

Separation of americium(III) from europium(III) with tridentate heterocyclic nitrogen ligands and crystallographic studies of complexes formed by 2,2':6',2''-terpyridine with the lanthanides

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Phenyl-substituted derivatives of 2,2':6',2''-terpyridine and a corresponding bipyridine-pyrazine derivative have been shown to have metal extraction properties and separation factors for americium(III) over europium(III) which are comparable to those previously obtained for 2,2':6',2''-terpyridine (L^1). The extracting agents in either *tert*-butylbenzene (TBB) or hydrogenated tetrapropene (TPH) gave D_{Am}/D_{Eu} separation factors (SFs) between 7 and 9 when used to extract the metal ions from 0.01–0.1 M nitric acid solution in synergistic combination with 2-bromodecanoic acid. In contrast to L^1 , the new hydrophobic ligands have little or no solubility in the aqueous phase. In an effort to better understand the nature of the species which may be involved in the extraction process, a series of metal- L^1 complexes which cover the lanthanides have been prepared. Five different structural types have been established for the lanthanide coordination complexes. In type 1, $[M(NO_3)_3(L^1)(H_2O)]$ ($M = Nd$), the metal is 10-coordinate being bonded to one terdentate L^1 ligand, three bidentate nitrates and a water molecule. In type 2, $[M(NO_3)_2(L^1)_2]^+[M(NO_3)_4(L^1)]^-$ ($M = Nd, Sm, Tb, Dy$ and Ho), the metal atom in the cation is 10-coordinate, being bonded to two terdentate L^1 ligands and two bidentate nitrates; in the anion the metal is also 10-coordinate, being bonded to one terdentate L^1 ligand and four nitrates, of which three are bidentate and one unidentate. In type 3, $[M(NO_3)_3(L^1)(H_2O)] \cdot L^1$ ($M = Ho, Er, Tm$ and Yb), the metal is 10-coordinate, being bonded to three bidentate nitrates, one terdentate L^1 and a water molecule. In addition, an L^1 ligand is found in the asymmetric unit which is hydrogen-bonded to the coordinated water molecule. In type 4, $[M(NO_3)_3(L^1)(H_2O)]$ ($M = Tm$), the metal is 9-coordinate, being bonded to two bidentate nitrates, one unidentate nitrate, one terdentate L^1 ligand and a water molecule. In type 5, $[M(NO_3)_3(L^1)]$ ($M = Yb$), the metal is 9-coordinate, being bonded to three bidentate nitrates and one terdentate L^1 ligand. A sixth structural type was observed for $M = La$ in the crystal structure $[(H_2L^1)(NO_3)]^+[(H_2L^1)]^{2+}[La(NO_3)_6]^{3-}$. The metal is not bound to L^1 but instead forms the well-known hexanitrate anion. This complex may give some indication of the type of species which could be formed at higher acid concentrations in the aqueous phase, where protonation of L^1 can occur.

Introduction

One of the aims 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 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.^{2–4} Various aza-aromatic bases have been shown to selectively extract actinides in preference to lanthanides from a nitric acid solution into an organic phase.^{5,6} 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 process and the proposed DIAMEX process.¹ The PUREX process is already used to separate uranium and plutonium from a concentrated nitric acid solution and the DIAMEX process will be used to coextract the trivalent lanthanide and actinide ions prior to their separation.

One of the tested ligands, 2,2':6',2''-terpyridine (L^1) shown in Fig. 1, in synergistic combination with 2-bromodecanoic acid, gave an $Am(III)/Eu(III)$ separation factor of 7 at 0.01 M HNO_3 .⁶ This promising result is tempered by the fact that the ligand has some solubility in the aqueous phase, even in its unprotonated form. In this work, we have used three, more hydrophobic, derivatives of terpyridine which should have little or no solubility in the aqueous phase. Thus, 4'-(4-nitrophenyl)-2,2':6',2''-terpyridine (L^2), 4'-(4-tolyl)-2,2':6',2''-terpyridine (L^3) and 4'-(4-dodecyloxyphenyl)-2,2':6',2''-terpyridine (L^4) have been synthesised and their $Am(III)/Eu(III)$ separation–extraction performance has been determined. A fourth ligand was also tested, 6'-pyrazin-2-yl-4'-(4-heptyloxyphenyl)-2,2'-bipyridinyl (L^5) in which one of the pyridine groups was replaced by pyrazine. All of the synthesised ligands are shown in Fig. 1.

In an effort to determine the nature of the species which may be involved in the extraction process, we have structurally characterised a series of lanthanide complexes formed with L^1 . It proved impossible to obtain crystals of complexes with ligands L^2 to L^5 but it seems likely that complexes with similar stoichiometries and coordination geometries will be found for the ligands L^1 to L^5 inclusive, as the bite angles of these planar

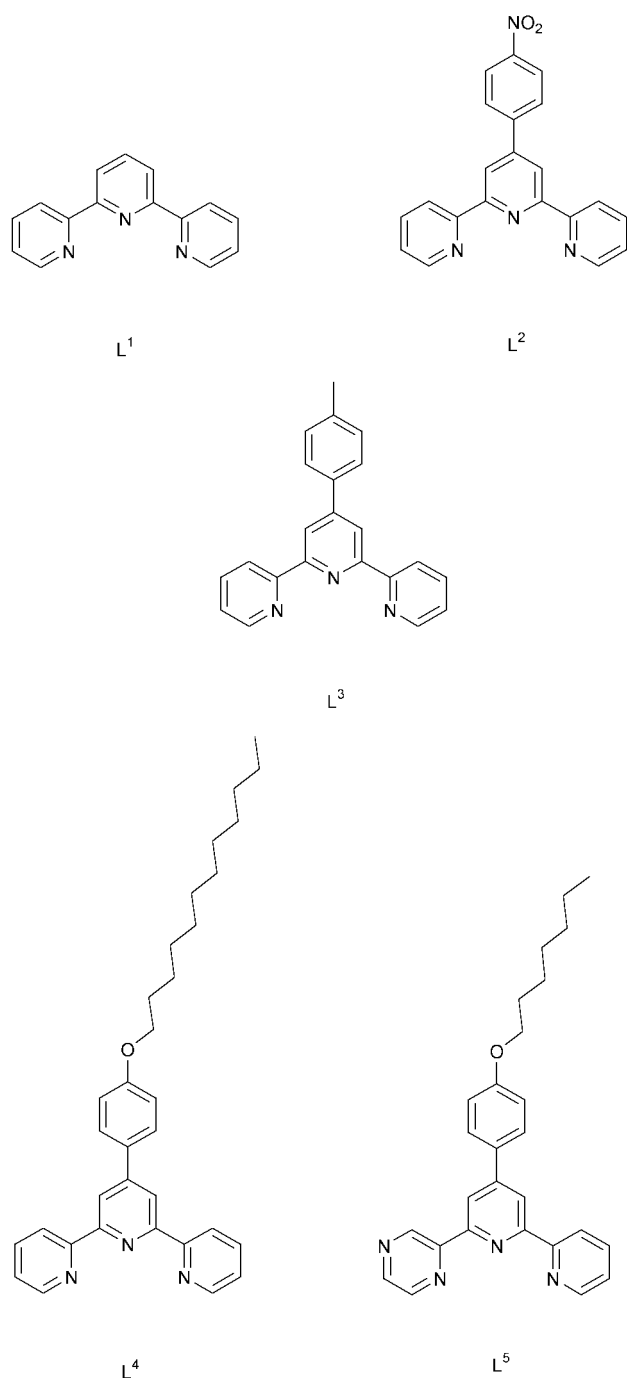


Fig. 1 Structures of the ligands.

terdentate ligands will be equivalent. Our aim is to gain an understanding of the processes involved in the extraction and, hence, to establish the best possible ligands for use in the An–Ln separations.

