DALTON
FULL PAPER

Synthesis, NMR, relaxometry and circularly polarised luminescence studies of macrocyclic monoamidetris(phosphinate) complexes bearing a remote chiral centre

Silvio Aime,[c] Mauro Botta,[c] Rachel S. Dickins,[a] Christine L. Maupin,[b] David Parker,*,†,[a] James P. Riehl[b] and J. A. Gareth Williams[a]

[a] *Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE*
[b] *Department of Chemistry, Michigan Technological University, Houghton, MI 49931-1295, USA*
[c] *Dipartimento di Chimica I. F. M., Universita degli Studi di Torino, via P. Giuria 7, Torino 10125, Italy*

Lanthanide complexes of macrocyclic monoamidetris(phosphinate) ligands are partially hydrated in aqueous solution. Introduction of a chiral centre into the amide group leads to the formation of only two non-interconverting complex diastereoisomers (2 : 1 for α-phenylethyl and 4 : 1 for α-1-naphthylethyl). Proton, ^{31}P NMR and circularly polarised luminescence studies indicated that the configuration at the chiral carbon centre determines the helicity of the layout of the pendent arms and the macrocyclic ring conformation, with an *RRR* or *SSS* configuration preferred at the phosphorus centres.

At the outset of a project directed towards the study of intramolecular stereoselective energy-transfer processes in lanthanide complexes, it was necessary first to understand the structural features which determine the relative energies of suitable complex stereoisomers in aqueous solution. For such a study, kinetically robust complexes are required that are relatively static on the NMR time-scale and tri- or tetra-N-substituted derivatives of 1,4,7,10-tetraazacyclododecane (cyclen) are well suited for this purpose.[1] Examples of such ligands are the monoamidetris(phosphinates), *e.g.* L^{1c} and L^{1d}, in which the four ring nitrogens and four pendent oxygens may bind cooperatively to a lanthanide ion to give a well defined complex.[2] The Y and Gd complexes of such ligands are kinetically stable with respect to dissociation both *in vitro* (k_{obs} is *ca.* 2×10^{-6} s^{-1} at pH 1, 310 K)[3] and *in vivo* (>99.7% of the complex is excreted intact over 7 d).[4] In the complexes with Eu, Y and Gd, it has been shown that one predominant stereoisomer exists in aqueous solution (as a 50 : 50 mixture of enantiomers) and partial, *that is non-integral*, hydration of the bound ion occurs.[2,5] The ligands examined to date in this series possess no stereogenic centres at carbon. It was of interest to determine the effect of introducing a chiral centre into the amide group examining the stereoisomerism in the derived lanthanide complexes. An added impetus for this study came from the observation that in the lanthanide complexes of enantiopure tetraamides, greater than 99% of one relatively rigid enantiopure complex is present in solution wherein the remote chiral centre at carbon determines both the helicity of the four pendent amide 'arms' and the configuration of the 12[ane]N_4 ring.[6,7] Accordingly, we have synthesised the chiral monoamidetris(phosphinate) ligands, H_3L^{1a}, H_3L^{1b} and H_3L^2 and examined the aqueous solution behaviour of their Eu, Gd and Tb complexes by NMR, luminescence and circularly polarised emission techniques.

Results and Discussion

Synthesis

The ligands and their lanthanide complexes were prepared according to established procedures (Scheme 1).[3,8,9] Monoalkylation of the molybdenumtricarbonyl complex of cyclen with the α-chloroamides **3a**, **3b**, **3c** or **4**, followed by oxidative deprotection yielded the monosubstituted derivatives **5a**, **5b**, **5c** and **6a** respectively. Co-condensation of these secondary amines with resublimed paraformaldehyde $(CH_2O)_n$ in the presence of $MeP(OEt)_2$ in dry THF led to phosphinoxymethylation of the three ring nitrogens. Subsequent base hydrolysis (10% aqueous KOH, 20 °C) gave the tris(phosphinates) L^{1a}, L^{1b} and L^2 and the lanthanide ion was introduced in water by reaction with the appropriate lanthanide acetate salt.

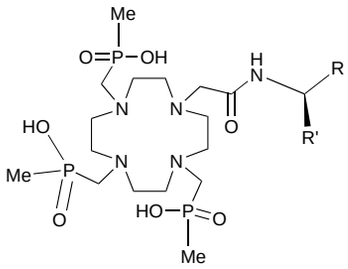
Stereochemical and NMR analysis

In the lanthanide complexes of L^{1c} and L^{1d}, there are 32 possible stereoisomers, *i.e.* 16 pairs of enantiomers which are distinguishable by NMR spectroscopy in an achiral environment.[2] These arise from three chiral elements: the *R* or *S* configuration at each phosphorus, the left- or right-handed helicity defining the lay-out of the four pendent arms and the overall Δ or Λ configuration of the 12[ane]N_4 ring. The introduction of a remote chiral centre in the amide moiety renders all 32 isomers diastereoisomeric and therefore distinguishable in principle by NMR spectroscopy. Prior work with an achiral amide substituent has revealed that one major diastereoisomer exists in solution, as was deduced from ^{31}P and ^{1}H NMR spectroscopy, and inspection at high-resolution of the emission band at 579.2 nm of the $\Delta J = 0$ transition of the Eu complex.[1,2]

The europium complexes of $L^{1a/1b}$ and L^2 were examined by ^{31}P NMR spectroscopy in D_2O (Fig. 1). Analysis of the spectra revealed the presence of two major species (appearing as three line singlets) and with $[EuL^2]$ at least three other minor species can be discerned. The ratio of the major isomers is dependent upon the steric bulk of the chiral amide group, being 2 : 1 for the phenyl and 4 : 1 for the 1-naphthyl containing complexes.‡ Addition of up to 5 equivalents of β-cyclodextrin to $[EuL^2]$ or $[EuL^{1a}]$ caused a shifting in all of the ^{31}P resonances but no change in the number of resonances observed. On the other

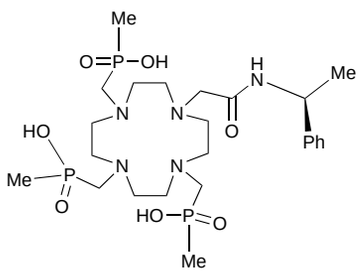
† E-Mail: david.parker@durham.ac.uk

‡ The complex $[EuL^{1a}]$ was analysed by analytical HPLC using a β-cyclodextrin chiral column. Two species were observed in ratio 4 : 1 [275 K; t = 0 min (95% H_2O, 5% MeOH), t = 25 min (100% MeOH)] using a simple gradient, but the baseline separation (Δt_R = 0.4 min) was insufficient to allow semi-preparative resolution.

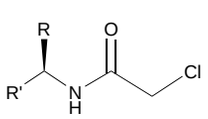


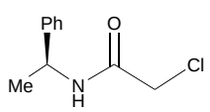
(*R*)- H_3L^{1a} R = 1-$C_{10}H_7$, R' = Me
(*S*)- H_3L^{1b} R = Me, R' = 1-$C_{10}H_7$

H_3L^{1c} R = H, R' = 1-$C_{10}H_7$
H_3L^{1d} R = H, R' = H



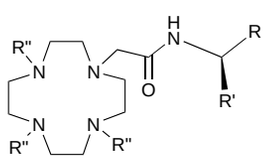
(*S*)-H_3L^2



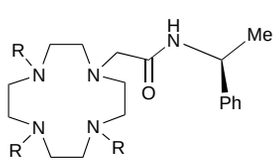


(*S*)-**4**

(*R*)- **3a** : R' = 1-$C_{10}H_7$, R = Me
(*S*)- **3b** : R' = Me, R = 1-$C_{10}H_7$
3c : R = H, R' = 1-$C_{10}H_7$



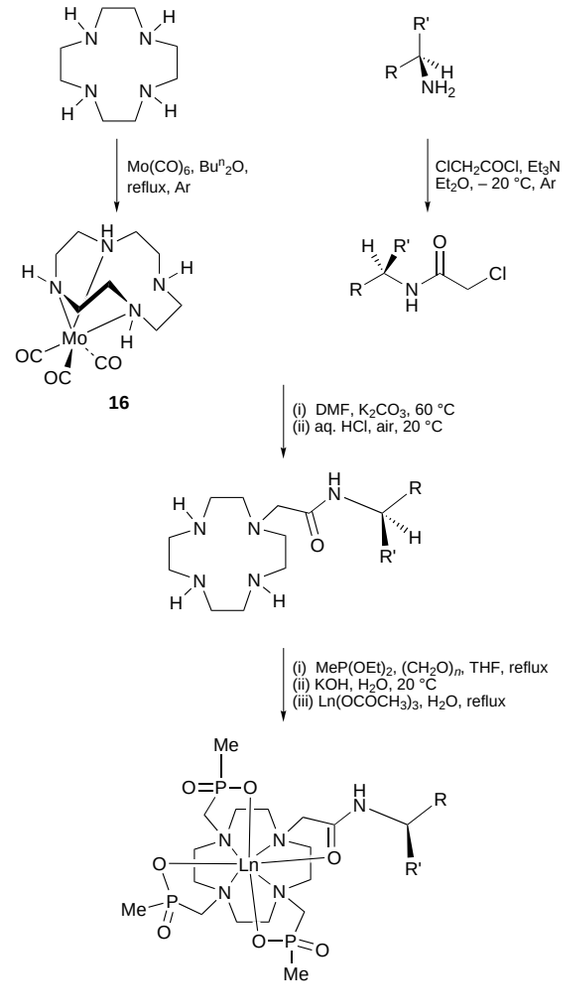
(*R*)- **5a** : R = 1-$C_{10}H_7$, R' = Me, R'' = H
(*S*)- **5b** : R = Me, R' = 1-$C_{10}H_7$, R'' = H
5c : R'' = R = H, R' = 1-$C_{10}H_7$
5d : R = 1-$C_{10}H_7$, R' = Me, R'' = CH_2PMeO_2Et
5e : R = Me, R' = 1-$C_{10}H_7$, R'' = CH_2PMeO_2Et
5f : R = H, R' = 1-$C_{10}H_7$, R'' = CH_2PMeO_2Et



(*S*)-**6a** : R = H
6b : R = CH_2PMeO_2Et

hand, when 2 equivalents of β-cyclodextrin was added to [EuL^{1c}], the three resonances at δ 96.6, 84.4 and 67.4 associated with the major isomer (≈90%), shifted and resolved to give three pairs of resonances of equal intensity at δ 96.7, 96.5, 84.1, 83.2, 61.1 and 60.8. In this case, the β-cyclodextrin is acting as a chiral solvating agent and is binding weakly to the enantiomers of [EuL^{1c}] to give two diastereoisomeric species.

