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Lanthanide complexes of a new nonadentate ligand derived from 1,4,7-triazacyclononane: synthesis, structural characterisation and NMR spectroscopic studies

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A new route to the synthesis of 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane has been introduced. This polyamino derivative of 1,4,7-triazacyclononane has been used to synthesise a new ligand (L) by Schiff-base condensation with sodium pyruvate in the presence of lanthanide(III) (Ln) ions as templating agents to form the complexes [Ln(L)] (Ln = Y, La, Sm, Yb). The ligand L has nine donor atoms comprising three amine and three imine N-donors and three carboxylate O-donors, and forms thermodynamically and kinetically stable Ln(III) complexes in which the three pendant arms of the ligand wrap around the nine-co-ordinate Ln(III) centres. Complexes with La(III), Sm(III) and Y(III) have been structurally characterised. All the complexes are isostructural and the co-ordination polyhedron about the lanthanide centre is in each case slightly distorted tricapped trigonal prismatic, with the two triangular faces of the prism formed by the macrocyclic N-donors and the carboxylate O-donors. NMR spectroscopic studies on the diamagnetic Y(III) and La(III) complexes and on the paramagnetic Yb(III) and Sm(III) complexes indicate that L imposes a very rigid co-ordination cage around the metal centre.

Introduction

Over the past years there has been increasing interest in the co-ordination chemistry of the lanthanides due to the wide variety of potential applications of their complexes. One of the most important is the application of paramagnetic Gd(III) complexes as contrast agents for magnetic resonance imaging (MRI).[1] Work on MRI agents has focused predominantly on poly(amino)carboxylate and related ligands[2] and especially on 1,4,7,10-tetrakis(carboxymethyl)-1,4,7,10-tetraazacyclododecane (DOTA) and its derivatives.[3,4] 1,4,7,10-Tetraazacyclododecane (cyclen) is the macrocyclic core in a large family of ligands suitable for lanthanide complexation. These ligands are formed by addition of pendant arms containing carboxylate,[5] phosphonate[6] and related groups[7] to afford octadentate macrocyclic ligands. Considering that the most common co-ordination numbers for lanthanide ions are either eight or nine, these ligands would be expected to form very stable complexes with all the lanthanides.

With 1,4,7-triazacyclononane as a macrocyclic core, the addition of pendant arms leads to the formation of exodentate ligands which form very stable complexes with divalent and trivalent first row transition elements.[8] The only comparable results with lanthanide ions consist of NMR solution studies of La(III) and Lu(III) complexes with the tricarboxylic derivative of [9]aneN$_3$.[9] We report herein the synthesis of a new poly(imino)carboxylate ligand (L) by Schiff-base condensation of a polyamine derivative of [9]aneN$_3$ with sodium pyruvate in the presence of Ln(III) ion as templating agent. The ligand L is the first example of a [9]aneN$_3$ derivative where the arms have been extended to obtain a set of nine donor atoms, and is therefore capable of fully encapsulating a Ln(III) centre. It is interesting to note that L has a tripodal disposition of the three arms with the [9]aneN$_3$ moiety acting as a capping group. This co-ordination mode is comparable with tripodal ligands based on tris(2-aminoethyl)amine (tren). A large variety of tripodal ligands derived from tren have been synthesised by Schiff-base condensation with 2,6-diformyl-4-methylphenol,[10] 2,6-diformine-pyridine,[11] salicylaldehyde,[12] acetylacetone[12] and sodium pyruvate.[13] All of these ligands have proven to be effective for the co-ordination of lanthanide ions as they have seven or more donor atoms. In this context, L has a co-ordination mode that is intermediate between that of the tripodal system based upon derivatives of tren and the macrocyclic capping systems derived from cyclen. The synthesis of L together with the crystal structures of its complexes with La(III), Sm(III) and Y(III) and the NMR spectra of all the complexes [Ln(L)] (Ln = Y, La, Sm, Yb) are described herein.

Results and discussion

Synthesis and characterisation of L^1

The previous route for the synthesis of 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (L^1) was by reductive alkylation of 1,4,7-triazacyclononane with phthalimidoacetaldehyde in the presence of $NaBH_3CN$, followed by acid hydrolysis of the recovered product to remove the protecting phthalol groups.[14] The first reaction step has to be performed under anhydrous conditions in MeCN using phthalimidoacetaldehyde which has previously been dehydrated by azeotropic removal of water with benzene: the product formed could only be partially purified by chromatography.