Experimental

Lanthanum nitrate hexahydrate (99.9%), neodymium nitrate hexahydrate (99.9%), samarium nitrate hexahydrate (99.9%), terbium nitrate pentahydrate (99.9%), dysprosium nitrate pentahydrate (99.9%), holmium nitrate pentahydrate (99.9%), erbium nitrate pentahydrate (99.9%), thulium nitrate pentahydrate (99.9%), ytterbium nitrate pentahydrate (99.9%), 2-acetylpyridine, 2,2':6',2''-terpyridine (all Aldrich), 2-acetylpyrazine, 4-heptyloxybenzaldehyde, 4-dodecyloxybenzaldehyde (Lancaster Synthesis), *tert*-butylbenzene (TBB; Acros), 2-bromodecanoic acid (Fluka) and hydrogenated tetrapropene, an industrial aliphatic diluent with highly branched chains,

(TPH; Prochrom, France) were used as received. Acetonitrile was dried and stored over 3 Å molecular sieves. NMR spectra were run on a JEOL JNM-EX 400 spectrometer. Microanalyses were carried out by Medac Ltd., Brunel Science Centre and mass spectra were run on a VG autospec machine. Uncorrected melting points were obtained on a Stuart melting point apparatus.

Preparation of ligands

4'-(4-Nitrophenyl)-2,2':6',2''-terpyridine (L^2) and 4'-(4-tolyl)-2,2':6',2''-terpyridine (L^3) were prepared according to the literature methods.^{7,8}

4'-(4-Dodecyloxyphenyl)-2,2':6',2''-terpyridine (L^4). A mixture of *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide⁹ (8.29 g, 0.0254 mol), 1-(2-pyridyl)-3-[4-dodecyloxyphenyl]propen-1-one (10 g, 0.0254 mol)¹⁰ and ammonium acetate (19.3 g) in 190 cm³ methanol was heated at reflux for 6 h. After removal of the solvent, the residue was partitioned between CH₂Cl₂ and water. The organic layer was separated and then the aqueous layer was extracted twice more with CH₂Cl₂. The combined organic extracts were then dried with sodium sulfate and the solvent was removed *in vacuo*. The oil was purified by column chromatography on Al₂O₃ with CH₂Cl₂ as eluant. The resulting yellow solid was recrystallised twice from ethanol to give 4.2 g (33%) of L^4 . Mp 85–87 °C. Found: C, 80.36; H, 8.10; N, 8.37. C₃₃H₃₉N₃O requires C, 80.29; H, 7.96; N, 8.51%. ¹H NMR (CDCl₃): δ 0.88 (3H, t), 1.17–1.41 (8H, m), 1.47 (2H, qt), 1.81 (2H, qt), 4.01 (2H, t), 7.00–7.03 (2H, m), 7.32–7.36 (2H, m), 7.84–7.88 (4H, m), 8.65–8.74 (6H, m).

1-(2-pyrazinyl)-3-[4-(heptyloxy)phenyl]propen-1-one. 2-Acetylpyrazine (0.5 g, 0.0041 mol) was added dropwise to a stirred emulsion of 4-heptyloxybenzaldehyde (0.90 g, 0.0041 mol) containing 10 cm³ EtOH and 5 cm³ 1.5 M NaOH. After stirring overnight at room temperature under a nitrogen atmosphere, the yellow solid was filtered and recrystallised from MeOH to give 0.5 g (38%) of pure product. Mp 92–94 °C. Found: C, 73.77; H, 7.36; N, 8.56. C₂₀H₂₃N₂O₂ requires C, 74.28; H, 7.17; N, 8.66%. ¹H NMR (CDCl₃): δ 0.91 (3H, t), 1.25–1.41 (8H, m), 1.81 (2H, qt), 4.07 (2H, t), 6.88–6.98 (2H, m), 7.60–7.73 (2H, m), 7.90–8.10 (2H, m), 8.65–8.80 (2H, m), 9.38 (1H, s).

6'-Pyrazin-2-yl-4'-(4-heptyloxyphenyl)-2,2'-bipyridinyl (L^5). A mixture of *N*-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide (5.03 g, 0.0154 mol), 1-(2-pyrazinyl)-3-[4-(heptyloxy)phenyl]propen-1-one (5 g, 0.0154 mol) and ammonium acetate (12 g) in 120 cm³ methanol was heated at reflux for 6 h. After cooling, a small amount of a light green solid precipitated. This was filtered, washed with water and dried under vacuum (yield 1.1 g, 17%). Mp 119–121 °C. Found: C, 76.33; H, 6.66; N, 13.26. C₂₇H₂₈N₄O requires C, 76.39; H, 6.65; N, 13.26%. ¹H NMR (CDCl₃): δ 0.92 (3H, t), 1.02–1.57 (8H, m), 1.84 (2H, qt), 4.02 (2H, t), 7.00–7.08 (2H, m), 7.33–7.41 (1H, m), 7.80–7.94 (3H, m), 8.60–8.78 (6H, m), 9.89 (1H, m).

Preparation of metal complexes of L^1

The complexes are numbered as *n*-M, where M is the metal and *n* the structure type.

1-Nd. Nd(NO₃)₃·6H₂O (0.0186 g, 0.04 mM) in 1 cm³ of CH₃CN was added dropwise to a stirred solution containing L^1 (0.0099 g, 0.04 mM) dissolved in 1 cm³ CH₃CN. Crystals suitable for structure analysis formed after standing overnight (yield 14 mg, 60%). Found: C, 31.03; H, 2.28; N, 14.61. C₁₅H₁₃N₆O₁₀Nd requires C, 30.98; H, 2.25; N, 14.45%.

2-Nd. Nd(NO₃)₃·6H₂O (0.0186 g, 0.04 mM) in 1 cm³ of CH₃CN was added dropwise to a stirred solution containing L^1

(0.0397 g, 0.17 mM) dissolved in 1 cm³ CH₃CN. Crystals suitable for structure analysis formed almost immediately (yield 6 mg, 11%). Found: C, 39.92; H, 2.46; N, 15.45. C₄₅H₃₃N₁₅O₁₈Nd₂ requires C, 39.73; H, 2.44; N, 15.44%. Thus, the two acetonitrile molecules found in the crystal structures were not present in the analysed sample.

2-Sm. Sm(NO₃)₃·6H₂O (0.0189 g, 0.04 mM) in 7 cm³ of CH₃CN (at approx. 60 °C) was added dropwise to a stirred solution containing L¹ (0.0397 g, 0.17 mM) dissolved in 7 cm³ of CH₃CN at the same temperature. Crystals suitable for X-ray crystallography were obtained after 2 days at room temperature (yield 16 mg, 29%). Found: C, 39.19; H, 2.43; N, 15.39. C₄₅H₃₃N₁₅O₁₈Sm₂ requires C, 39.38; H, 2.42; N, 15.30%.

