bonds. Clearly these hydrogen bonds are likely to be found in solution and will have a significant effect on the extraction properties. With L^1 it is the larger lanthanides that form a 10-coordinate cation with a 1 : 2 ratio but this stoichiometry is not possible for the smaller lanthanides. The reverse is true for the 1 : 3 ratio with L^5 which is only obtained with the smaller lanthanides, as the coordination number of 9 is too small to satisfy the larger metals. The remarkable extraction and separation properties of the L^5 ligand must be connected with its ability to form this $[M(L^5)_3]^{3+}$ species which is not possible for L^1, L^2, L^3 or L^4 in the presence of coordinating anions and is clearly due not only to the different electronic properties of the nitrogen atoms in the L^5 triazine but to the hydrophobic exterior of the ligand.

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