We have introduced a new sequence of reactions which leads to the synthesis of L^1 (Scheme 1). The first is the addition of chloroacetonitrile to [9]aneN$_3$·3HBr **1** in EtOH in the presence of an excess of Et_3N. The oil obtained after evaporation of the solvent was dissolved in $CHCl_3$ and washed with water, and the product **2** was obtained as a solid without further purification. Compound **2** was characterised satisfactorily by ^{1}H and ^{13}C

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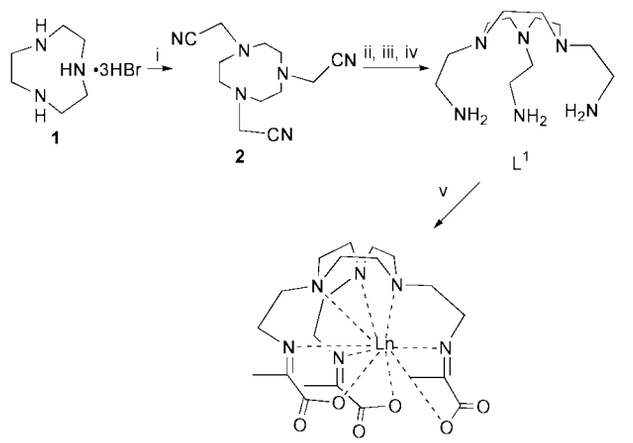

Scheme 1 Ln = Y, La, Sm, Yb. i: $ClCH_2CN$, NEt_3, EtOH, 18 h; ii: BH_3·THF 1 M, 48 h; iii: HCl 6 M, 24 h; iv: Dowex; v: 3 CH_3CO-COONa, LnX, MeOH, 2 h.

NMR, IR spectroscopy and elemental analysis. The EI mass spectrum of **2** shows peaks due to the product with loss of two and three nitrile arms.

The reduction of the nitrile groups in **2** using 1 M BH_3 solution in THF followed by hydrolysis of the borane complexes in refluxing concentrated HCl solution affords the hydrochloride salt of 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (L^1). The free amine is obtained by passing an aqueous solution of this salt through a Dowex column. The NMR spectra (^1H and ^{13}C) show all the expected resonances and satisfactory elemental analytical data were obtained. The EI mass spectrum of **2** shows peaks due to the product having lost two arms, two arms and one NH_2 group, and all three arms.

Synthesis and structural characterisation of [Ln(L)]

The synthesis of the complexes [Ln(L)] (Ln = Y, Sm, Yb, La) is achieved by Schiff-base condensation of the triamine L^1 with sodium pyruvate in the presence of an Ln(III) ion as the templating agent. As a representative of the early lanthanides, we have crystallised complexes where Ln = La, Sm Y, and fully characterised the Yb analogue. It is worth noting that only in the case of [Ln(L)] is it necessary to remove the $NaNO_3$ formed with the complex by passing a solution of the mixture in MeOH through a Sephadex column. In the other cases, the sodium salts formed do not interfere with the isolation of the complex. Elemental analysis and mass spectra for all the complexes are consistent with the formulation [Ln(L)].

Single-crystal X-ray diffraction studies confirm that the compounds [Y(L)], [La(L)] and [Sm(L)] are isostructural. In each, the Ln(III) centre is nine-co-ordinate, using all nine donor atoms of the ligand, namely the three amino N-donors of the macrocycle, the three imino N-donors and the three carboxylate O-donors. Bond lengths are in the range 2.622(4)–2.717(3) Å for the bonds between the Ln(III) and the macrocyclic N-donors, in the range 2.534(4)–2.643(3) Å for the bonds to the N-donors of the imine moiteies, and in the range 2.331(3)–2.441(3) Å for those to the carboxylate O-donors. The trend of the bond lengths moving from La to Y shows, as expected, a general shortening due to the lanthanide contraction (Table 1). Two different views of the crystal structure of [La(L)] are shown in Fig. 1 and 2. There is a high degree of planarity in the fragments C(2)–C(8) of all the structures due to the conjugation between the imine and carboxylate groups, with the mean deviation from the least squares mean plane being only 0.003–0.045 Å. It is interesting to note the difference in the opening of the three arms by looking at the pitch angle between the plane of the macrocycle and the plane of each pyruvate. The average of the three pitch angles decreases from 52.2° for [La(L)], to 51.0° for [Sm(L)], and to 49.6° for [Y(L)]. This variation is due to the different effective ionic radii of the three ions:

Table 1 Selected bond lengths (Å) in the [Y(L)], [Sm(L)] and [La(L)] structures

	[Y(L)]	[Sm(L)]	[La(L)]
Ln–N(1)	2.627(4)	2.669(4)	2.717(3)
Ln–N(4)	2.640(4)	2.677(4)	2.717(3)
Ln–N(7)	2.622(4)	2.690(4)	2.707(3)
Ln–N(3A)	2.552(4)	2.602(4)	2.643(3)
Ln–N(3B)	2.534(4)	2.588(4)	2.620(3)
Ln–N(3C)	2.544(4)	2.579(4)	2.630(3)
Ln–O(6A)	2.346(3)	2.403(3)	2.441(3)
Ln–O(6B)	2.331(3)	2.391(4)	2.436(3)
Ln–O(6C)	2.332(3)	2.391(4)	2.430(3)

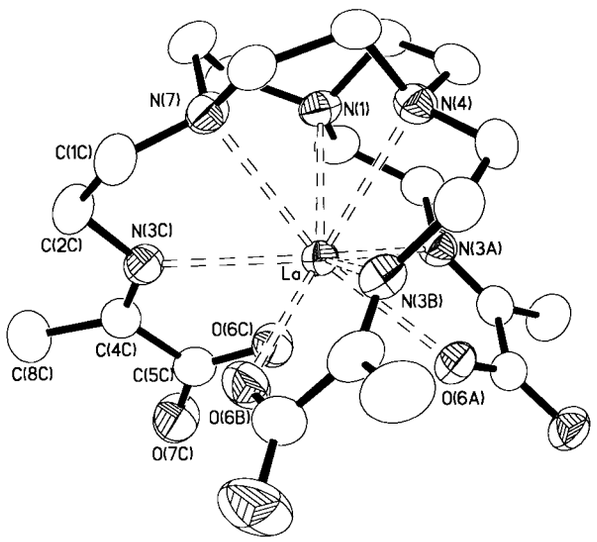

Fig. 1 Crystal structure of [La(L)] **4** with numbering scheme adopted. Hydrogen atoms and solvating MeOH molecules have been omitted for clarity. Displacement ellipsoids are drawn at 50% probability.