The transverse relaxation times, T_2, of the proton resonances in [$EuL^{1a/1b}$] and [EuL^2] are sufficiently long to permit the detection of coupling patterns at low applied magnetic fields (*e.g.* 90 MHz), whereas at higher field this coupling information is lost



(*R*)-L^{1a} R = 1-$C_{10}H_7$, R' = Me
(*S*)-L^{1b} R = Me, R' = 1-$C_{10}H_7$
L^{1c} R = H, R' = 1-$C_{10}H_7$
L^{1d} R = H, R' = H
(*S*)-L^2 R = Me, R' = Ph

Scheme 1

due to line-broadening.[10,11] A partial analysis of the ^1H–^1H COSY spectrum for [EuL^2] was carried out (see Experimental section for details). The presence of two major isomers was confirmed and was most evident in the appearance of two sets of P-Me doublets in ratio 2:1, consistent with the ^{31}P NMR analysis. Variable-temperature ^1H and ^{31}P-{^1H} NMR studies of [EuL^{1a}] were carried out in the range 290 to 363 K. The ^{31}P NMR study revealed a selective broadening of the resonances due to the minor isomers: at 315 K they had broadened, whereas the major resonances remained sharp (Fig. 2). At 333 K, the resonances of the major isomers also begin to broaden, and at 363 K one set had overlapped but for the pair around δ 90/93 the shift non-equivalence was the same as it was at 248 K. Allowing for the expected rather complex *T* dependence of the ^{31}P NMR shift in Eu complexes, such behaviour is consistent with exchange between the two major isomers and the other minor isomers, but the two major isomers themselves are *not* in rapid exchange with each other (on the NMR time-scale) over this temperature range.

By comparison with reported[12,13] crystal structures for the La, Y, Eu, Gd and Yb complexes of a related tetra(benzylphosphinate)–12[ane]N_4 ligand (revealing an *RRRR* or *SSSS* configuration at P), and by consideration of minimisation of *steric* hindrance, it is most likely that in the observed major

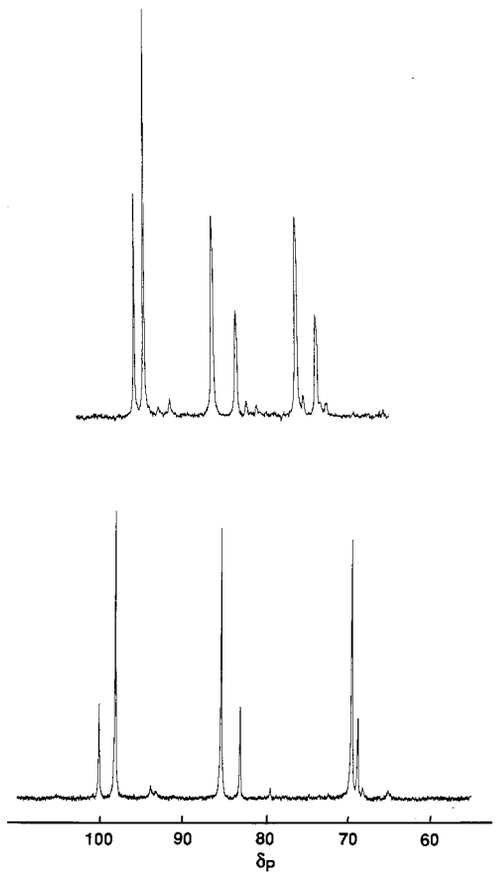


Fig. 1 The ^{31}P NMR spectra of [EuL^2] (upper) and [EuL^{1a}] (lower) showing the formation of two major diastereoisomers in solution (101.2 MHz, pD 5.5, 298 K)

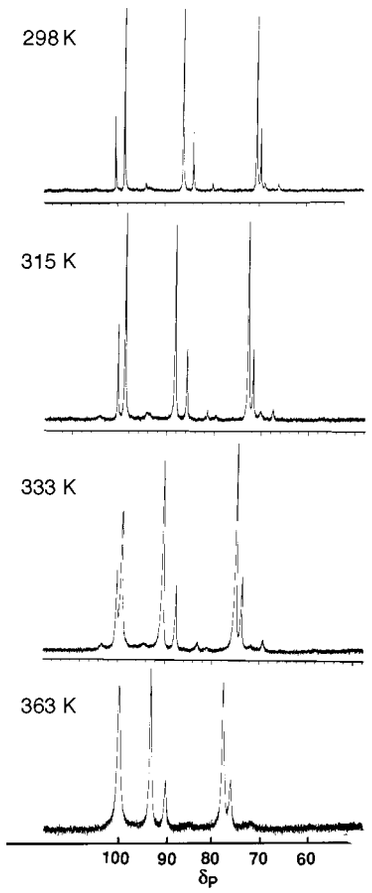


Fig. 2 Variable-temperature ^{31}P NMR spectra for [EuL^{1a}] at 298, 315, 333 and 363 K (161.9 MHz, pD 5.5)

isomers of [EuL^{1a}] and [EuL^2], the complex adopts a twisted square-antiprismatic structure and the P-Me groups are directed away from the 12[ane]N_4 ring with an *RRR* or *SSS* configuration at phosphorus. It is then evident that the observed diastereoisomers will possess the same ring conformation and lay-out of the pendent arms, but will differ only in the configuration at phosphorus. The two major diastereoisomers of [EuL^2] that are observed are therefore likely to be (*S-SSS*) and (*S-RRR*), specifying chirality at C and P in turn. Similarly for [EuL^{1a}] and [EuL^{1b}], the observed diastereoisomers are (*R-RRR*) and (*R-SSS*), and (*S-SSS*) and (*S-RRR*). Such an analysis is consistent with the observation that ^{31}P and ^1H NMR spectra for the 1-naphthyl containing Eu complexes were identical, could not be resolved by addition of β-cyclodextrin and were not in exchange on the NMR time-scale. Interconversion between the major pair of isomers would require cleavage of the strong Ln–O bond (typically 2.4 Å),[12] whereas exchange between the minor isomers observed may occur by ring inversion or by a pendent arm rotation.[1,14] Such behaviour is then consistent with the solution dynamics of related 12[ane]N_4 complexes wherein a remarkable stability of the Ln–O bond, with respect to dissociation, had been previously identified.[15–17]

Relaxation properties of gadolinium complexes

The relaxation rate of the water proton in the presence of [GdL^{1a}] and [GdL^2] has been measured over a range of applied magnetic fields, and at various temperatures. The value of the measured relaxivity (the increment of the water proton relaxation rate per unit concentration) and analysis of the associated NMRD (magnetic field dependence of the relaxivity) profiles allows information to be deduced on the hydration state and on the various correlation times associated with solution relaxation. Details of the form of the analysis used, its interpretation and representative data are given in several recent references.[1,12,15,18]

Relaxivity values, R_{1p}, (29 MHz, 298 K) of 3.65 and 3.45 dm^3 mmol^{-1} s^{-1} were measured for [GdL^2] and [GdL^{1a}] respectively. These values remained fairly constant over the pH range 2 to 12, only increasing slowly at pH < 2, as the onset of complex dissociation led to the release of some of the free aquated Gd^{3+} ion. The values are higher than those reported for the related tetrabenzylphosphinate (R_{1p} = 1.85 dm^3 mmol^{-1} s^{-1}) and tetramethylphosphinate complexes (R_{1p} = 2.44 dm^3 mmol^{-1} s^{-1}) which are known to possess *no* bound water molecules.[12] The replacement of a phosphinate group by an amide binding site allows a water molecule to approach the lanthanide more closely, but may not lead to the water molecule being bound by oxygen.[2,5] Analysis of the NMRD profiles of [GdL^2] and [GdL^{1a}] (Fig. 3 and Table 1), suggested that there was a relatively long Gd–OH distance (3.40 and 3.44 Å respectively) consistent with the presence of a well defined 'second-sphere' co-ordinated water.[5,12] This second co-ordination sphere contribution may result from the ability of the carboxamide oxygen to act as a hydrogen-bond acceptor, thereby bringing the water molecule sufficiently close to the paramagnetic centre to affect the solvent relaxation (Scheme 2). Partial hydration of this type has been reported previously in related complexes,[2] and in this case the water molecule approaches more closely to the Gd in the less-encumbered complex [GdL^2] (3.40 Å), compared to [GdL^{1a}] (3.44 Å).

Solution NMR studies had revealed that addition of β-cyclodextrin to [EuL^2] and [EuL^{1a}] led to shifts in the ^{31}P NMR resonance of the non-equivalent P atoms. The strength of the interaction with [GdL^{1a}] may be evaluated by measuring the dissociation constant, K_d, for the β-cyclodextrin complex with [GdL^{1a}] using the proton relaxation enhancement technique.[19] This involves monitoring the increase in relaxivity, at a

Table 1 The NMR relaxation parameters obtained by fitting the experimental NMRD profiles of [GdL^2] and [GdL^{1a}]

	[GdL^2]		[GdL^{1a}]		
Parameter[a]	298 K	312 K	278 K	298 K	312 K
τ_{so}/ps	122	91	118	124	113
τ_v/ps	18.3	9.1	24.4	15.7	8.4
τ_r/ps	100	61	190	91	60
τ_m/ns	0.9	0.5	1.3	0.8	0.6
q	1	1	1	1	1
r/Å[b]	3.40	3.40	3.44	3.44	3.44
a/Å	4.0	4.0	4.0	4.0	4.0
10^{-5} D/cm^2 s^{-1}	2.40	3.15	1.0	2.4	3.15

[a] τ_{so} is the electronic relaxation time at zero field, τ_v is the field-independent correlation time, τ_m is the exchange rate for the proximate water molecule and τ_r is the rotational correlation time for the complex; q is the nearest integral hydration number and r is the mean proton Gd distance; a is the mean distance of approach of 'outer-sphere' water molecules and D is the diffusion coefficient of the complex. [b] Structural analyses show that Gd–H distances are *ca.* 3.0 in $q = 1$ complexes and >4.0 Å in $q = 0$ complexes.[1]

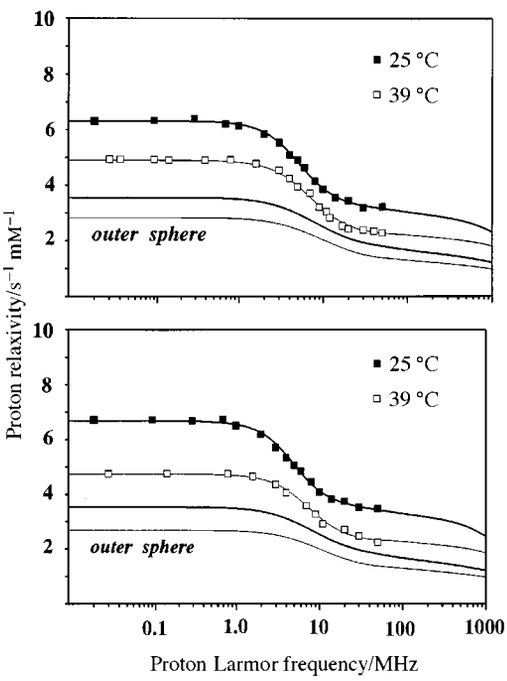
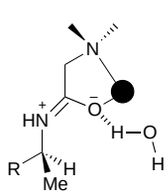