2-Tb. Tb(NO₃)₃·5H₂O (0.0185 g, 0.04 mM) in 2 cm³ of CH₃CN (at approx. 60 °C) was added dropwise to a stirred solution containing L¹ (0.0397 g, 0.17 mM) dissolved in 2 cm³ of CH₃CN at the same temperature. Crystals formed after standing overnight (yield 19 mg, 32%). Found: C, 38.75; H, 2.42; N, 15.30. C₄₇H₃₈N₁₆O₂₀Tb₂ requires C, 38.54; H, 2.61; N, 15.29%. The sample sent for analysis indicated the presence of one water molecule and one acetonitrile rather than the two acetonitriles that were observed in the crystal structure.

2-Dy and 2-Ho. The dysprosium (2-Dy) and holmium (2-Ho) complexes were prepared in the same way as the Tb complex (yield: Dy 10 mg, 17%; Ho 21 mg, 36%). Found: C, 38.55; H, 2.49; N, 15.88. C₄₇H₃₈N₁₆O₁₉Dy₂ requires C, 38.77; H, 2.63; N, 15.39%. Found: C, 38.33; H, 2.49; N, 15.10. C₄₇H₃₈N₁₆O₁₉Ho₂ requires C, 38.64; H, 2.62; N, 15.34%. In both 2-Dy and 2-Ho, one additional acetonitrile and one water molecule were found in the analysed samples which were not observed in the crystal structures.

3-Ho. 3-Ho was prepared in a similar manner to 2-Ho except that the metal solution was added to the L¹ solution at room temperature. On mixing, a precipitate began to form so a further 3 cm³ of CH₃CN was added and the solution was heated to redissolve the solid. Small crystals of 3-Ho appeared after standing overnight at room temperature.

3-Er. 3-Er was prepared according to the method described above for 2-Tb. Crystals appeared after slowly evaporating the solvent for one week at room temperature (yield 14 mg, 39%). Found: C, 42.80; H, 2.83; N, 14.93. C₃₀H₂₄N₉O₁₀Er requires C, 43.01; H, 2.89; N, 15.04%. The three solvent acetonitrile molecules found in the crystal structure were not found in the analysis of the bulk sample.

3-Tm and 4-Tm. Tm(NO₃)₃·5H₂O (0.0189 g, 0.04 mM) in 1.5 cm³ of CH₃CN (at approx. 60 °C) was added dropwise to a stirred solution containing L¹ (0.0397 g, 0.17 mM) dissolved in 1.5 cm³ of CH₃CN at the same temperature. A precipitate appeared on standing overnight at room temperature and, on closer inspection, there appeared to be two different crystal forms whose structures were determined to be those of 3-Tm and 4-Tm (yield 15 mg). The elemental analysis indicated that the mixture was almost all 3-Tm with a small amount of 4-Tm. As in the 3-Er case, the solvent acetonitrile molecules found in the crystal structure were not found in the bulk sample. Found: C, 42.32; H, 2.87; N, 14.98. C₃₀H₂₂N₉O₉Tm (3-Tm) requires C, 42.92; H, 2.88; N, 15.01%.

3-Yb and 5-Yb. A mixture of 3-Yb and 5-Yb was prepared in a similar manner to the mixture of 3-Tm and 4-Tm. Only crystals of 5-Yb were suitable for a structure determination even though the analysis indicated that the precipitate was almost exclusively 3-Yb (yield 17 mg). Found: C, 42.31; H, 2.75;

N, 14.27. C₃₀H₂₂N₉O₉Yb (3-Yb) requires C, 42.71; H, 2.87; N, 14.94%.

An attempt was then made to prepare pure 5-Yb by adding one mole equivalent of L¹ to the metal. The analysis indicated that the formula of the precipitated complex is Yb(NO₃)₃·(L¹)·H₂O (yield 6 mg, 24%). Found: C, 29.33; H, 2.20; N, 13.57. C₁₅H₁₃N₆O₁₀Yb requires C, 29.52; H, 2.15; N, 13.77%. If the water molecule is coordinated the product could be structure type 4, if H₂O is uncoordinated then it is likely to be type 5.

6-La. Diprotonated L¹ was prepared as described previously.⁴ 6-La was prepared using the same method as for 3[H₂L¹]²⁺·2[La(NO₃)₆]³⁻·3H₂O.⁴ It appears that the initial solid diprotonated L¹ must have contained more nitric acid than the previous sample used to prepare 3[H₂L¹]²⁺·2[La(NO₃)₆]³⁻·3H₂O. This resulted in the formation of a different product, [(H₂L¹)-(NO₃)₃]⁺[(H₂L¹)(CH₃CN)]²⁺[La(NO₃)₆]³⁻, in which NO₃⁻ and CH₃CN were located in the diprotonated L¹ cavities, as compared to 3[H₂L¹]²⁺·2[La(NO₃)₆]³⁻·3H₂O in which only water molecules were found in the L¹ cavity. The sample sent for analysis contained an additional mole of water. Found: C, 34.73; H, 2.65; N, 17.55. C₃₂H₂₉N₁₄O₂₁La·H₂O requires C, 34.85; H, 2.87; N, 17.79%.

Solvent extraction experiments

Mixtures of 2-bromodecanoic acid and the oligopyridine extractant in either TBB or TPH were vigorously shaken with aqueous phases containing tracer amounts of ²⁴¹Am and ¹⁵²Eu for 5 min (TBB) or 30 min (TPH). After phase disengagement by centrifugation at 4500 rpm, aliquots of each phase were withdrawn for radiometric analysis. The γ-activities at 59.54 and 121.78 keV, for ²⁴¹Am and ¹⁵²Eu, respectively, were measured using a HPGe detector (EG&G ORTEC or Eurysis Mesures). Distribution ratios *D_M* were calculated according to the equation *D_M* = [Activity]_{org}/[Activity]_{aq}, where [Activity]_{org} and [Activity]_{aq} are the radioactivity in counts s⁻¹ of ²⁴¹Am and ¹⁵²Eu at equilibrium for equal volumes of organic and aqueous phases respectively. Separation factors, SF_{Am/Eu}, were calculated as the *D_{Am}*/*D_{Eu}* ratio for the same experimental conditions.

Crystallography

The crystal structures of 12 lanthanide metal complexes of 2,2':6',2''-terpyridine (L¹) were determined. 1-Nd is [M(L¹)-(NO₃)₃(H₂O)], 2-Nd, 2-Sm, 2-Tb, 2-Dy and 2-Ho are [M(L¹)₂-(NO₃)₂][M(L¹)(NO₃)₄], 3-Ho, 3-Er, 3-Tm are [M(L¹)(NO₃)₃·(H₂O)]·L¹, 4-Tm is [M(L¹)(NO₃)₃(H₂O)], 5-Yb is [M(L¹)(NO₃)₃] and 6-La is [(H₂L¹)(NO₃)₃]⁺(H₂L¹)²⁺[La(NO₃)₆]³⁻. Crystal data for 1-Nd, 2-Nd, 2-Sm, 2-Tb, 2-Dy, 2-Ho, 3-Ho, 3-Er, 3-Tm, 4-Tm, 5-Yb and 6-La are given in Table 1, together with refinement details. Data for all 12 crystals were collected with Mo-Kα 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.¹¹ Structures were solved using direct methods with the SHELX86 program.¹² All non-hydrogen atoms in the metal complexes were refined anisotropically. Hydrogen atoms on the carbon 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 included. Heavy atoms in solvent molecules were refined anisotropically or isotropically where appropriate. Empirical absorption corrections were made for all structures using the DIFABS program.¹³ All structures were refined on *F*² until convergence, using SHELXL.¹⁴ All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Bond lengths in the metal coordination sphere of each structure are shown in Table 2. Hydrogen bonds are detailed in Table 3.