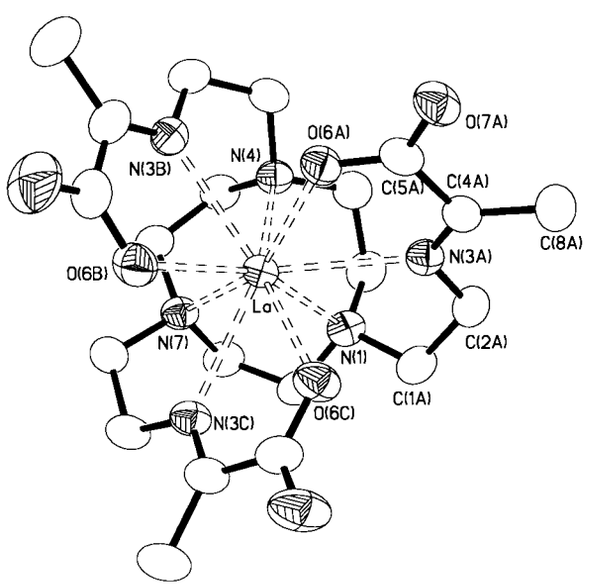

Fig. 2 View of the crystal structure of [La(L)] **4** along the non-crystallographic 3-fold axis. Displacement ellipsoids are drawn at 50% probability.

1.36 for La^{3+}, 1.27 for Sm^{3+} and 1.21 Å for Y^{3+} (values are for the nine-co-ordinate ions).[15] The co-ordination geometry about the lanthanide centre is slightly distorted tricapped trigonal prismatic (Fig. 3a). It is well known[16] that the two most common geometries for nine-co-ordinate complexes are capped square antiprismatic and tricapped trigonal prismatic. The presence of 1,4,7-triazacyclononane as a capping moiety forces the Ln(III) ion to assume a trigonal prismatic structure as the

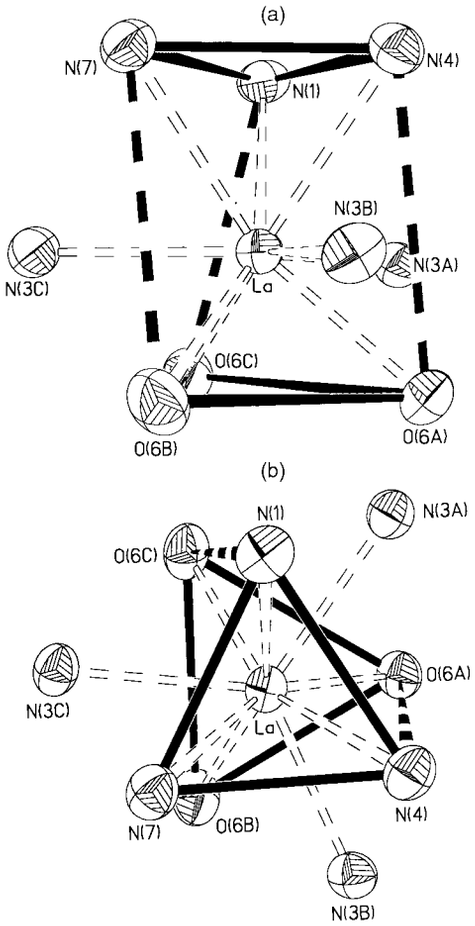

Fig. 3 (a) Co-ordination geometry about the metal centre in [La(L)] **4**. (b) View of the co-ordination geometry in complex **4** down the non-crystallographic 3-fold axis.