Fig. 3 The NMRD profiles at 298 and 312 K for [GdL^2] (upper) and [GdL^{1a}] (lower). The solid line through the experimental points shows the simulated behaviour using a best-fitting procedure to relaxation theory. The lower curves show the outer-sphere contributions to the observed relaxivity



Scheme 2

fixed Larmor frequency, when a given concentration of the gadolinium complex is titrated with increasing amounts of β-cyclodextrin. On formation of the adduct, the molecular volume of the gadolinium complex is increased, leading to a slower rotational correlation time, τ_R, and an associated increase in relaxivity. The titration data were handled as a plot of the relaxivity enhancement factor, ε* (representing the ratio of the paramagnetic relaxation rates in the presence and absence of β-cyclodextrin), as a function of β-cyclodextrin concentration. Using the quadratic expression in equation (1),[13]

$$\varepsilon^* = \left(\frac{1}{\varepsilon_b}\right) \frac{C_T + nM_T + K_d - [(C_T + nM_T + K_d)^2 - 4nM_TC_T]^{\frac{1}{2}}}{2C_T} + 1 \quad (1)$$

wherein C_T = total concentration of complex, M_T = total β-cyclodextrin concentration, $n = 1$ and ε_b = relaxivity of the bound complex, a value for K_d of 2.6×10^{-2} dm^3 mol^{-1} was obtained by an iterative best fitting procedure. This is a relatively weak interaction in comparison to the dissociation constant for β-cyclodextrin with 1-methylnaphthalene (K_d = 3.2×10^{-3} dm^3 mol^{-1}, H_2O, 298 K).[20]

Luminescence behaviour of Eu and Tb complexes

The UV absorption spectra of [LnL^2] and [LnL^{1a}] revealed the presence of a phenyl ππ* absorption at 254 nm (ε = 200 dm^3 mol^{-1} cm^{-1}) and a naphthyl ππ* absorption band at 286 nm (ε = 9300 dm^3 mol^{-1} cm^{-1}). The aromatic chromophore serves as a useful antenna group in these complexes allowing sensitised emission of the proximate lanthanide to occur, following intramolecular energy transfer.[1] The metal-based emission lifetimes and quantum yields were measured in H_2O and D_2O (Table 2). As expected with the Eu complexes, quantum yields were low due to efficient deactivation of the singlet excited state involving a photoinduced electron transfer to the readily reduced europium ($Eu^{3+/2+} = -0.35$ V) centre. The [TbL^{1a}] complex also exhibited a weak emission in aereated aqueous solution, but a quantum yield of 0.1 was measured in deaereated solution. This behaviour may be attributed to a competitive thermally activated back energy transfer process from the emissive $^5D_4$ state to the naphthyl triplet. The naphthyl triplet is quenched by molecular oxygen: removal of molecular oxygen eliminates this deactivation pathway and strong emission is then observed. The photophysical details of such processes have recently been reported in analogous mononaphthyl[2] and tetranaphthyl tetraamide complexes.[21,22]

The lifetimes of the emissive state in H_2O and D_2O were determined by observing the intensity of the luminescence after a range of delay times (Table 2). The amide NH protons undergo rapid exchange in D_2O,[22] so that comparison of the radiative rate constants in H_2O and D_2O allows the effect of the quenching amide NH and closely diffusing OH oscillators to be discerned. Recent analysis of over a dozen eight- and nine-coordinate Eu complexes of 12[ane]N_4[2,5,23] has shown that a secondary amide NH oscillator contributes about 0.08 ms^{-1} in terms of k [equation (2)] (k_{nat} is the natural radiative lifetime, k_{nr}

$$k_{obs}^{H_2O} = k_{nat} + k_{nr} + \Sigma k_{XH} + \Sigma k_{C=O} \quad (2)$$

is the rate constant for non-radiative deactivation and Σk_{XH}/$\Sigma k_{C=O}$ is the sum of the rate constants for energy transfer to proximate, energy matched XH or C=O oscillators). For terbium complexes this amide NH quenching effect is much smaller and may be ignored. A hydrophilic 12[ane]N_4 Eu complex gives rise to quenching of the Eu $^5D_0$ state from the unbound, but closely diffusing OH oscillators.[23] Again, analysis of >12 related complexes reveals that this effect contributes on average *ca.* 0.25 ms^{-1} to the measured k value. After allowing for these effects (Table 2), a corrected hydration state, q, may be estimated. The values obtained reveal that the Eu complexes examined are only partially hydrated (non-integral values) with the naphthyl complex giving a lower q value than the phenyl. The analogous Tb complexes are even less hydrated. This pattern of behaviour has been observed previously with 'achiral' monoamidetris(phosphinate) lanthanide complexes,[2,5] and is consistent with the NMRD derived distance parameter (Table 1), which was in an intermediate

Table 2 Luminescence lifetimes and observed radiative rate constants for the europium and terbium complexes in H_2O and D_2O and their use in estimating the hydration state of the metal

Complex[a,d]	τ_{H_2O}/ms	τ_{D_2O}/ms	k_{H_2O}/ms^{-1}	k_{D_2O}/ms^{-1}	Δk[c]/ms^{-1}	$\Sigma_{OH_{os}+NH}$	q^{1c}_{corr}
[EuL^{1d}][b]	0.76	1.85	1.32	0.54	0.78	−0.33	0.56
[EuL^{2}]	0.68	1.74	1.47	0.57	0.90	−0.33	0.71
[EuL^{1a}]	0.73	1.70	1.37	0.59	0.78	−0.33	0.56
[TbL^{1d}][b]	3.20	4.30	0.31	0.23	0.08	−0.06	0.1
[TbL^{2}]	3.00	4.00	0.33	0.25	0.08	−0.06	0.1

[a] Quantum yields for [EuL^2] were 1×10^{-3} and 2×10^{-3} in H_2O and D_2O respectively, for [TbL^2] 0.12 and 0.18 and for [EuL^{1a}] 0.8×10^{-3} (H_2O) and 1.7×10^{-3} (D_2O). [b] Data from refs. 2, 5. [c] Values of q^{1c}_{corr} for Eu complexes were obtained by subtracting 0.08 ms^{-1} from Δk to compensate for the amide NH quenching, and 0.25 ms^{-1} to allow for quenching by 'outer-sphere' (unbound) OH oscillators. Using $q = A'\Delta k$ (A' is an empirically derived proportionality constant reflecting the sensitivity of the given lanthanide to quenching by OH oscillators); for Eu, $A' = 1.25$. For the Tb complexes, a correction of 0.06 ms^{-1} was applied to allow for 'outer-sphere' OH quenching only. Full details of this modified method of analysis will be reported subsequently. [d] For complexes of L^2 and L^{1d}, excitation was at 254 nm; for the complex of L^{1a}, at 290 nm.

range between that found for a metal-bound water and a purely 'outer-sphere' hydrated complex. The lower hydration of the Tb complexes has now been seen consistently in many 12[ane]N_4 complexes, and is also apparent in aqua ion chemistry. The change in co-ordination number of hydrated ions ('the gadolinium break') halfway along the 'f'-block series is well known despite the small (2.4 pm) difference in ionic radius between Eu and Tb.[24]

Circularly polarised luminescence

Circularly polarised luminescence (CPL) is the emission analogue of circular dichroism, and may be used to probe the chiral environment of the lanthanide excited state.[25–27] The total emission and CPL spectra associated with the $^5D_4 \longrightarrow {}^7F_5|{}^7F_4|{}^7F_3$ transitions, following direct laser excitation of the $^7F_6 \longrightarrow {}^5D_4$ transition in [TbL^2] at 488 nm were measured in water (Fig. 4). The measured emission dissymmetry factors, g_{em}, were quite large and measured +0.17 ($\Delta J = -1$, 543 nm), −0.06 ($\Delta J = 0$, 584 nm) and −0.12 ($\Delta J = +1$, 621 nm) for the observed transitions. The CPL spectra obtained were independent of the nature of the excitation: identical CPL spectra were obtained with left- or right-handed circularly polarised light. Although there may, in theory, be preferential absorption of left- or right-handed CP light, the circularly polarised emission is independent of the handedness of the excitation source. It is the chirality (helicity) about the metal centre that determines the sign and magnitude of the CPL.

Strong CPL was also observed with [TbL^{1a}] in degassed aqueous solution either following direct laser excitation or indirect excitation into the proximate naphthyl chromophore ($\lambda_{ex} = 300$ nm) (Fig. 5). The CPL spectra obtained with [TbL^{1a}] were remarkably similar to those obtained with [TbL^2]. The values of g_{em} (+0.18 for $\Delta J = -1$ at 540 nm) were essentially the same and were independent of the mode of excitation. The similarity of behaviour between the two complexes is not particularly surprising, since the complexes only differ in the aryl substituent in the amide moiety.

Proton and ^{31}P NMR studies on the corresponding Eu complexes had revealed that two diastereoisomers are not exchanging and exist in solution in a ratio of 2 : 1 for [LnL^2] and 4 : 1 for [LnL^{1a}]. If the diastereoisomers have identical ring conformations and the same layout of the pendent arms, then the observed CPL will be due to contributions from *both* isomers. On the other hand, if the two diastereoisomers have enantiomeric ring conformations and pendent arm helicities, then equal and opposite CPL spectra will be observed for each isomer: the CPL from the major isomer would then cancel out the contribution to the CPL from the minor isomer, so the measured CPL is due to the diastereoisomer in excess. As the ratio of the major to minor isomer is greater for [TbL^{1a}], then a larger g_{em} value might have been anticipated compared to [TbL^2]. The fact that the observed dissymmetry values and CPL spectra were almost identical, strongly suggests that the two diastereoisomers in solution have the same macrocyclic ring conformation and pendent arm helicities, and differ only in the configuration at the P centres. Such a conclusion accords with the interpretation of the NMR data, discussed earlier.

Conclusion

In the Eu and Tb complexes of L^2 and L$^{1a/1b}$, NMR and CPL measurements strongly indicate that the configuration of the chiral centre in the amide group determines the helicity of the pendent arms and probably the macrocyclic ring conformation. The complexes exist in solution as two non-interconverting diastereoisomers, differing only in the configuration at P (*RRR* or *SSS*), in a ratio which is dependent on the size of the remote chiral group.

Experimental

General procedures and characterisation techniques

Reactions requiring anhydrous or inert conditions were carried out using Schlenk-line techniques under an atmosphere of dry argon. Anhydrous solvents when required were freshly distilled over the appropriate drying agent. Water was purified by the 'Purite$_{STILL}$plus' system.