Table 1 Crystal data and structure refinement for the compounds

Code	1-Nd	2-Nd	2-Sm	2-Tb	2-Dy	2-Ho	3-Ho	3-Er	3-Tm	4-Tm	5-Yb	6-La
Empirical formula	C ₁₅ H ₁₃ N ₆ ⁻	C ₄₀ H ₃₀ N ₁₇ ⁻	C ₄₅ H ₃₃ N ₁₅ ⁻	C ₄₀ H ₃₀ N ₁₇ ⁻	C ₄₅ H ₃₃ N ₁₅ ⁻	C ₄₅ H ₃₃ N ₁₅ ⁻	C ₃₆ H ₃₃ ⁻	C ₃₆ H ₃₃ ⁻	C ₃₄ H ₂₈ N ₁₁ ⁻	C ₁₅ H ₁₃ N ₆ ⁻	C ₁₅ H ₁₁ N ₆ ⁻	C ₃₂ H ₂₉ LaN ₁₄ ⁻
Formula weight	NdO ₁₀ 581.56	Nd ₂ O ₁₈ 1442.45	Sm ₂ O ₁₈ 1372.54	O ₁₈ Tb ₂ 1471.81	O ₁₈ Dy ₂ 1396.86	O ₁₈ Ho ₂ 1401.72	ErN ₁₂ O ₁₀ 961	ErN ₁₂ O ₁₀ 961	O ₁₀ Tm 919.60	O ₁₀ Tm 606.24	O ₉ Yb 592.34	O ₂₁ 542.30
Crystal system, space group	Triclinic, <i>P</i> 1̄	Triclinic, <i>P</i> 1̄	Triclinic, <i>P</i> 1̄	Triclinic, <i>P</i> 1̄	Triclinic, <i>P</i> 1̄	Triclinic, <i>P</i> 1̄	Triclinic, <i>P</i> 1̄	Triclinic, <i>P</i> 1̄	Triclinic, <i>P</i> 1̄	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions/Å, °												
<i>a</i>	8.327(9)	11.189(14)	10.518(12)	11.087(12)	10.452(13)	10.463(11)	9.994(12)	10.017(12)	10.263(19)	8.655(10)	9.090(9)	10.385(14)
<i>b</i>	10.985(12)	16.059(17)	15.595(17)	16.01(2)	15.531(17)	15.525(17)	14.967(17)	14.742(17)	14.487(17)	8.833(10)	16.693(17)	41.89(5)
<i>c</i>	11.160(14)	16.320(17)	16.116(17)	16.266(17)	16.107(19)	16.131(17)	14.954(17)	14.936(17)	14.816(17)	25.31(3)	13.636(15)	10.757(12)
<i>α</i>	93.76(1)	106.58(1)	100.72(1)	106.01(1)	101.06(1)	100.88(1)	70.01(1)	69.49(1)	64.87(1)	(90)	(90)	(90)
<i>β</i>	94.44(1)	95.16(1)	106.15(1)	95.80(1)	106.14(1)	106.22(1)	78.05(1)	78.11(1)	73.94(1)	90.86(1)	111.11(1)	115.70(1)
<i>γ</i>	101.42(1)	95.87(1)	95.78(1)	95.87(1)	95.84(1)	95.81(1)	79.78(1)	79.78(1)	78.88(1)	(90)	(90)	(90)
Volume/Å ³	994	2774	2462	2728	2431	2438	2006	2008	1909	1934	1140	4216
Z, Calculated density/Mg m ⁻³	2, 1.943	2, 1.727	2, 1.851	2, 1.792	2, 1.908	2, 1.910	2, 1.587	2, 1.589	2, 1.600	4, 2.082	4, 2.038	4, 1.709
Absorption coefficient/mm ⁻¹	2.680	1.940	2.455	2.662	3.144	3.004	3.336	3.144	2.393	4.657	4.909	1.114
Reflections measured	3414	8908	7591	8460	8252	8371	5583	6861	5396	3494	5514	11752
Unique reflections (<i>R</i> _{int})	3414	8908	7591	8460	8252	8371	5583	6861	5396	2111 (0.0566)	3449 (0.0756)	6846 (0.0689)
Data/restraints/parameters	3414/0/290	8908/0/763	7591/0/722	8460/0/767	8252/0/722	8252/0/722	5583/0/536	6861/0/491	5396/0/478	2111/54/290	3449/0/281	6846/36/616
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] <i>R</i> ₁	0.0733	0.0593	0.0800	0.0423	0.0700	0.0452	0.0638	0.0610	0.0949	0.0604	0.0652	0.1111
<i>wR</i> ₂	0.1979	0.1617	0.2042	0.1144	0.2000	0.1201	0.1623	0.1941	0.2208	0.1822	0.1852	0.2245
<i>R</i> indices (all data) <i>R</i> ₁	0.1199	0.0781	0.1879	0.0582	0.1214	0.0735	0.1258	0.0748	0.2745	0.0720	0.0797	0.1372
<i>wR</i> ₂	0.2179	0.1783	0.2471	0.1237	0.2306	0.1405	0.1887	0.2100	0.2859	0.1945	0.2014	0.2367
Largest diff. peak and hole/e Å ⁻³	0.888, -1.492	1.656, -2.125	2.719, -1.477	1.976, -1.116	2.767, -1.650	1.542, -0.965	1.993, -1.588	1.924, -2.492	0.927, -0.655	1.180, -1.505	3.447, -3.278	1.214, -2.924

Table 2 Bond lengths (Å) in the metal coordination spheres

Type 1: 1-Nd	
Nd(1)–O(100)	2.488(8)
Nd(1)–O(41)	2.530(9)
Nd(1)–O(42)	2.553(10)
Nd(1)–O(62)	2.556(9)
Nd(1)–O(52)	2.560(8)
Nd(1)–O(61)	2.570(8)
Nd(1)–N(31)	2.586(10)
Nd(1)–N(11)	2.625(10)
Nd(1)–O(51)	2.632(9)
Nd(1)–N(21)	2.703(13)

Type 2: 2-Nd, 2-Sm, 2-Tb, 2-Dy and 2-Ho

Cation	2-Nd	2-Sm	2-Tb	2-Dy	2-Ho
M(1)–O(22)	2.526(5)	2.475(13)	2.462(5)	2.440(10)	2.421(6)
M(1)–O(11)	2.550(6)	2.483(12)	2.479(6)	2.413(10)	2.405(6)
M(1)–N(31)	2.592(7)	2.609(13)	2.542(7)	2.539(9)	2.538(7)
M(1)–O(12)	2.591(6)	2.598(13)	2.539(6)	2.596(9)	2.598(6)
M(1)–O(21)	2.598(6)	2.550(12)	2.541(6)	2.555(10)	2.545(6)
M(1)–N(41)	2.630(6)	2.572(14)	2.563(6)	2.543(10)	2.559(7)
M(1)–N(11)	2.631(6)	2.583(15)	2.567(6)	2.587(10)	2.558(7)
M(1)–N(61)	2.638(7)	2.675(15)	2.585(6)	2.613(11)	2.605(7)
M(1)–N(51)	2.645(6)	2.621(13)	2.586(6)	2.560(9)	2.560(7)
M(1)–N(21)	2.651(6)	2.555(13)	2.587(6)	2.528(9)	2.541(7)