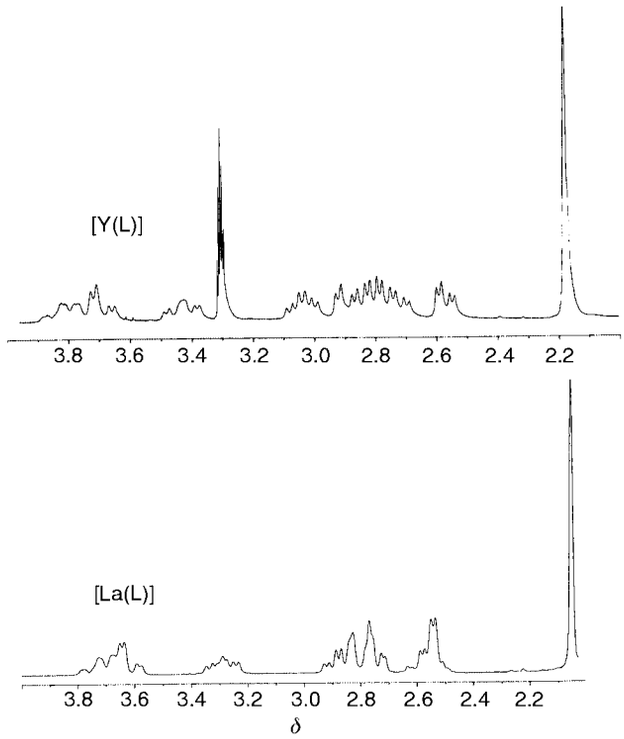

Fig. 4 ^{1}H NMR spectra of diamagnetic [Y(L)] (above) and [La(L)] (below) in CD_3OD and D_2O, respectively at 298 K.

macrocyclic nitrogen donors impose the first triangular face. The other triangular face of the prism is formed by the carboxylic oxygens with the imine nitrogens capping the three rectangular faces of the prism. The upper and lower triangular faces of the prism are essentially equilateral (angle range 58.2–61.6°) and parallel (the angle between the plane defined by the triangle of three oxygen donors and that defined by the three nitrogen donors is never more than 3°), but the oxygen triangular faces are always slightly twisted around the 3-fold axis compared to the nitrogen triangular face. The twist between the two triangular faces is illustrated in Fig. 3b and can be quantified looking at the torsion angles formed by the four atoms of each rectangular face of the prism. In [Y(L)] the average of the three torsion angles (one for every triangular side) is 20.2, in [Sm(L)] is 22.9 and in [La(L)] is 27.0°. Consequently, we observe that the distortion from the trigonal prismatic geometry is more evident as the size of the encapsulated metal ion increases.

Comparing this co-ordination geometry with the polyhedra observed in the corresponding complexes of DOTA, we observe that in the latter, with a tetradentate macrocycle as a capping group, the nine-co-ordinate complexes assume a square antiprismatic stereochemistry with the macrocyclic N-donors forming one square face.[17] Nevertheless, the complexes with DOTA and its derivatives[6,17,18] are similar to the complexes obtained with L in that their structures are monomeric with all the donor atoms involved in the co-ordination. The difference is that in DOTA examples the Ln(III) ions are eight-co-ordinate having one co-ordination site available for occupation by a solvent molecule (usually water in these examples[17]), while in complexes of L the ligand can completely fulfil the co-ordination requirements of the Ln(III) ion, leaving no space for co-ordination of a solvent molecule.

It is interesting to note that using tris(2-aminoethyl)amine (tren) as the tripodal triamine and the same sodium pyruvate as the ketone for the Schiff-base condensation,[13] polymeric structures have been obtained. These polymers are formed in two different ways: either with one carboxylate group from each ligand bridging to the next metal centre or with Na^+ cations joined to carboxylate oxygens linking together two or more units. Our complexes, like those of DOTA, form only monomeric structures because the Ln(III) ion has a complete co-ordination sphere. When the tripodal ligand has only seven donor atoms,[13] the lanthanide ion can complete its co-ordination sphere using donor atoms from adjacent complexes, thereby forming polymeric structures. However, crystallisation of these polymeric materials from water affords monomers with two water ligands bound to the metal centre.[13]

NMR spectroscopic studies

NMR spectroscopic studies on diamagnetic [Ln(L)] (Ln = La, Y) and on paramagnetic [Ln(L)] (Ln = Yb, Sm) have been carried out and compared to the similar studies reported for $[Ln(DOTA)]^-$ complexes.[5,6,19] The ^{1}H NMR spectrum of [Y(L)] (300 MHz, 298 K, CD_3OD) shows a complex series of multiplets and doublets of doublets (Fig. 4). A 2D-COSY experiment combined with a ^{1}H-^{13}C coupling 2D experiment allowed an accurate assignment of the resonances (see Fig. 5 for labelling scheme). The protons of the methyl group of the pyruvate appear as a singlet at δ 2.18; the axial protons of the CH_2CH_2 moiety of each arm appear as a pair of complicated triplets due to vicinal and geminal coupling [a broad triplet at δ 3.81 for the axial proton of the CH_2 close to the imine nitrogen (H_{4a}) and a triplet of doublets at δ 3.03 for the axial proton of the CH_2 close to the macrocycle (H_{3a})]; the equatorial protons appear as a pair of doublet of doublets (δ 3.68 for H_{4e} and δ 2.80 for H_{3e}). J_{gem} is 17.2 Hz for H_{4e} and 12.3 Hz for H_{3e} while J_{trans}, due to the coupling between equatorial and axial protons of different CH_2 groups, are 5.7 and 5.1 Hz respectively. The CH_2CH_2 moiety of the macrocycle forms a series of multiplets that can be assigned as follows: the axial protons afford a pair of multiplets at δ 3.42 and δ 2.74 while the equatorial protons afford a pair of doublet

Table 2 ^{13}C NMR chemical shifts (ppm) for [Y(L)]

CH_3 (pyruvate)	16.0
CH_2–N (imine)	47.4
CH_2–N (arm)	59.1
N–CH_2–CH_2–N	52.6
N–CH_2–CH_2–N	59.2
C=N	171.5
COO^-	172.7