Thin layer chromatography was carried out on neutral alumina plates (Merck Art 5550) or silica plates (Merck 5554) and detection was made following irradiation at 254 nm or by staining with iodine. Column chromatography was carried out using neutral alumina (Merck Aluminium Oxide 90, activity II-III, 70-230 mesh) pre-soaked in ethyl acetate, or silica (Merck Silica Gel 60, 230-400 mesh). Analytical and semi-preparative HPLC were performed on a Varian 9010/9065 Polychrom system using a chiral cyclodextrin column (Shodex OR pak CDB-853 HQ series, β-cyclodextrin) and a flow rate of 1.4 cm^3 min^{-1} ($T = 2$ °C; $t = 0$ min, 95% H_2O, 5% MeOH; $t = 25$ min, 100% MeOH, end time).

Melting points were measured with a Köfler block and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1600 FT spectrometer with GRAMS Analyst software, and a Graseby-Specac 'Golden Gate' Diamond ATR accessory spectrometer. Oils were examined as thin films and solids incorporated into KBr discs as stated.

The NMR spectra were acquired using a Brüker AC250 spectrometer operating at 250.13, 62.9, 101.1 and 235.3 MHz for ^{1}H, ^{13}C-{^{1}H}, ^{31}P-{^{1}H} and ^{19}F-{^{1}H} measurements respectively; a Varian VXR 200 operating at 200 MHz for ^{1}H; a JEOL EX-90 operating at 90 and 36 MHz for ^{1}H and ^{31}P-{^{1}H} respectively; a JEOL EX-400 operating at 400, 100.6 and 161.8 MHz for ^{1}H, ^{13}C-{^{1}H} and ^{31}P-{^{1}H} respectively and a Varian VXR400 operating at 400 MHz for ^{1}H. Two-dimensional spectra were run on a JEOL EX-90 and a Varian VXR 200 spectrometer. Variable-temperature ^{1}H NMR studies were carried out on a Varian VXR 400; a JEOL EX-90 and a JEOL

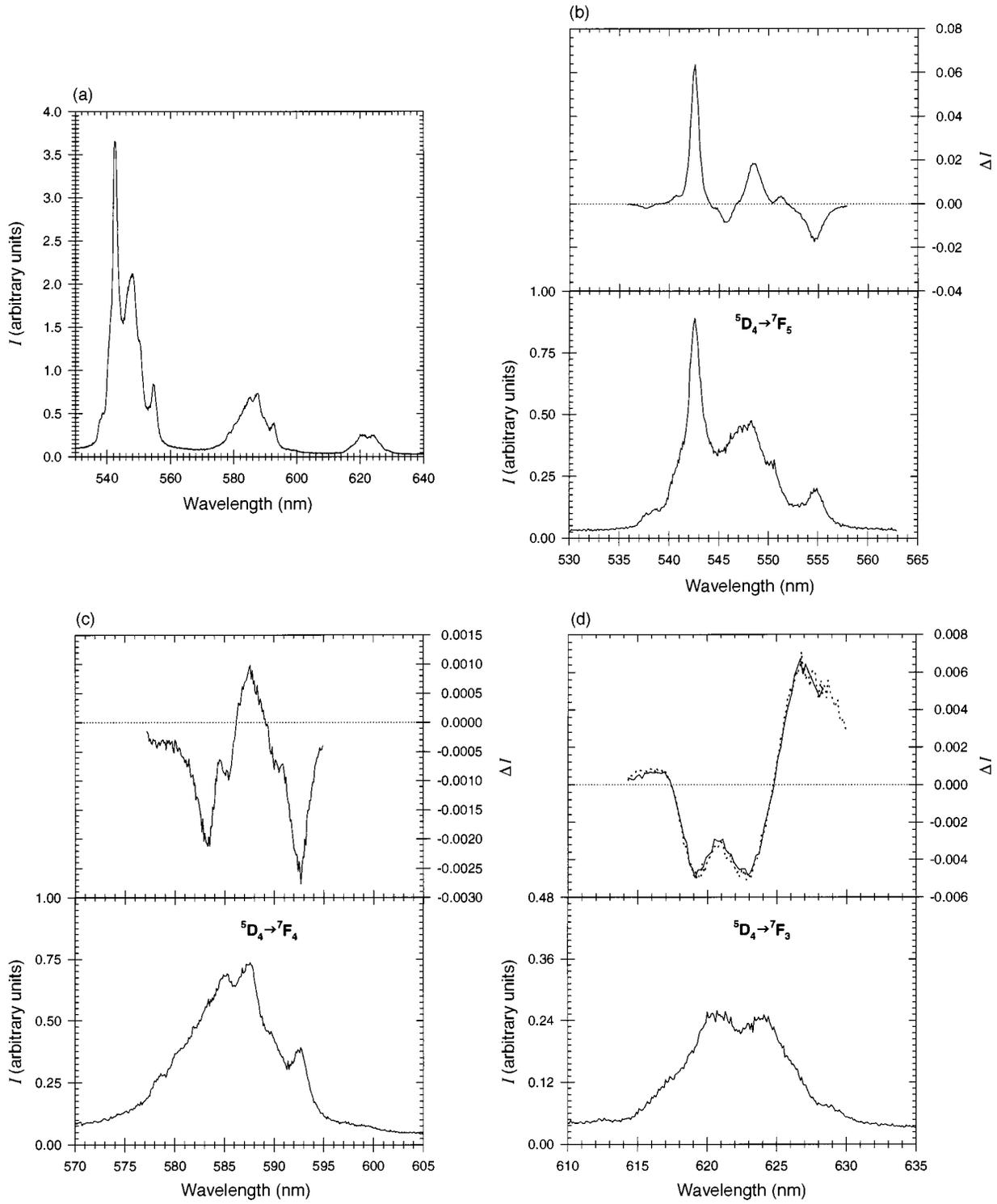


Fig. 4 (a) Total emission spectrum for [TbL^2]. Total emission spectrum (lower) and circularly polarised luminescence (CPL) spectrum (upper) showing (b) the $\Delta J = -1$ ($g_{em} = +0.17$), (c) $\Delta J = 0$ ($g_{em} = -0.06$) and (d) $\Delta J = +1$ ($g_{em} = -0.12$) transitions following excitation at 488 nm (pH 5.5, 298 K). The solid and dotted lines for the $\Delta J = +1$ transition show the CPL spectrum obtained with left- or right-handed circularly polarised excitation

EX-400 instruments. Proton relaxivities were measured at 25 °C on a 20 MHz Spin-Master spectrometer (Stelar) by means of the inversion recovery technique. Proton and ^{13}C-{^1H} spectra were referenced internally relative to *tert*-butyl alcohol (1 drop; δ_H 0; δ_C 31.3) for paramagnetic complexes or to the residual protio-solvent resonances which are reported relative to $SiMe_4$. The ^{31}P-{^1H} spectra were referenced externally relative to H_3PO_4 in D_2O (δ 0).

Mass spectra were recorded on a VG 7070E spectrometer operating in DCI (ammonia) or FAB (glycerol matrix) mode. Electrospray mass spectra were recorded on a VG Platform II (Fisons instrument) operating in positive or negative ion mode as stated. The FAB and accurate mass spectra were recorded by the EPSRC Mass Spectrometry Service at Swansea.

Luminescence and absorption spectra

Ultraviolet absorbance spectra were recorded on a Unicam UV/VIS spectrometer UV2-100 with Unicam Vision Software Version 2.11. Fluorescence spectra were recorded on a Perkin-

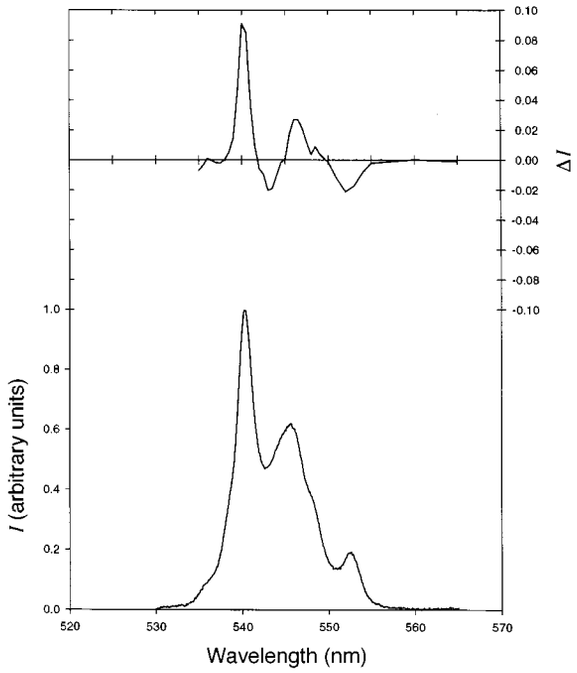


Fig. 5 Total emission spectrum (lower) and circularly polarised luminescence spectrum (upper) for [TbL[1a]], showing the $\Delta J = -1$ ($^{540}_{g_{em}} = +0.18$) transition following UV excitation of the naphthyl chromophore (298 K degassed, H_2O)

Elmer LS50B spectrofluorimeter using FL Winlab Version 1.10 software, equipped with a Hamamatsu R928 photomultiplier tube using quartz fluorescence cuvettes of pathlength 1 cm.

Phosphorescence emission and excitation spectra were recorded on the same instrument operating in time-resolved mode with a delay time of 0.1 ms and a gate time of 10 ms. Emission spectra were corrected for the wavelength dependence of the photomultiplier tube and the most highly resolved spectra were obtained with slit widths (half-height bandwidth) of 10 nm (excitation) and 2.5 nm (emission). The spectrometer automatically corrects the phosphorescence excitation spectra through a reference photomultiplier tube and the spectra were obtained by monitoring the emission at 590 or 619 nm for Eu^{3+} and 545 nm for Tb^{3+} complexes.

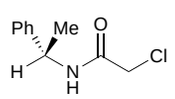
Luminescence quantum yields, φ, were measured according to the procedure described by Haas and Stein,[28] using [Ru(2,2′-bipy)]$^{2+}$ (φ = 0.028 in H_2O)[29] and quinine sulfate (φ = 0.546 in 0.5 mol dm^{-3} H_2SO_4)[30] as standards for Eu^{3+} and Tb^{3+} complexes respectively.