Anion

M(2)–O(31)	2.644(7)	2.547(13)	2.645(7)	2.507(10)	2.509(6)
M(2)–O(32)	2.548(6)	2.497(12)	2.468(6)	2.428(9)	2.439(6)
M(2)–O(41)	2.598(6)	2.613(13)	2.567(6)	2.580(11)	2.580(7)
M(2)–O(42)	2.571(7)	2.570(13)	2.514(7)	2.488(10)	2.495(8)
M(2)–O(51)	2.567(7)	2.497(13)	2.520(6)	2.460(9)	2.435(7)
M(2)–O(52)	2.559(6)	2.596(13)	2.466(6)	2.573(11)	2.556(7)
M(2)–O(61)	2.434(7)	2.370(14)	2.374(6)	2.346(10)	2.323(6)
M(2)–N(71)	2.600(6)	2.556(14)	2.528(6)	2.527(10)	2.531(7)
M(2)–N(81)	2.591(7)	2.590(13)	2.513(6)	2.554(11)	2.544(7)
M(2)–N(91)	2.577(7)	2.561(16)	2.519(6)	2.506(10)	2.541(7)

Types 3 and 4: 3-Ho, 3-Er, 3-Tm and 4-Tm

	3-Ho	3-Er	3-Tm	4-Tm
M(1)–O(100)	2.328(7)	2.326(6)	2.317(12)	2.313(10)
M(1)–O(41)	2.478(10)	2.451(8)	2.407(14)	2.500(14)
M(1)–O(42)	2.463(9)	2.460(7)	2.444(13)	2.371(14)
M(1)–O(51)	2.518(9)	2.523(7)	2.480(12)	2.402(14)
M(1)–O(52)	2.436(8)	2.435(6)	2.473(14)	2.410(13)
M(1)–O(61)	2.431(8)	2.414(8)	2.313(16)	2.251(13)
M(1)–O(62)	2.725(11)	2.858(12)	[3.534(20)]	[3.576(16)]
M(1)–N(11)	2.503(11)	2.478(7)	2.494(19)	2.441(15)
M(1)–N(21)	2.545(8)	2.505(7)	2.463(17)	2.482(17)
M(1)–N(31)	2.510(9)	2.489(7)	2.475(16)	2.526(14)

Type 5: 5-Yb

Yb(1)–O(42)	2.364(8)
Yb(1)–O(61)	2.373(8)
Yb(1)–O(52)	2.382(10)
Yb(1)–O(41)	2.385(7)
Yb(1)–N(21)	2.395(8)
Yb(1)–O(62)	2.406(10)
Yb(1)–N(11)	2.417(7)
Yb(1)–N(31)	2.419(8)
Yb(1)–O(51)	2.456(9)

Type 6: 6-La

La(1)–O(42)	2.624(10)
La(1)–O(21)	2.646(11)
La(1)–O(12)	2.653(10)
La(1)–O(51)	2.645(10)
La(1)–O(62)	2.659(9)
La(1)–O(32)	2.658(10)
La(1)–O(41)	2.660(10)
La(1)–O(22)	2.667(10)
La(1)–O(11)	2.672(11)
La(1)–O(31)	2.678(11)
La(1)–O(52)	2.685(10)
La(1)–O(61)	2.742(20)

Table 3 Hydrogen bonds (Å) in the structures

1-Nd			
O(100)···O(64) ^a	2.92		
O(100)···O(52) ^b	2.96		
O(100)···O(62) ^b	2.97		
3-M			
	M = Ho	M = Er	M = Tm
O(100)···N(41)	2.87	2.87	2.83
O(100)···N(51)	2.97	2.93	2.92
O(100)···N(61)	2.81	2.80	2.79

Angle (°) between adjacent pyridine rings of uncoordinated L¹ in 3-M

	23.8, 29.9	22.8, 31.4	16.9, 27.2
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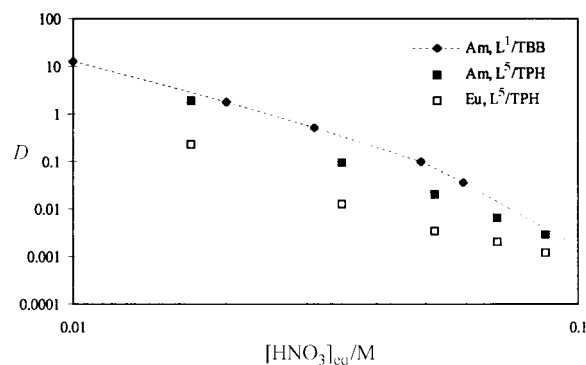
4-Tm

O(100)···O(62) ^c	2.75
O(100)···O(51) ^d	2.84

6-La

N(11)···N(100)	2.91
N(31)···N(100)	2.91
N(41)···O(71)	2.73
N(61)···O(71)	2.76

Symmetry operations: ^a 1 – x, –y, –z; ^b –x, –y, –z; ^c –x + 1/2, y – 1/2, –z + 1/2; ^d 1/2 – x, y + 1/2, 1/2 – z.

**Fig. 2** Distribution ratios for the extraction of americium(III) and europium(III) with 0.02 M L²–L⁴ and 1 M 2-bromodecanoic acid in TBB.

CCDC reference number 186/1805.

See <http://www.rsc.org/suppdata/dt/a9/a907077j/> for crystallographic files in .cif format.

Discussion

Solvent extraction

Solvent extraction studies were carried out with the different nitrogen heterocycles (L²–L⁵) in synergy with 2-bromodecanoic acid (HA) in *tert*-butylbenzene (TBB) or hydrogenated tetrapropene (TPH). Distribution ratios (*D*) for the extraction of Am(III) and Eu(III) from aqueous solutions containing HNO₃ (*ca.* 0.005–0.1 M) by 1 M 2-bromodecanoic acid and by 0.02 M solutions of ligands L¹–L⁴ containing 1 M 2-bromodecanoic acid in *tert*-butylbenzene are shown in Fig. 2. The extraction of Am(III) and Eu(III) when 0.02 M of L⁵ in synergistic combination with 1 M 2-bromodecanoic acid was used in TPH is shown in Fig. 3, together with the data previously obtained for L¹ in TBB.⁶ The data for L¹ extracted from initial HNO₃ are included in Fig. 3 for comparison, even though the data for L⁵ are plotted *versus* the equilibrium HNO₃ concentration.

Metal extraction with TPH and *tert*-butylbenzene has been shown to be almost identical when using L¹ and 2-bromo-

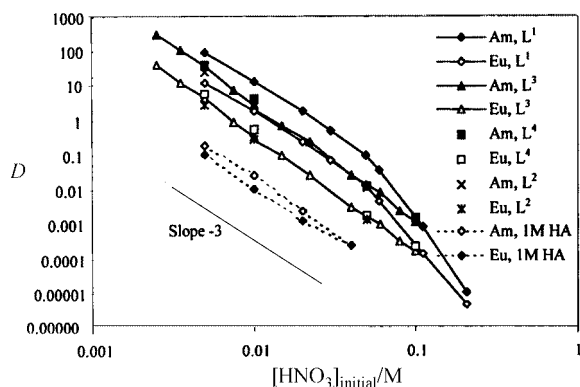


Fig. 3 Distribution ratios for the extraction of americium(III) and europium(III) with 1 M 2-bromodecanoic acid and either 0.02 M L^1 (in TBB) or 0.02 M L^5 (in TPH).