Table 3 ^1H NMR chemical shifts (ppm) for [La(L)] and [Sm(L)]

	Multiplicity	[La(L)]	[Sm(L)]
H_{4a}	t	3.73	2.37 (overlapping)
H_{4e}	d	3.61	3.09
H_{3a}	t	2.88	5.20
H_{3e}	d	2.75	3.24
H_{ax}	t	3.29	2.95
H_{eq}	d	2.80	2.39 (overlapping)
H_{ax}	t	2.58	0.83
H_{eq}	d	2.54	2.25
H_{pyruv}	s	2.05	1.88

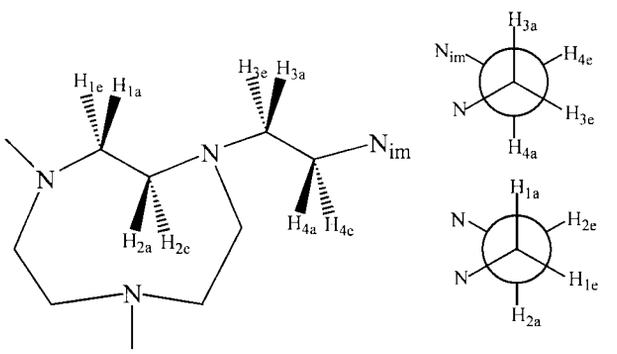

Fig. 5 Labelling scheme for the CH_2CH_2 linkers of the macrocycle and the arms and their Newman projections.

of doublets at δ 2.89 and δ 2.56. The 2D-COSY experiment allowed us to assess that the equatorial proton at δ 2.56 is geminal to the axial resonances at δ 2.74 (and H_{eq} at δ 2.89 to H_{ax} at δ 3.42). The geminal couplings are 12.9 and 16.1 Hz and the *trans* (eq–ax) couplings are 4.8 and 5.3 Hz. The ^{13}C NMR spectrum of [Y(L)] shows one peak less than expected, but with the help of the ^1H-^{13}C coupling experiment, we were able to determine that the "missing" peak is overlapped by the solvent peak (CD_3OD) and consequently we have assigned all the peaks as reported in Table 2.

The ^1H NMR spectrum of [La(L)] has also been recorded (300 MHz, 298 K, D_2O) and shows the same splitting pattern already described for [Y(L)] (Fig. 4). The peaks have been assigned and are reported in Table 3. The coupling constants are: 13.91 Hz for J_{gem} of H_4 (J_{trans} is 4.83 Hz), 12.77 Hz for J_{gem} of H_3 (J_{trans} is 5.33 Hz) and 14.16 and 11.51 Hz for J_{gem} of H_2 and H_1 (J_{trans} are 6.11 and 5.57 Hz). The equatorial proton at δ 2.80 is geminal to the axial resonances at δ 3.29 and H_{eq} at δ 2.54 to H_{ax} at δ 2.58.

Proton NMR spectra for paramagnetic lanthanide complexes are shifted over an expanded spectral region. The ^1H NMR spectrum of [Yb(L)] (300 MHz, 298 K, D_2O) shows nine resonances in the range between δ 36.4 to δ −29.0 (Fig. 6) due to nine different protons (H_{pyruv}, four axial and four equatorial protons). All the resonances have been assigned with the help of a 2D-COSY experiment (Table 4). The paramagnetic shift observed in the ^1H NMR spectrum of [Sm(L)] is much smaller and all the resonances lie between δ 0.83 and δ 5.20 (Fig. 6), and a coupling pattern similar to that for [Y(L)] and [La(L)] is observed. Resonances have been assigned on the basis of 2D-COSY experiments and are given in Table 3. The geminal

Table 4 Variable temperature ^1H NMR chemical shifts (ppm) for paramagnetic [Yb(L)]

	278 K	298 K	323 K	343 K
H_{3a}	40.7	36.4	32.0	28.1
H_{4e}	20.8	18.8	16.8	15.1
H_{4a}	15.3	14.0	14.2	11.6
H_{1a}	10.0	9.4	8.8	8.4
H_{pyruv}	9.7	9.0	8.3	7.7
H_{3e}	8.6	8.1	7.6	7.2
H_{1e}	−10.4	−8.6	−6.7	−5.0
H_{2e}	−12.6	−10.7	−8.5	−6.7
H_{2a}	−33.6	−29.0	−24.1	−19.9