Lifetimes were measured on a Perkin-Elmer LS50B spectrofluorimeter using software written for this purpose by Dr. A. Beeby, University of Durham. Reported lifetimes, τ, are the average of at least three separate measurements calculated by monitoring the emission intensity at 590 or 619 nm for Eu^{3+} and 545 nm for Tb^{3+} complexes after at least 20 different delay times covering two or more lifetimes. The gate time was 0.1 ms and slit widths of 15 nm and 5 nm or less were employed for Eu^{3+} and Tb^{3+} complexes respectively. The phosphorescence decay curves were fitted by an equation of the form $I(t) = I(0)\exp(-t/\tau)$ using a curve fitting program (Kaleidagraph software on an Apple Macintosh or Grafit software on a PC), where $I(t)$ is the intensity at time t after the excitation flash, $I(0)$ the initial intensity at $t = 0$ and τ is the phosphorescence lifetime. High correlation coefficients were observed, τ is reproducible to at least ±0.06 ms and independent of concentration over the range examined (solution absorbance 0.05–0.5).

Circularly polarised luminescence spectra were recorded at Michigan Technological University, USA. Excitation of the $^7F_6 \longrightarrow {}^5D_4$ transition of Tb^{3+} was accomplished with the 488 nm line of a Coherent Innova 70 argon-ion laser. Excitation of the Eu^{3+} (560–581 nm) was accomplished by using a Coherent-599 tunable dye laser (0.03 nm resolution) using the argon-ion laser as a pump source. The laser dye used in the measurement was Rhodamine 110 in ethylene glycol. Calibration of the emission monochromator (and subsequently the dye laser) was accomplished by passing scattered light from a low power He–Ne laser through the detection system. The error in the dye laser wavelength was assumed to be equal to the resolution of the emission detection. The optical detection system consisted of a photoelastic modulator (PEM, Hinds Int.) operating at 50 kHz, and a linear polariser which together act as a circular analyser, followed by a long pass filter, focusing lens, and a 0.22 nm monochromator. The emitted light was detected by a cooled EM1-9558QB photomultiplier tube operating in photon counting mode. The output pulses from the photomultiplier tube were passed through a variable gain amplifier/discriminator and input into a specially built differential photon counter. The 50 kHz reference signal from the photoelastic modulator was used to direct the incoming pulses into two separate counters, an up-counter which counts every photon pulse and thus is a measure of the total luminescence signal $I = I_{left} + I_{right}$, and an up/down counter which adds pulses when the analyser is transmitting left circularly polarised light and subtracts when the analyser is transmitting right circularly polarised light. This second counter provides a measure of the differential emission intensity $\Delta I = I_{left} - I_{right}$. The differential photon counter allows for the selection of a time window for counting which is centred around the maximum in the modulation cycle. For the measurements reported here, the window was set to 50%.

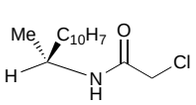
Ligand synthesis

2-Chloro-*N*-[(*S*)-methylbenzyl]ethanamide (*S*)-2.



Chloroacetyl chloride (0.78 cm^3, 9.9 mmol) in dry diethyl ether (20 cm^3) was added dropwise to a stirred solution of (*S*)-α-methylbenzylamine (1.1 cm^3, 8.3 mmol) and triethylamine (1.4 cm^3, 9.9 mmol) in dry diethyl ether (30 cm^3) at −20 °C. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The resulting white precipitate was dissolved in water (60 cm^3) and the organic layer washed with hydrochloric acid (0.1 mol dm^{-3}, 50 cm^3), water (3 × 30 cm^3), dried (K_2CO_3) and the solvent removed *in vacuo* to yield a white solid. Recrystallisation from diethyl ether yielded white needles (0.95 g, 60%); m.p. 95–96 °C; ν_{max}(KBr)/cm^{-1} 3265 (N–H), 1652 (C=O); δ_H(250 MHz; $CDCl_3$) 7.41–7.34 (5 H, m, C_6H_5), 6.82 (1 H, br s, NH), 5.18 (1 H, m, CH), 4.11 (1 H, d, ^2J 15.1, CH_2), 4.08 (1 H, d, ^2J 15.1, CH_2), 1.58 (3 H, d, ^3J 6.7 Hz, CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 165.0 (CO), 142.4 (*q*-C_6H_5), 128.8 (*m*-C_6H_5), 127.6 (*p*-C_6H_5), 126.1 (*o*-C_6H_5), 49.2 (CHN), 42.6 (CH_2), 21.7 (CH_3); *m*/*z* (DCI) 198 (100%, M^+) (Found: C, 60.6; H, 6.15; N, 6.90. $C_{10}H_{12}ClNO$ requires C, 60.8; H, 6.12; N, 7.08%).

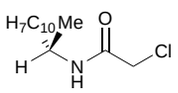
2-Chloro-*N*-[(*R*)-1-naphthyl]ethylethanamide (*R*)-3a.



This compound was prepared following a method similar to that for compound **2** using (*R*)-1-(1-naphthyl)ethylamine (0.94 cm^3, 5.8 mmol) and triethylamine (0.98 cm^3, 7 mmol) in dry diethyl ether (30 cm^3) and treating with a solution of chloroacetyl chloride (0.56 cm^3, 7 mmol) in dry diethyl ether

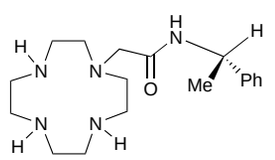
(30 cm^3). The product was recrystallised from diethyl ether and was isolated as white needles (1.1 g, 76%); m.p. 144–145 °C; ν_{max}(KBr)/cm^{-1} 3296 (N–H), 1648 (C=O); δ_H(250 MHz; $CDCl_3$) 8.12–7.48 (7 H, m, $C_{10}H_7$), 6.84 (1 H, br s, NH), 5.99 (1 H, m, CH), 4.13 (1 H, d, ^2J 15.3, CH_2), 4.11 (1 H, d, ^2J 15.3, CH_2), 1.75 (3 H, d, ^3J 7.0 Hz, CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 165.0 (CO), 137.5 ($C_{10}H_7$), 133.9 ($C_{10}H_7$), 130.9 ($C_{10}H_7$), 128.9 ($C_{10}H_7$), 128.6 ($C_{10}H_7$), 126.8 ($C_{10}H_7$), 126.0 ($C_{10}H_7$), 125.3 ($C_{10}H_7$), 123.1 ($C_{10}H_7$), 122.6 ($C_{10}H_7$), 45.2 (CH), 42.6 (CH_2), 20.9 (CH_3); *m*/*z* (DCI) 248 (100%, MH^+), 212 (18%, $M^+ - Cl$), 155 (70%, $M^+ - NHCOCl$) (Found: C, 68.1; H, 5.64; N, 5.59. $C_{14}H_{14}ClON$ requires C, 67.8; H, 5.69; N, 5.65%).

2-Chloro-*N*-[(*S*)-1-naphthyl]ethylethanamide (*S*)-3b.



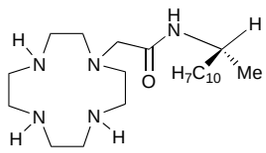
This compound was prepared following a method similar to that for compound **2** using (*S*)-1-(1-naphthyl)ethylamine (4.72 cm^3, 29.2 mmol) and triethylamine (4.9 cm^3, 35.1 mmol) in dry diethyl ether (100 cm^3) and treating with a solution of chloroacetyl chloride (2.79 cm^3, 35.1 mmol) in dry diethyl ether (50 cm^3). The product was recrystallised from diethyl ether and was isolated as white needles (3.5 g, 48%). Characterisation data are the same as those reported for **3a** (Found: C, 68.0; H, 5.60; N, 5.54. $C_{14}H_{14}ClON$ requires C, 67.8; H, 5.69; N, 5.65%).

1-[(*S*)-1-(1-Phenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (*S*)-6a.



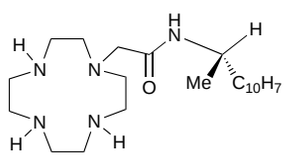
1,4,7,10-Tetraazacyclododecane (0.4 g, 2.3 mmol) and molybdenum hexacarbonyl (0.6 g, 2.3 mmol) in dry dibutyl ether (20 cm^3) were heated at reflux under argon for 2 h to give a bright yellow precipitate of the 1,4,7,10-tetraazacyclododecane–molybdenum–tricarbonyl complex (**16**) which was filtered under argon and dried *in vacuo*. The complex (**16**) (0.8 g, 2.3 mmol) and fine mesh anhyhdrous potassium carbonate (0.4 g, 2.8 mmol) were taken into degassed dimethylformamide (30 cm^3) and a solution of 2-chloro-*N*-[(*S*)-methylbenzyl]ethanamide **2** (0.45 g, 2.3 mmol) in dry dimethylformamide (1 cm^3) was added under argon by steel cannula. The reaction mixture was heated at 60 °C for 4 h under an argon atmosphere. The solvent was removed by distillation *in vacuo* and the brown residue was taken into hydrochloric acid (1 mol dm^{-3}, 13 cm^3) and the resulting acidic brown suspension was stirred open to the air for 18 h. Molybdenum residues were removed by centrifugation and filtration and the aqueous layer was washed with dichloromethane (30 cm^3) and chloroform (20 cm^3). The pH of the solution was raised to 14 by addition of sodium hydroxide pellets, with cooling. The product was extracted into dichloromethane (3 × 30 cm^3), washed with water (3 × 30 cm^3), dried (K_2CO_3) and the solvent removed *in vacuo* to yield a yellow-brown oil (620 mg, 81%); R_f (Al_2O_3; 10% CH_3OH–CH_2Cl_2; I_2 and UV detection) 0.44–0.1; ν_{max}(film)cm^{-1} 3285 (N–H), 1666 (C=O); δ_H(250 MHz; $CDCl_3$) 8.23 (1 H, d, ^3J 7.7, NHCO), 7.45–7.28 (5 H, m, C_6H_5), 5.21 (1 H, m, CH), 3.20 (2 H, s, CH_2), 2.92–2.54 (16 H, m, ring-CH_2), 2.00–1.90 (3 H, m, ring-NH), 1.56 (3 H, d, ^3J 5.0 Hz, CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 170.3 (CO), 143.3 (*q*-C_6H_5), 128.2 (*m*-C_6H_5), 126.8 (*p*-C_6H_5), 126.1 (*o*-C_6H_5), 58.8 (CH_2CO), 52.9 (ring-CH_2), 48.0 (CHN), 46.7 (ring-CH_2), 46.4 (ring-CH_2), 45.3 (ring-CH_2), 21.3 (CH_3); *m*/*z* (DCI) 334 (100%, M^+).

1-[(*R*)-1-(1-Naphthyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (*R*)-5a.