decanoic acid⁶ and the extractions presented in Fig. 2 and 3 are thus comparable. It has been previously shown that Am(III) and Eu(III) extraction by L^1 itself is negligible.⁶ Fig. 2 shows that 2-bromodecanoic acid (HA) only extracts to a small degree and an Am(III)/Eu(III) separation factor around 2 is obtained at low acid concentrations. The synergistic combination of L^1 – L^5 and 2-bromodecanoic acid, however, results in increased distribution coefficients and Am(III)/Eu(III) separation factors between 7 and 9 are observed. In each case, the extraction decreases with increasing HNO_3 concentration. This would seem to indicate that all of the ligands become protonated, at higher acid concentrations. It has been previously shown that when L^1 becomes protonated, it can pass into the aqueous phase although the amount passing into the aqueous phase is reduced in the presence of the synergist 2-bromodecanoic acid.⁶ In the case of the more hydrophobic ligands L^2 and L^3 , precipitates were observed at higher nitric acid concentrations indicating that the protonated species were not soluble in either the aqueous or organic phases. Substitution with a hydrophobic group on the terpyridine was expected to increase the Am and Eu distribution ratios because the hydrophobic derivatives would be more likely to remain in the organic phase during the extractions. The opposite was, however, observed and treatment with the unsubstituted terpyridine (L^1) shows a slightly higher metal extraction when compared to those using the substituted nitrogen heterocycles (L^2 – L^5). It seems more likely that a factor such as the basicity of the ligand has a bigger effect than hydrophobicity on the Am and Eu distribution ratios. The extraction results show that substitution of one terminal pyridine with pyrazine does not change either the distribution ratios or the separation factors to any significant degree. It seems likely that further substitution by pyrazine or by a more weakly basic heterocyclic nitrogen ligand such as triazine or triazole will be necessary before an effect can be seen. This was shown in a recently published study involving the separation of Am and Eu by 2,6-di(5,6-dipropyl-1,2,4-triazin-3-yl)pyridine, which gave D_{Am} values of between 22 and 45 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 .¹⁵ The substituted terpyridines whose efficacies are compared in Fig. 2 and 3 also show similar nitric acid dependency, distribution ratios and separation factors for americium and europium. The different substituents on the central pyridyl groups do not seem to affect the extraction considerably. These results indicate that the nature of the metal complexes formed by ligands L^1 to L^5 with the lanthanide series are likely to be equivalent and the following crystallographic studies were only carried out on complexes containing the unsubstituted terpyridine (L^1). Acetonitrile was found to be an excellent solvent for the crystallisation of all the studied lanthanide complexes.

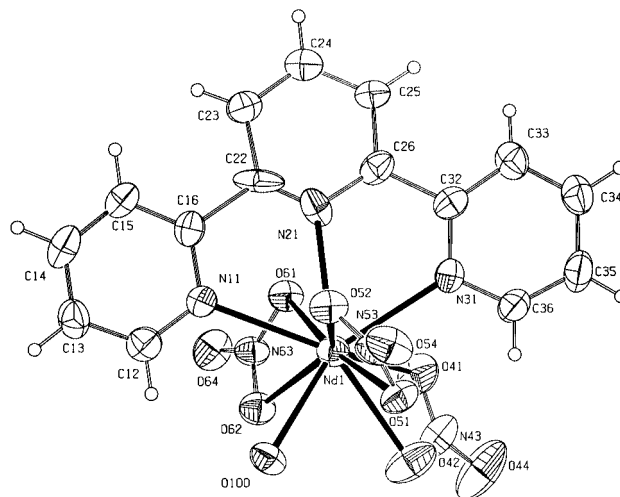


Fig. 4 The structure of 1-Nd with the atomic numbering scheme. Ellipsoids at 30% probability.

Solid state structures

When this work was initiated there were very few lanthanide structures containing L^1 , apart from a series of 1:1 lanthanide chloride– L^1 complexes.¹⁶ However in the last year a systematic survey has been reported of lanthanide structures containing L^1 with a variety of anions, such as acetate, trichloroacetate¹⁷ and perchlorate¹⁸ as well as nitrate.¹⁹ Remarkably, although 7 structures containing nitrate are reported in 3 groups, not one was the same as those reported here, despite all having a metal: L^1 ratio of 1:1. While the preparations were subtly different, the variations in stoichiometry are clearly significant and indicate the complexity of the lanthanide–nitrate– L^1 system.

The complex 1-Nd was prepared by adding the metal to the ligand in a ratio of 1:1 and shows the metal ion coordinated to three bidentate nitrates, one tridentate L^1 ligand and a water molecule (Fig. 4). By contrast, the previously determined complexes¹⁹ with lanthanide, nitrate, L^1 and water have structures $[ML^1(NO_3)_2(H_2O)_n](NO_3)_n$, with $n = 3$ for the La, Eu and Gd compounds, which are 10-coordinate and form an isomorphous set, and $n = 2$ for the Tb, Lu and Yb products, which are nine-coordinate and form another isomorphous set. A previous structure determination of the Gd complex has also been published.²⁰ In all these compounds then, one nitrate remains unbound to the metal and it seems likely, though the Nd complex was not studied, that a 10-coordinate complex of formulation $[NdL^1(NO_3)_2(H_2O)_3](NO_3)$ does exist in solution and in the solid state. The only difference between this cation and 1-Nd is that two water molecules in the former are replaced by one nitrate in the latter to form a neutral complex but the coordination number remains at 10. An interesting feature of the coordination sphere, as has been previously observed,^{17,19} is the close interaction between C(12) and O(100) of 3.13 Å [$H(12) \cdots O(100)$ 2.48 Å] (see Fig. 4), which is indicative of a stabilising intramolecular hydrogen bond between L^1 and water in the coordination sphere. The water molecule is only 0.59 Å from the plane of the pyridine ring. The dimensions in 1-Nd are as expected. The shortest metal–ligand bond is to the water molecule [2.488(8) Å] with similar bond lengths to the three nitrates [2.530(9)–2.632(9) Å]. The Nd–N bond lengths show some variation, such that the Nd–N_c [c = central, thus N(21)] bond length of 2.703(13) Å is significantly longer than Nd–N_o [o = outer, thus N(11), N(31)] at 2.625(10) and 2.586(10) Å.

The complex 2-Nd was prepared by adding the metal nitrate to the ligand in a ratio of 1:4 and shows the presence of both a cation and an anion in the asymmetric unit, with a formulation of $[Nd(NO_3)_2(L^1)_2][Nd(NO_3)_4(L^1)]$. As shown in Fig. 5(a), the cation $[Nd(NO_3)_2(L^1)_2]^+$ is 10-coordinate with the metal bonded to two tridentate L^1 ligands and two bidentate nitrate anions.