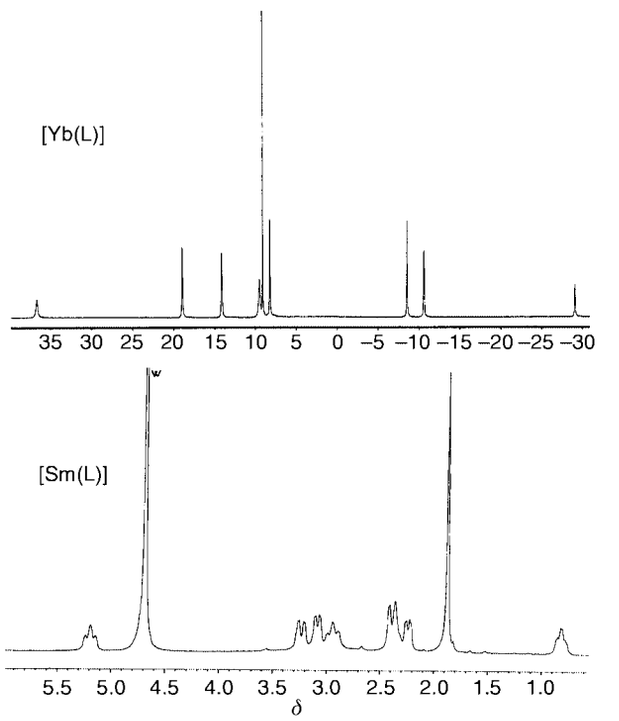

Fig. 6 ^1H NMR spectra of paramagnetic [Yb(L)] (above) and [Sm(L)] (below) in D_2O at 298 K.

coupling constants are for H_2, 10.14 Hz for H_4, 13.05 Hz for H_3, 14.03 Hz and 11.94 Hz for H_1. The equatorial proton at δ 2.39 is geminal to the axial resonances at δ 2.95 and H_{eq} at δ 2.25 to H_{ax} at δ 0.83. It is interesting to note that in all the ^1H NMR spectra of the paramagnetic complexes $[Ln(DOTA)]^-$ a coupling pattern has not been detected.[19]

The solution behaviour of various lanthanide poly(amino)-carboxylate complexes has been studied by variable temperature ^1H NMR and reported in the literature. The spectra of the DTPA (H_5DTPA = *N*,*N*,*N*′,*N*″,*N*″-diethylenetriaminepentaacetic acid) complexes of La(III), Pr(III), Eu(III) and Yb(III) in D_2O[20,21] all show signal coalescence as the temperature is raised. In addition, the lanthanide complexes of the macrocyclic ligand DOTA show this coalescence behaviour above about 45 °C in D_2O.[19]

The variable-temperature ^1H NMR behaviour of [Y(L)] and [Yb(L)] has therefore been investigated. Significantly, the ^1H NMR spectra of [Y(L)] in CD_3OD recorded between 223 and 333 K show a splitting pattern almost unchanged over this temperature range. This behaviour is indicative of a highly rigid cage formed by the ligand and it is particularly interesting with respect to the dynamic process involving the CH_2CH_2 moieties of the macrocycle observed in DOTA complexes at high temperature.[5,19] The dynamic behaviour of DOTA and DTPA lanthanide complexes has been attributed to a rotation about the metal ion involving a "shuffling" of co-ordinated acetates along with a backbone "ethylenic flip"[19,20] or "wagging" motion.[22]

None of these dynamic processes are observed for [Y(L)] suggesting not only that the metal ion is rigidly encapsulated by the three arms, but also that the macrocyclic framework remains bound and rigid even at high temperatures.

The temperature dependence of paramagnetic NMR shifts for Ln(III) complexes is quite complex.[23,24] Upon varying the temperature from 5 to 70 °C, the nine peaks observed in the ^{1}H NMR spectrum of [Yb(L)] are all shifted upfield (Table 4). The absence of coalescence or dynamic processes which have been observed in VT ^{1}H NMR studies of $[Pr(DOTA)]^{-}$[19] is again indicative of the high rigidity of the cage.

Experimental

NMR spectra were recorded on a Bruker DPX 300 (^{1}H, ^{13}C NMR and 2D coupling experiments) and IR spectra on a Perkin-Elmer 1600 spectrometer (FTIR, samples on KBr discs). All ^{1}H chemical shifts were referenced to residual protons in the deuterated solvents used and ^{13}C NMR spectra were referenced to the ^{13}C resonances of the solvents. Elemental analytical data were obtained by the Microanalytical Service (Perkin-Elmer 240B analyser) at the University of Nottingham and EI (electron impact) mass spectra were measured using a V6 Autospec V67070E spectrometer. Electrospray and FAB (fast atom bombardment) mass spectra were obtained by the EPSRC National Mass Spectrometry Service at the University of Swansea.

1,4,7-Triazacyclononane trihydrobromide ([9]aneN_3·3HBr, **1** in Scheme 1, was prepared as described in the literature.[25] All starting materials were obtained from Aldrich Chemical Co. and were used without further purification.