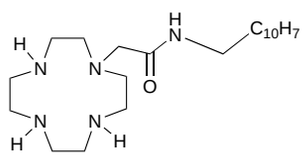
This compound was prepared following a similar method to that for compound **6a** using 1,4,7,10-tetraazacyclododecane–molybdenum–tricarbonyl complex (1 g, 2.86 mmol), 2-chloro-*N*-[(*R*)-1-naphthyl]ethylethanamide **3a** (0.71 g, 2.86 mmol) and potassium carbonate (0.55 g, 4.0 mmol) in degassed, dry dimethylformamide (30 cm^3) to yield a brown oil (0.55 g, 50%) after purification; ν_{max}(film)/cm^{-1} 3421 (N–H), 1643 (C=O); δ_H(250 MHz; $CDCl_3$) 8.52 (1 H, d, ^3J 8.0, NHCO), 8.12–7.49 (7 H, m, $C_{10}H_7$), 5.95 (1 H, m, CH), 3.25 (1 H, d, ^2J 17.5, CH_2CO), 3.19 (1 H, d, ^2J 17.5, CH_2CO), 2.59–2.20 (19 H, m, ring-CH_2, ring-NH), 1.71 (3 H, d, ^3J 6.9 Hz, CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$), 170.6 (CO), 138.2 (*q*-$C_{10}H_7$), 133.6 (*q*-$C_{10}H_7$), 131.2 (*q*-$C_{10}H_7$), 128.6 ($C_{10}H_7$), 128.0 ($C_{10}H_7$), 126.4 ($C_{10}H_7$), 125.8 ($C_{10}H_7$), 125.2 ($C_{10}H_7$), 123.5 ($C_{10}H_7$), 122.9 ($C_{10}H_7$), 58.9 (CH_2CO), 53.4 (ring-CH_2), 46.8 (ring-CH_2), 45.6 (ring-CH_2), 44.5 (ring-CH_2), 43.9 (CHN), 20.0 (CH_3); *m*/*z* (DCI) 384 (100%, MH^+).

1-[(*S*)-1-(1-Naphthyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane (*S*)-5b.



This compound was prepared following a similar method to that for compound **6a** using 1,4,7,10-tetraazacyclododecane–molybdenum–tricarbonyl complex (4.2 g, 12.1 mmol), 2-chloro-*N*-[(*S*)-1-naphthyl]ethylethanamide **3b** (3.0 g, 12.1 mmol) and potassium carbonate (2.34 g, 17 mmol) in degassed, dry dimethylformamide (60 cm^3) to yield a brown oil (2.3 g, 50%) after purification. Characterisation data are the same as those reported for (*R*)-**5a**.

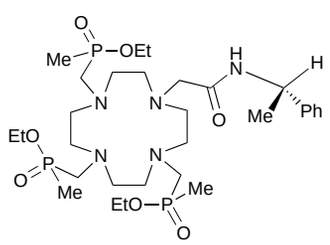
1-[(1-Naphthyl)methylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane 5c.



This compound was prepared following a method similar to that for compound **6a** using 1,4,7,10-tetraazacyclododecane–molybdenum–tricarbonyl complex (0.75 g, 2.14 mmol), 2-chloro-*N*-(naphthylmethyl)ethanamide[5] (0.5 g, 2.14 mmol) and potassium carbonate (0.35 g, 2.57 mmol) in degassed, dry dimethylformamide (30 cm^3) to yield a yellow oil (0.2 g, 25%) after purification; ν_{max}(film)/cm^{-1} 3365 (N–H), 1652 (C=O); δ_H(250 MHz; $CDCl_3$) 8.50–8.40 (1 H, br m, NHCO), 7.82–7.76 (4 H, m, $C_{10}H_7$), 7.48–7.41 (3 H, m, $C_{10}H_7$), 4.61 (2 H, d, ^3J 5.0, $CH_2C_{10}H_7$), 3.24 (2 H, s, CH_2CO), 2.69–2.39 (19 H, m, ring-CH_2, ring-NH); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 171.3 (CO), 135.9 ($C_{10}H_7$), 133.0 ($C_{10}H_7$), 132.3 ($C_{10}H_7$), 128.1 ($C_{10}H_7$), 127.5 ($C_{10}H_7$), 127.4 ($C_{10}H_7$), 126.4 ($C_{10}H_7$), 126.2 ($C_{10}H_7$), 126.1 ($C_{10}H_7$), 125.7 ($C_{10}H_7$), 59.1 (CH_2CO), 53.1 (ring-CH_2), 46.9 (ring-CH_2), 46.3 (ring-CH_2), 45.6 (ring-CH_2), 43.1 ($CH_2C_{10}H_7$); *m*/*z* (DCI) 370 (100%, MH^+).

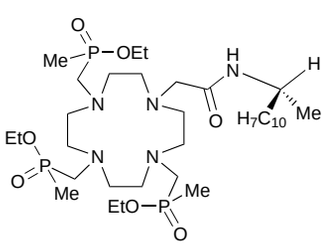
Methyldiethoxyphosphine. Diethylchlorophosphite (14.3 cm^3, 0.1 mol) was added dropwise, over 1 h, to a cooled solution of methylmagnesium bromide (33.3 cm^3 of a 3 mol dm^{-3} solution in diethyl ether, 0.1 mol) under argon at 20 °C. The mixture was allowed to warm to room temperature and stirred for 1 h. The resulting precipitate was filtered off under argon by cannula transfer. Distillation under reduced pressure yielded methyldiethoxyphosphine as a solution in diethyl ether whose molarity was established by addition of a known mass of diethylphenylphosphonite followed by ^{31}P NMR integration of the two distinct singlets, $\delta_P\{^1H\}$ (101.3 MHz) 176.4. On other occasions this compound was purchased from Strem Chemicals and used as received, following ^{31}P analysis.

Triethyl 10-[(*S*)-1-(1-phenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triyltrimethylenetri(methylphosphinate) 6b.



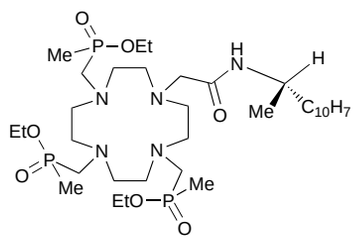
The monosubstituted macrocycle **6a** (0.56 g, 1.68 mmol) was allowed to heat at reflux temperature in dry tetrahydrofuran (40 cm^3), under argon over 4 Å molecular sieves for 30 min. Methyldiethoxyphosphine (26.3 cm^3 of a 1.1 mol dm^{-3} solution in diethyl ether, 7.56 mmol) was added to the cooled solution. After heating for 10 min at reflux, paraformaldehyde (0.25 g, 8.4 mmol) was added and the solution was heated at reflux for a further 18 h. The solvent was removed *in vacuo* to yield a brown oil. The product was purified by alumina column chromatography (gradient elution from dichloromethane to 2% methanol–dichloromethane) giving a yellow oil (0.6 g, 55%); R_f (Al_2O_3; 10% MeOH–CH_2Cl_2; I_2 and UV detection) 0.61; ν_{max}(film)/cm^{-1} 3384 (br) (N–H), 1665 (C=O); δ_H(250 MHz; $CDCl_3$) 8.15 (1 H, ^3J 8.2, NH), 7.32–7.18 (5 H, m, C_6H_5), 5.12 (1 H, m, CH), 4.03–3.94 (6 H, m, C$H_2$$CH_3$), 3.11–2.48 (24 H, br m, CH_2CO, CH_2P, ring-CH_2), 1.50–1.36 (12 H, m, PCH_3, CH_3), 1.25 (9 H, t, ^3J 7.0 Hz, CH_2CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 170.2 (CO), 143.5 (*q*-C_6H_5), 128.2 (*m*-C_6H_5), 126.9 (*p*-C_6H_5), 126.4 (*o*-C_6H_5), 59.9 (CH_2CH_3), 55.4 (ring-CH_2), 53.9 (d, ^3J 88, CH_2P), 47.9 (CHN), 21.3 (CH_3), 16.5 (CH_2CH_3), 13.6 (d, ^1J 89 Hz, PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; $CDCl_3$) 52.0 (3 P, br); *m*/*z* (DCI) 694 (100%, M^+).

Triethyl 10-[(*R*)-1-(1-naphthyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triyltrimethylenetri(methylphosphinate) 5d.



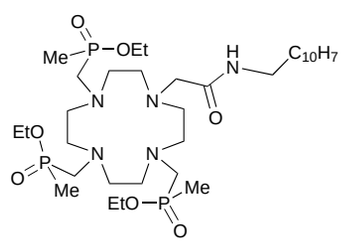
This compound was prepared following a method similar to that for compound **6b** using the monosubstituted macrocycle **5a** (0.16 g, 0.42 mmol), methyldiethoxyphosphine (**18**) (6.5 cm^3 of a 1.1 mol dm^{-3} solution in diethyl ether, 1.9 mmol) and paraformaldehyde (0.06 g, 2.1 mmol) in dry tetrahydrofuran (20 cm^3) to yield a yellow oil (0.17 g, 54%) after purification; R_f (Al_2O_3; 10% CH_3OH–CH_2Cl_2; I_2 and UV detection) 0.68; ν_{max}(film)/cm^{-1} 3397 (br) (N–H), 1652 (C=O); δ_H(250 MHz; $CDCl_3$) 8.45–7.47 (7 H, m, $C_{10}H_7$), 5.93 (1 H, m, CH), 3.99 (6 H, m, C$H_2$$CH_3$), 3.19–2.32 (24 H, br m, ring-CH_2, CH_2P, CH_2CO), 1.54 (9 H, d, ^2J 13.0 Hz, PCH_3), 1.37–1.28 (12 H, m, CH_2CH_3, CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 170.3 (CO), 138.5 (*q*-$C_{10}H_7$), 133.7 (*q*-$C_{10}H_7$), 131.5 (*q*-$C_{10}H_7$), 128.5 ($C_{10}H_7$), 128.1 ($C_{10}H_7$), 126.4 ($C_{10}H_7$), 125.8 ($C_{10}H_7$), 125.0 ($C_{10}H_7$), 123.7 ($C_{10}H_7$), 123.0 ($C_{10}H_7$), 60.0 (CH_2CH_3), 55.7–53.0 (ring-CH_2, CH_2CO), 43.6 (CHN), 20.1 (CH_3), 16.6 (CH_2CH_3), 13.7 (d, ^1J 89 Hz, PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; $CDCl_3$) 53.3–51.4 (3 P, br m); *m*/*z* (DCI) 744 (100%, MH^+).

Triethyl 10-[(*S*)-1-(1-naphthyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triyltrimethylenetri(methylphosphinate) 5e.



This compound was prepared following a method similar to that for compound **5d** using the monosubstituted macrocycle **5b** (2.0 g, 5.2 mmol), methyldiethoxyphosphine (77 cm^3 of a 0.3 mol dm^{-3} solution in diethyl ether, 23.6 mmol) and paraformaldehyde (0.8 g, 26.2 mmol) in dry tetrahydrofuran (100 cm^3) to yield a yellow oil (2 g, 52%) after purification. Characterisation data are the same as those reported for **5d**.

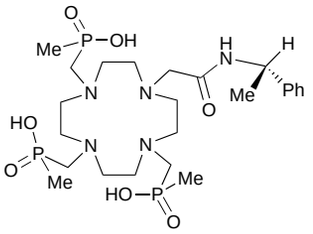
Triethyl 10-[(1-naphthyl)methylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triyltrimethylenetri(methylphosphinate) 5f.