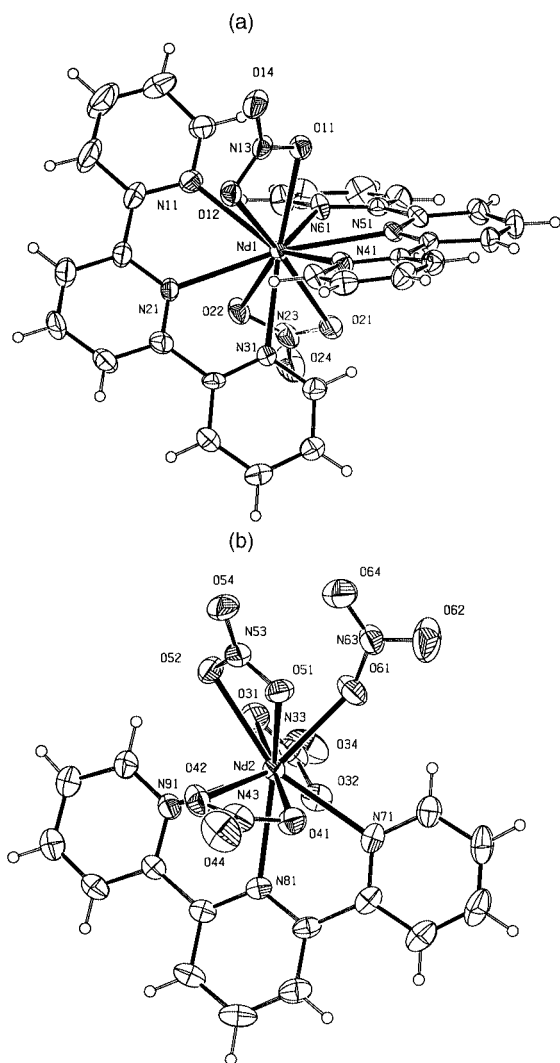


Fig. 5 The structure of (a) the cation and (b) the anion in 2-Nd with the atomic numbering scheme. Ellipsoids at 30% probability. The structures of 2-Sm, 2-Tb, 2-Dy and 2-Ho are similar.

The two L^1 ligands intersect at 55.7° . The dimensions in the cation are remarkably regular, with Nd–O ranging from 2.526(5)–2.598(6) Å and Nd–N from 2.592(7)–2.651(6) Å. The anion $[Nd(NO_3)_4(L^1)]^-$, shown in Fig. 5(b), is also 10-coordinate with the metal bonded to only one tridentate L^1 and four nitrate anions, one of which is unidentate. The bond lengths in the anion show a greater variation than in the cation, with a short bond to the unidentate nitrate [Nd(2)–O(61) 2.434(7) Å], but the other Nd–O distances [2.548(6)–2.644(7) Å] and Nd–N distances [2.577(7)–2.600(6) Å] are more regular. There is a weak C–H \cdots O interaction to the unidentate nitrate (H \cdots O 2.55 Å), but there are no such contacts in the cations. The asymmetric unit is completed by two solvent acetonitrile ligands, but these are not involved in intermolecular hydrogen bonding. This $[M(NO_3)_2(L^1)_2][M(NO_3)_4(L^1)]$ formulation has been observed before for $M=La$,²¹ with the significant difference that the metal atom in the anion is 11-coordinate with all 4 nitrates bidentate.

Lanthanides bonded to more than one L^1 ligand are relatively rare in the literature. Apart from this example,²¹ the others all show three L^1 ligands bonded to a 9-coordinate metal ion. Examples include $[Ln(L^1)_3](ClO_4)_3$, $Ln = Eu$ ²² and Ce, Pr, Sm, Eu (form A), Eu, Lu and Y (form B).¹⁸ Both forms A and B show similar discrete $[Ln(L^1)_3]^{3+}$ cations. The fact that these cations have only been found in the presence of a weakly coordinating anion such as perchlorate is significant particularly as they have not been observed in the presence of the more

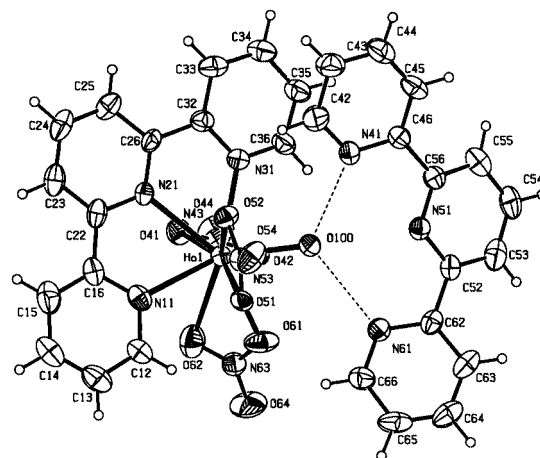


Fig. 6 The structure of 3-Ho with the atomic numbering scheme. Ellipsoids at 30% probability. Hydrogen bonds shown as dotted lines. The structures of 3-Er and 3-Tm are similar.

strongly coordinating nitrate ion or indeed of the acetate and trichloroacetate anions.¹⁷

The structure of 2-Sm is equivalent to that of 2-Nd, but while the unit cell is similarly triclinic, the lattice dimensions are different and there is no solvent in the unit cell. We have analysed LnL^1 structures in the Cambridge Structural Database²³ as implemented at the Daresbury Laboratory²⁴ and have found that, on average, when the M–N_c distances are greater than 2.58 Å, M–N_o < M–N_c, and for distances less than 2.58 Å, M–N_o > M–N_c. While distances in 1-Nd conform to this pattern, the distances in 2-M are much more disparate, no doubt because of the steric constraints of the coordination sphere and because the differences will be small as M–N_c distances are close to 2.58 Å for these early lanthanides. The structure of 2-Tb is isomorphous with that of 2-Nd, while 2-Dy and 2-Ho are both isomorphous with 2-Sm. The only noticeable difference in structure is that in 2-Tb and 2-Nd, both L^1 ligands are closely planar (inter-pyridine angles $<10^\circ$) while in 2-Dy, 2-Ho and 2-Sm, one of the L^1 ligands is highly distorted (inter-pyridine angles *ca.* 25°) while the other is more closely planar (angles $<10^\circ$).

It is interesting that the anions in all five ionic complexes contain three bidentate nitrates and one unidentate nitrate. A search of the CSD^{23,24} shows the presence of only a few examples of the unidentate nitrate with lanthanides although the recent study of acetate and trichloroacetate structures¹⁷ did show many unidentate anions. Dimensions of the metal coordination spheres in the five compounds are compared in Table 2; the only differences are due to the decrease in metal size with the lanthanide series.

The structure of 3-Ho is shown in Fig. 6. The asymmetric unit contains $[Ho(L^1)(NO_3)_3(H_2O)]$ together with an unbonded L^1 molecule. The metal atom is 10-coordinate, being bonded to three bidentate nitrate anions, one tridentate L^1 and a water molecule. However, the bond to O(62), at 2.725(11) Å, is much longer than the other nitrate bonds [range 2.431(8)–2.518(9) Å], suggesting that this particular nitrate is intermediate between unidentate and bidentate. The water molecule forms the shortest bond at 2.328(7) Å. The uncoordinated L^1 molecule in the asymmetric unit forms hydrogen bonds to the water molecule which is coordinated to the holmium. The O(100) \cdots N(41) and O(100) \cdots N(61) distances are 2.87 and 2.81 Å, while O(100) \cdots N(51) is 2.97 Å, thus suggesting that water hydrogen atoms form donating hydrogen bonds to the outer two nitrogen atoms. Previous calculations⁴ have shown that a water molecule (or equivalent) is necessary to stabilise this conformation of the uncoordinated L^1 where the nitrogen atoms are mutually *cis* (the *cis*, *cis* conformation) because in its absence the *trans*, *trans* conformation is found, which reduces steric interactions. The