Synthesis of 1,4,7-tris(cyanomethyl)-1,4,7-triazacyclononane 2

[9]aneN_3·3HBr **1** (3.0 g, 8.07 mmol), chloroacetonitrile (1.9 g, 25.2 mmol), and Et_3N (10 g, 0.099 mol) in EtOH (150 cm^3) were refluxed under N_2 for 18 h. After cooling, the solvent was removed by rotary evaporation to yield a red oil which was dissolved in $CHCl_3$ (100 cm^3) and washed with H_2O (3 × 100 cm^3). The organic phase was collected and dried over $MgSO_4$, filtered, and dried by rotary evaporation. The resulting yellow oil was dried *in vacuo* to yield a pale yellow solid (1.052 g, 4.27 mmol, yield 53%). ^{1}H NMR: δ ($CDCl_3$) 2.85 (12 H, s, NCH_2), 3.59 (6 H, s, NCH_2CN). ^{13}C NMR: δ ($CDCl_3$) 54.12 (N*C*H$_2$), 46.49 (N*C*HCN), 116.14 (*C*N). EI mass spectrum: *m*/*z* found 163.2, 138.1, 124.1 for 166.2 [$M^+ - 2CH_2CN$], 140.2 [$M^+ - 2CH_2CN - CN$] and 126.1 [$M^+ - 3CH_2CN$] respectively. IR (KBr disk), ν/cm^{-1}: 2937m, 2840m, 2227m (CN stretch), 1455m, 1132w, 1099w, 887w, 844w. (Found %: C, 58.2; H, 7.6; N, 34.0. Calc. for $C_{12}H_{18}N_6$: C, 58.5; H, 7.4; N, 34.1).

Synthesis of 1,4,7-tris(2-aminoethyl)-1,4,7-triazacyclononane (L^1)

1,4,7-Tris(cyanomethyl)-1,4,7-triazacyclononane **2** (0.320 g, 1.23 mmol) and BH_3·THF (40 cm^3, 1 M solution in THF) were refluxed under N_2 for 48 h. After cooling, excess borane was destroyed by adding water (5 cm^3), then the solution was dried *in vacuo*. The white solid obtained was dissolved in 6 M HCl (50 cm^3) and heated under reflux for 24 h. After cooling, the solution was dried *in vacuo* to yield a white solid. The solid was dissolved in the minimum amount of water and the solution obtained was passed through a Dowex 1 × 8–200 column (10 g) activated with a solution 1 M of sodium hydroxide. The solvent was removed under reduced pressure to yield a colourless oil (0.270 g, 1.045 mmol, yield 85%). ^{1}H NMR: δ ($CDCl_3$) 2.76 (12 H, s, NCH_2), 2.75, 2.59 (12 H, tt, CH_2CH_2N), 1.63 (6 H, broad, NH_2). ^{13}C NMR: δ ($CDCl_3$) 56.90 (N*C*H$_2$), 62.21 (N*C*H$_2$CH$_2$NH$_2$), 40.26 (NCH$_2$*C*H$_2$NH$_2$). EI mass spectrum: *m*/*z* found 213.2, 199.2, 185.2 and 159.2 for 214.3 [$M^+ - CH_2CH_2NH_2$], 198.3 [$M^+ - CH_2CH_2NH_2 - NH_2$], 184.3 [$M^+ - CH_2CH_2NH_2 - CH_2NH_2$], 154.2 [$M^+ - 2CH_2CH_2NH_2$] respectively (Found %: C, 55.5; H, 11.9; N, 32.3. Calc. for $C_{12}H_{30}N_6$: C, 55.8; H, 11.7; N, 32.5).

Synthesis of [Y(L)] 3

1,4,7-Tris(2-aminoethyl)-1,4,7-triazacyclononane (L^1) (39.8 mg, 0.154 mmol), sodium pyruvate (50.9 mg, 0.462 mmol) and $Y(NO_3)_3$ (56.2 mg, 0.154 mmol) were heated under reflux in MeOH (30 cm^3) for 2 h. After cooling, the solvent volume was reduced, Et_2O was added and a pale yellow solid was obtained. The solid was filtered off and dried under reduced pressure. $NaNO_3$ was removed from the yttrium complex product by passing a concentrated solution of the solid in MeOH through an LH-20 Sephadex column. Addition of Et_2O yielded a white solid (61.2 mg, 0.11 mmol, yield 71.4%). Single crystals suitable for X-ray structural analysis were obtained by diffusion of Et_2O vapour into a solution of the complex in MeOH at room temperature. Mass spectrum (electrospray) *m*/*z* = 577 (M^+ [$C_{21}H_{33}N_6O_6Y + Na^+$]) (Found %: C, 44.5; H, 6.6; N, 13.4. Calc. for $C_{21}H_{33}N_6O_6Y$·2CH_3OH: C, 44.7; H, 6.7; N, 13.6). IR (KBr disk), ν/cm^{-1}: 2920w, 2854w, 1654s and 1617s ($\nu_{C=N,C=O}$), 1384m, 1206m, 1110w.

Synthesis of [La(L)] 4

1,4,7-Tris(2-aminoethyl)-1,4,7-triazacyclononane (L^1) (39.8 mg, 0.154 mmol), sodium pyruvate (50.9 mg, 0.462 mmol) and $La(OTf)_3$·H_2O (90.3 mg, 0.154 mmol) were heated under reflux in MeOH (30 cm^3) for 2 h. After cooling, the solvent volume was reduced, and Et_2O was added to afford a white solid. The product was collected and dried *in vacuo* (65.4 mg, 0.108 mmol, yield 70.3%). Single crystals suitable for X-ray structural analysis were obtained by diffusion of Et_2O vapour into a solution of the complex in MeOH at room temperature. Mass spectrum (FAB) *m*/*z* = 627 (M^+ [$C_{21}H_{33}N_6O_6La + Na^+$]) (Found %: C, 41.0; H, 6.0; N, 12.4. Calc. for $C_{21}H_{33}N_6O_6La$·2CH_3OH: C, 41.3; H, 6.2; N, 12.6). IR (KBr disk), ν/cm^{-1}: 2914w, 2849w, 1653s and 1610s ($\nu_{C=N,C=O}$), 1384m, 1364m, 1274s, 1201s, 1134m, 1111m, 1031m, 641m, 573w, 518w.