This compound was prepared following a method similar to that for compound **5d** using the monosubstituted macrocycle **5c** (0.2 g, 0.55 mmol), methyldiethoxyphosphine, (26.7 cm^3 of a 0.09 mol dm^{-3} solution in diethyl ether, 2.46 mmol) and paraformaldehyde (0.08 g, 2.73 mmol) in dry tetrahydrofuran (30 cm^3) to yield a yellow oil (0.1 g, 29%) after purification; R_f (Al_2O_3; 10% CH_3OH–CH_2Cl_2; I_2 and UV detection) 0.57; δ_H(250 MHz; $CDCl_3$) 8.70 (1 H, s, NH), 7.89–7.86 (4 H, m, $C_{10}H_7$), 7.55–7.52 (3 H, m, $C_{10}H_7$), 4.73 (2 H, d, ^3J 6.8, $CH_2C_{10}H_7$), 4.04 (6 H, m, C$H_2$$CH_3$), 3.29 (2 H, s, CH_2CO), 3.10–2.46 (22 H, ring-CH_2, CH_2P), 1.50–1.30 (18 H, m, PCH_3, CH_2CH_3); $\delta_C\{^1H\}$ (62.9 MHz; $CDCl_3$) 171.5 (CO), 136.7 (*q*-$C_{10}H_7$), 133.3 (*q*-$C_{10}H_7$), 132.6 (*q*-$C_{10}H_7$), 128.2 ($C_{10}H_7$), 127.6 ($C_{10}H_7$), 126.6 ($C_{10}H_7$), 126.3 ($C_{10}H_7$), 125.8 ($C_{10}H_7$), 60.1 (CH_2CH_3), 55.5–53.3 (ring-CH_2, CH_2P, CH_2CO), 43.2 (CH_2N), 16.7 (CH_2CH_3), 13.9 (d, ^1J 88 Hz, PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; $CDCl_3$) 52.5 (1 P), 52.2 (1 P), 52.1 (1 P). (A satisfactory accurate mass spectrum could not be obtained for this product.)

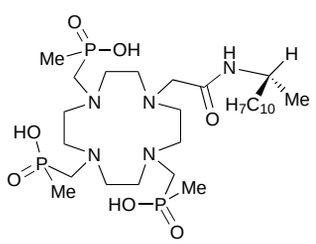
10-[(*S*)-1-(1-Phenyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triyltrimethylenetri(methylphosphinic acid) L^2.

The monoamidetris(phosphinate ester) **6b** (0.3 g, 0.4 mmol) was stirred in a solution of potassium hydroxide (10 cm^3 of a 10%



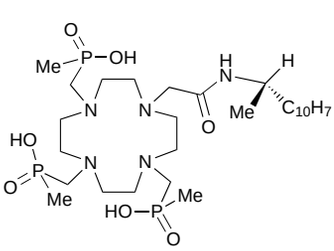
solution in water) at room temperature for 18 h. The solution was neutralised to pH 6.5 with hydrochloric acid (0.1 mol dm^{-3} solution) and the solvent removed by lyophilization. The resulting solid was dissolved in hot ethanol (5 cm^3) and the remaining salts removed by centrifugation followed by filtration. The solvent was removed *in vacuo* to give a pale yellow solid (0.2 g, 82%); m.p. >200 °C; ν_{max}(solid)/cm^{-1} 3288 (br) (N–H), 1639 (C=O); δ_H(250 MHz; D_2O) 8.09 (1 H, s, NH), 7.07–6.97 (5 H, m, C_6H_5), 4.58 (1 H, m, CH), 3.33–2.14 (24 H, br m, ring-CH_2, CH_2P, CH_2CO), 1.11 (3 H, d, ^3J 6.8, CH_3), 0.95 (9 H, d, ^2J 13.0 Hz, PCH_3); $\delta_C\{^1H\}$ (62.9 MHz; D_2O) 171.1 (CO), 143.5 (*q*-C_6H_5), 128.7 (*m*-C_6H_5), 127.3 (*p*-C_6H_5), 125.7 (*o*-C_6H_5), 55.0–47.0 (ring-CH_2, *C*H_2CO, CH_2P, CHN), 21.2 (CH_3), 16.6 (d, ^1J 91 Hz, PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 40.0–28.6 (3 P, br); *m*/*z* (FAB) 610 (100%, *M*H^+) (Found: *M*H^+, 610.2689. $C_{24}H_{47}N_5O_7P_3$ requires *M*H^+, 610.2688).

10-[(*R*)-1-(1-Naphthyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triyltrimethylenetri(methylphosphinic acid) L^{1a}.



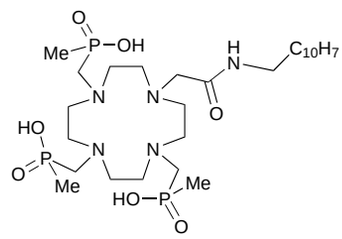
This compound was prepared following a method similar to that for compound L^2 using the monoamidetris(phosphinate ester) **5d** (0.16 g, 0.2 mmol) in a solution of potassium hydroxide (10 cm^3 of a 10% solution in water) to give a pale yellow solid (0.13 g, 92%); m.p. >200 °C; ν_{max}(solid)/cm^{-1} 3243 (N–H), 1652 (C=O); δ_H(250 MHz; D_2O) 7.80–7.10 (7 H, m, $C_{10}H_7$), 5.36 (1 H, m, CH), 3.30–2.00 (24 H, br m, ring-CH_2, CH_2P, CH_2CO), 1.20 (3 H, d, ^3J 6.7 Hz, CH_3), 0.93–0.79 (9 H, br m, PCH_3); $\delta_C\{^1H\}$ (62.9 MHz; D_2O) 170.1 (CO), 138.6 (*q*-$C_{10}H_7$), 133.4 (*q*-$C_{10}H_7$), 130.0 (*q*-$C_{10}H_7$), 127.3–123.8 ($C_{10}H_7$), 121.3 ($C_{10}H_7$), 53.7–45.0 (br m, CH_2P, ring-CH_2, CHN, *C*H_2CO), 20.0–15.0 (br m, CH_3, PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 39.6–27.0 (3 P, br m); *m*/*z* (FAB) 660 (100%, *M*H^+) (Found: *M*H^+, 660.2850. $C_{28}H_{49}N_5O_7P_3$ requires *M*H^+, 660.2844).

10-[(*S*)-1-(1-Naphthyl)ethylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triyltrimethlenetri(methylphosphinic acid) L^{1b}.



This compound was prepared following a method similar to that for compound L^{1a} using the monoamidetris(phosphinate ester) **5e** (0.65 g, 0.87 mmol) in a solution of potassium hydroxide (10 cm^3 of a 10% solution in water) to give a pale yellow solid (0.53 g, 92%). Characterisation data are the same as those reported for L^{1a} (Found: *M*Na^+, 682.2662. $C_{28}H_{48}N_5NaO_7P_3$ requires *M*Na^+, 682.2664).

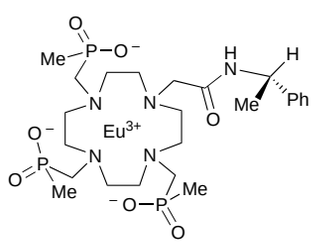
10-[(1-Naphthyl)methylcarbamoylmethyl]-1,4,7,10-tetraazacyclododecane-1,4,7-triyltrimethylenetri(methylphosphinic acid) L^{1c}.



This compound was prepared following a method similar to that for compound L^{1b} using monoamidetris(phosphinate ester) **5f** (0.1 g, 0.16 mmol) in a solution of potassium hydroxide (10 cm^3 of a 10% solution in water) to give a pale yellow solid (0.07 g, 67%); m.p. >200 °C; ν_{max}(solid)/cm^{-1} 3291 (br) (N–H), 1644 (C=O); δ_H(250 MHz; D_2O) 7.60–7.16 (7 H, br m, $C_{10}H_7$), 4.22 (2 H, s, $CH_2C_{10}H_7$), 3.23–2.59 (24 H, br m, ring-CH_2, CH_2CO, CH_2P), 0.88 (9 H, d, ^2J 13.4 Hz, PCH_3); $\delta_C\{^1H\}$ (62.9 MHz; D_2O) 172.1 (CO), 135.5 (*q*-$C_{10}H_7$), 132.8 (*q*-$C_{10}H_7$), 132.2 (*q*-$C_{10}H_7$), 128.3 ($C_{10}H_7$), 127.5 ($C_{10}H_7$), 126.5 ($C_{10}H_7$), 126.1 ($C_{10}H_7$), 125.7 ($C_{10}H_7$), 56.4 (*C*H_2CO), 54.2–50.5 (ring-CH_2, CH_2P), 43.0 (CH_2N), 16.9 (d, ^1J 96 Hz, PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 39.4 (2 P), 33.0 (1 P); *m*/*z* (ES^-) 645 (100%, *M*). (A satisfactory accurate mass spectrum could not be obtained for this product.)

Lanthanide complexes

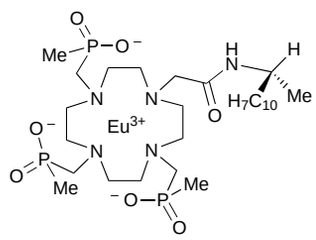
[EuL^2].