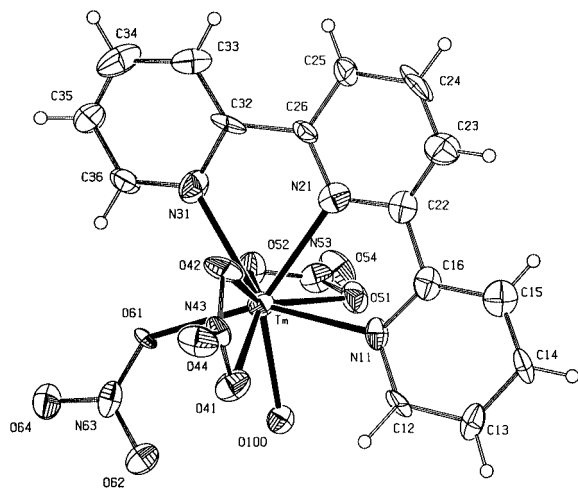


Fig. 7 The structure of 4-Tm with the atomic numbering scheme. Ellipsoids at 30% probability.

angles between adjacent rings in the uncoordinated L^1 are 23.8 and 29.9°, compared to 10.4 and 4.0° in the coordinated L^1 . It is noteworthy that O(100) also forms a weak interaction of 2.59 Å with H(35) and could be considered to form an acceptor hydrogen bond from C(35)–H, as well as the two donor hydrogen bonds to N(41) and N(61). Indeed, the two pyridine rings 3 and 4 are stacked (angle of intersection 21.3°) with a closest contact of 3.28 Å between the two hydrogen bonded atoms N(41) and C(35) (Fig. 6). Rather surprisingly, the three acetonitrile solvent molecules do not form any intermolecular hydrogen bonds.

It is interesting that 2-Ho and 3-Ho were prepared under almost identical conditions. It has been noted previously 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 and the solvent:water ratio. The results obtained here for Ho indicate that the volume of solvent and temperature are also important factors which may have an influence on the precipitated complex.²⁵

3-Er and 3-Tm are isomorphous with 3-Ho, although in 3-Tm there are only two acetonitrile solvent molecules and the unit cell is significantly smaller by *ca.* 2%. In 3-Er the bonds are just slightly shorter than for 3-Ho (see Table 2), except for the M–O(62) bond which is 2.858(12) Å. This is not unexpected as it indicates that the smaller size of Er compared to Ho forces the nitrate to be more unidentate. This pattern is also observed in 3-Tm, but here the nitrate is clearly unidentate, with a Tm–O(62) distance of 3.534(20) Å, so that the metal is 9-coordinate. The Tm–O(61) bond, at 2.313(16) Å, is remarkably short, and indeed comparable to the Tm–O(100) water molecule bond of 2.317(12) Å. In both 3-Er and 3-Tm, the hydrogen bond pattern and twist in the uncoordinated ligand is similar to that observed in the 3-Ho structure. Details are provided in Table 3. It is interesting that in all three structures the oxygen atom of the unidentate nitrate forms a shorter bond to the metal than any oxygen atoms of the bidentate nitrates.

The structure of 4-Tm is shown in Fig. 7. Here the metal atom is also 9-coordinate, being bonded to three nitrates, one of which is unidentate, one L^1 ligand and one water molecule. The dimensions are given in Table 2. It is interesting that two different structures are obtained for Tm, one with an extra L^1 ligand (3-Tm) and one without (4-Tm). It is noteworthy that the dimensions of the metal coordination spheres are very similar, indicative of the fact that the size of the metal ion is consistent with a 9-coordinate metal environment. In 4-Tm, the Tm–O(61) bond to the unidentate nitrate is even shorter at 2.251(13) Å. This oxygen atom is in the ML^1 plane and forms a hydrogen bond to C(12)–H (H...O 2.36 Å). In the absence of the extra L^1 molecule, the water molecule in 4-Tm is hydrogen bonded to

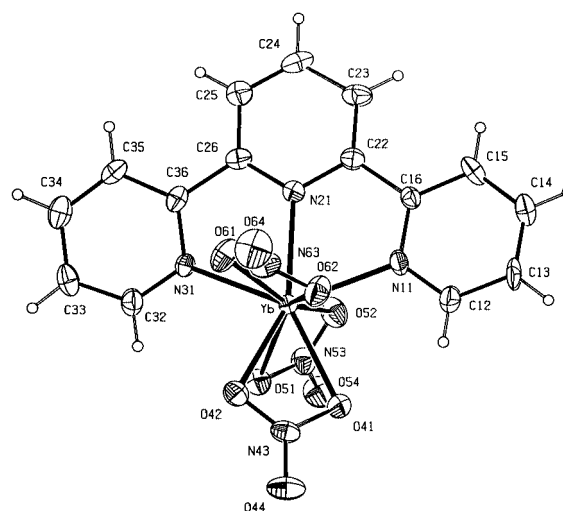


Fig. 8 The structure of 5-Yb with the atomic numbering scheme. Ellipsoids at 30% probability.

two oxygen atoms from two different nitrates coordinated to two different metal atoms (Table 3), at distances of 2.75 and 2.84 Å. The stoichiometry of 4-Tm is equivalent to that of 1-Nd but, in the latter case, the large size of the cation permits the formation of a 10-coordinate complex with L^1 , three bidentate nitrates and a water molecule all bonded to the metal.

The structure of 5-Yb (Fig. 8) shows that the metal ion is bonded to three bidentate nitrates and one terdentate L^1 ligand. There is a short C(12)–H...O(41) contact of 2.48 Å, indicative of weak hydrogen bond formation. The Yb–O distances range from 2.364(8)–2.406(10) Å, apart from Yb–O(51) which is 2.456(9) Å. The Yb–N_o distances, at 2.417(7) and 2.419(8) Å, are just larger than the M–N_c distance of 2.395(8) Å, which is consistent with the pattern observed in the CSD. Analysis of the precipitate obtained on addition of four mol equivalents of the ligand indicates that it contains a mixture of complexes and that the majority of the mixture is made up of 3-Yb. A further preparation involving the addition of only one molar equivalent of L^1 produced a precipitate of formula Yb(NO₃)₃·(L^1)·H₂O, which is consistent with a formulation as 1-, 4- or 5-M. It is unlikely to be 1-M as the smaller Yb(III) generally forms complexes with coordination numbers of nine or less, which are observed in both 4-M and 5-M, but it could also be an example of the [M(NO₃)₂(L^1)(H₂O)₂](NO₃) family of ref. 19.

The prevalence of the unidentate nitrate in the present work is unprecedented. A search of the CSD for structures containing the nitrate anion bonded to a lanthanide found 729 examples. The mean difference between the two shortest Ln–O distances was calculated as 0.069 Å. There were only eight examples with a difference greater than 1.00 Å and none with a difference between 0.5 and 1.0 Å. In this work alone we have almost doubled the number of examples of the unidentate nitrate anion. It seems likely a significant reason for these is the relative inflexibility of the L^1 ligand which is necessarily terdentate and planar. Thus, the Ln(L^1)(NO₃)₃(H₂O) formulation with three bidentate nitrates is too crowded for all but the largest lanthanide and stable complexes can be formed either by excluding one nitrate from the coordination sphere¹⁹ or by one of the nitrates becoming unidentate.

The crystal structure of the 6-La structure is shown in Fig. 9 together with the atomic numbering scheme. There are two independent (H₂ L^1)²⁺ cations, an [La(NO₃)₆]^{3–} anion, a nitrate ion and a solvent acetonitrile in the asymmetric unit. In the hexanitrate anion, the metal ion is 12-coordinate, with La–O dimensions ranging from 2.62(1) to 2.74(2) Å. As is usually found for diprotonated L^1 cations, the two outer nitrogens are protonated and form donor hydrogen bonds to atoms that are encapsulated within the plane of the ligand. One cation forms

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