Synthesis of [Sm(L)] 5

1,4,7-Tris(2-aminoethyl)-1,4,7-triazacyclononane (L^1) (39.8 mg, 0.154 mmol), sodium pyruvate (50.9 mg, 0.462 mmol) and $SmCl_3$·6H_2O (56.2 mg, 0.154 mmol) were heated under reflux in MeOH (30 cm^3) for 2 h. After cooling, the solvent volume was reduced and Et_2O was added to afford a pale yellow solid. The product was collected and dried *in vacuo* (69.1 mg, 0.112 mmol, yield 72.7%). Single crystals suitable for X-ray structural analysis were obtained by diffusion of Et_2O vapour into a solution of the complex in MeOH at room temperature. Mass spectrum (FAB) *m*/*z* = 640 (M^+ [$C_{21}H_{33}N_6O_6Sm + Na^+$]) (Found %: C, 39.8; H, 6.4; N, 12.2. Calc. for $C_{21}H_{33}N_6O_6Sm$·2CH_3OH·H_2O: C, 39.6; H, 6.2; N, 12.0). IR (KBr disk), ν/cm^{-1}: 2924w, 2851w, 1653s and 1616s ($\nu_{C=N,C=O}$), 1387m, 1204s, 1110m, 1030w.

Synthesis of [Yb(L)] 6

1,4,7-Tris(2-aminoethyl)-1,4,7-triazacyclononane (L^1) (39.8 mg, 0.154 mmol), sodium pyruvate (50.9 mg, 0.462 mmol) and $YbCl_3$·6H_2O (59.7 mg, 0.154 mmol) were heated under reflux in MeOH (30 cm^3) for 2 h. After cooling, the solvent volume was reduced, and Et_2O added to afford a pale yellow solid. The product was collected and dried *in vacuo* (59.7 mg, 0.093 mmol, yield 60.7%). Mass spectrum (FAB) *m*/*z* = 662.3 (M^+ [$C_{21}H_{33}N_6O_6Yb + Na^+$]) (Found %: C, 38.0; H, 5.6; N, 12.1. Calc. for $C_{21}H_{33}N_6O_6Yb$·CH_3OH·H_2O: C, 38.4; H, 5.7; N, 12.2). IR (KBr disk), ν/cm^{-1} 2915w, 2845w, 1653s and 1617s ($\nu_{C=N,C=O}$), 1387m, 1209m, 1109m.

Table 5 Crystal data and X-ray experimental details for [Y(L)] **3**, [La(L)] **4** and [Sm(L)] **5**

	3	**4**	**5**
Formula	$C_{21}H_{33}N_6O_6Y\cdot 2CH_3OH\cdot 0.5H_2O$	$C_{21}H_{33}N_6O_6La\cdot 3CH_3OH\cdot H_2O$	$C_{21}H_{33}N_6O_6Sm\cdot 3CH_3OH\cdot 0.5H_2O$
M	627.03	718.59	721.02
Crystal system	Trigonal	Trigonal	Trigonal
Space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
$a = b$/Å	28.215(4)	28.215(4)	28.337(4)
c/Å	23.215(5)	23.170(5)	23.405(5)
V/Å^3	15974(5)	15974(5)	16276(5)
T/K	203(2)	203(2)	203(2)
Z	18	18	18
μ/mm^{-1}	1.688	1.256	1.673
Unique data	6634	8390	8051
Observed data	5393	6714	6489
$R1$, $wR2$[a]	0.0662, 0.2020	0.0434, 0.1289	0.0489, 0.1485

[a] $R1$ based on observed data with $I \geq 2\sigma(I)$, $wR2$ on all unique data.

Crystallography

Crystal data, data collection and refinement parameters for compounds [Ln(L)] (Ln = Y, Sm and La) are given in Table 5, with selected bond lengths in Table 1. Data were collected on a Stoe IPDS diffractometer equipped with a imaging plate area detector and a rotating anode generator, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). Semi-empirical absorption corrections based on the program HABITUS[26] were applied for all compounds.

In all the structures disorder was identified in methanol molecules and it was modelled as follows: in **3** one disordered MeOH molecule was modelled using partial occupancy models over one site for the C atoms (occupancy factors of 0.50) and over three sites for the O atoms (occupancy factors of 0.167). In **4** the two disordered MeOH molecules were modelled using partial occupancy models over three sites for both C and O atoms for one molecule and only for the O atoms in the other molecule (occupancy factors of 0.33). Finally, in **5** the two disordered MeOH molecules were modelled using partial occupancy models over two sites for both C and O atoms in one molecule and only for the O atoms for the other. Appropriate restraints to bond distances were applied in all the disordered molecules. In all the structures the largest residual electron density features lay near the disordered MeOH molecules.

CCDC reference number 186/1985.

See http://www.rsc.org/suppdata/dt/b0/b002794o/ for crystallographic files in .cif format.

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