Europium(III) acetate (0.05 g, 0.14 mmol) was added to a stirred solution of compound **2** (0.07 g, 0.12 mmol) in water (3 cm^3) and the solution was heated at reflux for 18 h. The solvent was removed by lyophilization and the resulting solid extracted into hot ethanol (4 cm^3). The remaining salts were removed by centrifugation followed by filtration and the solvent removed *in vacuo* to give a yellow-brown solid. Purification by column chromatography through a plug of alumina (5% CH_3OH–CH_2Cl_2) yielded a very pale yellow solid (0.02 g, 22%); m.p. >250 °C; R_f (Al_2O_3; 15% CH_3OH–CH_2Cl_2; I_2 detection) 0.4 (br); ν_{max}(solid)/cm^{-1} 3314 (br) (N–H), 1620 (C=O); *m*/*z* (ES^-) 758.05 (100%, *M*) (Found: *M*H^+, 760.1663. $C_{24}H_{44}EuN_5O_7P_3$ requires *M*H^+, 760.1666). Major isomer: δ_H(90 MHz; D_2O; 291 K) [partial assignment] 28.2 (1 H, br, ring-H_{ax}), 25.1 (1 H, br, ring-H_{ax}), 17.2 (1 H, br, ring-H_{ax}), 13.7 (1 H, br, ring-H_{ax}), 9.5 (1 H, br, ring-H_{ax}), 6.8–5.9 (5 H, m, C_6H_5), 2.1 (3 H, d, ^3J 6.2, CH_3), 1.6 to −0.7 (3 H, br, ring-H_{eq}), −1.5 (3 H, d, ^2J 16, PCH_3), −3.8 (3 H, d, ^2J 14, PCH_3), −4.5 to −5.9 (2 H, br, ring-H_{ax}), −6.4 (3 H, d, ^2J 14 Hz, PCH_3), −6.9 to −7.8 (2 H, br, ring-H_{eq}), −10.8 to −11.5 (2 H, br, ring-H_{ax}, ring-H_{eq}), −14.5 to −15.3 (2 H, br, ring-H_{eq}); $\delta_C\{^1H\}$ (62.9 MHz; D_2O) 200.9 (CO), 146.3 (*q*-C_6H_5), 128.7 (*m*-C_6H_5), 127.0 (*p*-C_6H_5), 125.5 (*o*-C_6H_5), 107.4–60.0

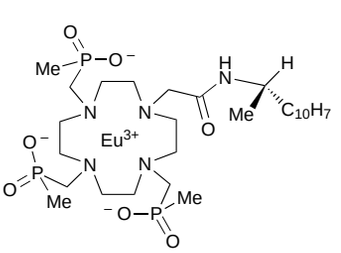
(ring-CH_2, CH_2P, CH_2CO), 52.6 (CHN), 24.8 (CH_3), 6.8–2.1 (PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 95.5 (1 P), 83.3 (1 P), 68.2 (1 P). Minor isomer: δ_H(90 MHz; D_2O; 18 K) [partial assignment] 27.6 (1 H, br, ring-H_{ax}), 25.1 (1 H, br, ring-H_{ax}), 17.2 (1 H, br, ring-H_{ax}), 13.7 (1 H, br, ring-H_{ax}), 11.0 (1 H, br, ring-H_{ax}), 6.8–5.9 (5 H, m, C_6H_5), 1.8 to −0.5 (3 H, br, ring-H_{eq}), 1.3 (3 H, d, ^3J 6.3, CH_3), −0.3 (3 H, d, ^2J 14, PCH_3), −4.4 (3 H, d, ^2J 14, PCH_3), −5.9 (3 H, d, ^2J 16 Hz, PCH_3), −7.6 to −15.5 (8 H, br, 3 ring-H_{ax}, 5 ring-H_{eq}); $\delta_C\{^1H\}$ (62.9 MHz; D_2O) 202.6 (CO), 134–125 (C_6H_5), 107.4–60.0 (ring-CH_2, CH_2P, CH_2CO), 53.7 (CHN), 23.3 (CH_3), 6.8–2.1 (PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; D_2O), 97.3 (1 P), 79.0 (1 P), 64.6 (1 P).

[EuL^{1a}].



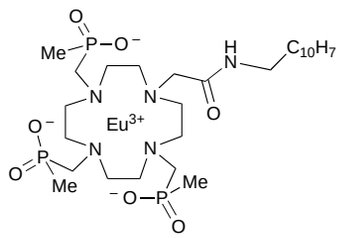
This compound was prepared following a method similar to that for [EuL^2] using europium(III) acetate (0.012 g, 0.13 mmol) and compound L^{1a} (0.06 g, 0.09 mmol) in water (3 cm^3) to yield a pale yellow solid (0.034 g, 46%); m.p. >250 °C; R_f (Al_2O_3; 15% CH_3OH–CH_2Cl_2; I_2 detection) 0.35 (br); ν_{max}(solid)/cm^{-1} 3256 (br) (N–H), 1620 (C=O); *m*/*z* (ES^-) 808 (100%, *M*) (Found: MH^+, 810.1783. $C_{28}H_{45}EuN_5O_7P_3$ requires MH^+, 810.1822). Major isomer: δ_H(90 MHz; D_2O; 278 K) [partial assignment] 28.7 (1 H, br, ring-H_{ax}), 25.7 (1 H, br, ring-H_{ax}), 17.6 (1 H, br, ring-H_{ax}), 2.2 (3 H, d, ^3J 6.6, CH_3), −2.3 (3 H, d, ^2J 14.7, PCH_3), −4.0 (3 H, d, ^2J 15.5, PCH_3), −6.6 (3 H, d, ^2J 15.5 Hz, PCH_3); $\delta_C\{^1H\}$ (400 MHz; D_2O; 278 K) 227 (CO), 145 (*q*-$C_{10}H_7$), 136 (*q*-$C_{10}H_7$), 135 (*q*-$C_{10}H_7$), 131 ($C_{10}H_7$), 130 ($C_{10}H_7$), 129 ($C_{10}H_7$), 128 ($C_{10}H_7$), 127 ($C_{10}H_7$), 125 ($C_{10}H_7$), 122 ($C_{10}H_7$), 134–127 (ring-CH_2, CH_2P, CH_2CO), 52 (CHN), 25 (CH_3), 8–4 (PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 96.0 (1 P), 82.3 (1 P), 66.8 (1 P). Minor isomer: δ_H(90 MHz; D_2O; 278 K) [partial assignment] 29.1 (1 H, br, ring-H_{ax}), 27.5 (1 H, br, ring-H_{ax}), 15.1 (1 H, br, ring-H_{ax}), 1.77 (1 H, d, ^3J 5.9, CH_3), −3.4 (3 H, d, ^2J 15.5, PCH_3), −5.1 (3 H, d, ^2J 15.5, PCH_3), −6.4 (1 H, d, ^2J 15.5 Hz, PCH_3); $\delta_C\{^1H\}$ (400 MHz; D_2O; 298 K) 250 (CO), 147 (*q*-$C_{10}H_7$), 141 (*q*-$C_{10}H_7$), 138 (*q*-$C_{10}H_7$), 134–127 ($C_{10}H_7$), 110–65 (ring-CH_2, CH_2P, CH_2CO), 53 (CHN), 24 (CH_3), 8–4 (PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 97.9 (1 P), 80.3 (1 P), 66.0 (1 P).

[EuL^{1b}].



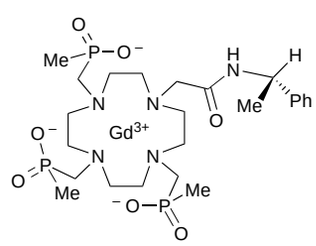
This compound was prepared following a method similar to that for complex [EuL^2] using europium(III) acetate (0.2 g, 0.3 mmol) and compound L^{1b} (0.2 g, 0.3 mmol) in water (3 cm^3) to yield a pale yellow solid (0.13 g, 53%). Characterisation data are the same as those reported for [EuL^{1a}] (Found: MH^+, 810.1843. $C_{28}H_{45}EuN_5O_7P_3$ requires MH^+, 810.1822) (Found: C, 37.0; H, 6.46; N, 7.35%. $C_{28}H_{45}EuN_5O_7P_3\cdot5H_2O$ requires: C, 37.4; H, 6.12; N, 7.78%).

[EuL^{1c}].



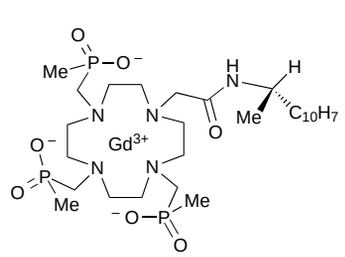
This compound was prepared using a method similar to that for complex [EuL^2] using europium(III) acetate (0.047 g, 0.14 mmol) and compound L^{1c} (0.055 g, 0.1 mmol) in water (3 cm^3) to yield a pale yellow solid (0.028 g, 41%); m.p. >250 °C; R_f (Al_2O_3; 10% CH_3OH–CH_2Cl_2; I_2 detection) 0.74–0.34; δ_H(90 MHz; D_2O; 301 K) [partial assignment] 27.7 (1 H, br, ring-H_{ax}), 24.6 (1 H, br, ring-H_{ax}), 17.1 (1 H, br, ring-H_{ax}), 12.9 (1 H, br, ring-H_{ax}), 9.41 (1 H, br, ring-H_{ax}), 8.44–6.58 (5 H, m, $C_{10}H_7$), 1.71 to −0.51 (3 H, br, ring-H_{eq}), −1.20 (3 H, d, ^2J 14, PCH_3), −3.62 (3 H, d, ^2J 14, PCH_3), −4.42 (1 H, br, ring-H_{ax}), −5.93 (3 H, d, ^2J 14 Hz, PCH_3), −6.01 to −7.4 (3 H, br, ring-H_{ax}, 2-ring-H_{eq}), −10.0 to −14.1 (4 H, br, ring-H_{ax}, 3 ring-H_{eq}); $\delta_C\{^1H\}$ (400 MHz; D_2O; 298 K) 203.5 (CO), 140.5 (*q*-$C_{10}H_7$), 137.0 (*q*-$C_{10}H_7$), 135.0 (*q*-$C_{10}H_7$), 131.5 ($C_{10}H_7$), 130.5 ($C_{10}H_7$), 130.0 ($C_{10}H_7$), 129.0 ($C_{10}H_7$), 128.5 ($C_{10}H_7$), 128.0 ($C_{10}H_7$), 127.5 ($C_{10}H_7$), 108.0 (ring-CH_2), 106.0 (ring-CH_2), 104.0 (ring-CH_2), 86.0 (ring-CH_2), 85.0 (d, ^1J 90, CH_2P), 82.0 (ring-CH_2), 72.5 (ring-CH_2), 69.5 (d, ^1J 90, PCH_2), 68.5 (ring-CH_2, CH_2CO), 63.0 (d, ^1J 90, PCH_2), 48.0 ($CH_2C_{10}H_7$), 7.5 (d, ^1J 90, PCH_3), 6.5 (d, ^1J 90, PCH_3), 4.5 (d, ^1J 90 Hz, PCH_3); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 96.6 (1 P), 84.4 (1 P), 67.4 (1 P); *m*/*z* (ES^-) 794 (100%, *M*) (Found: C, 36.3; H, 6.42; N, 7.40. $C_{23}H_{43}EuN_5O_7P_3\cdot5H_2O$ requires: C, 36.6; H, 5.99; N, 7.91%).

[GdL^2].



This compound was prepared following a method similar to that for complex [EuL^2] using gadolinium(III) acetate (0.046 g, 0.14 mmol) and compound L^2 (0.06 g, 0.1 mmol) in water (3 cm^3) to yield a colourless solid (0.02 g, 26%); m.p. >250 °C; R_f (Al_2O_3; 15% CH_3OH–CH_2Cl_2; I_2 detection) 0.60 (br); ν_{max}(solid)/cm^{-1} 3300 (br) (N–H), 1620 (C=O); *m*/*z* (ES^-) 762 (100%, *M*) (Found: *M*, 764.1621. $C_{24}H_{43}GdN_5O_7P_3$ requires *M*, 764.1616).

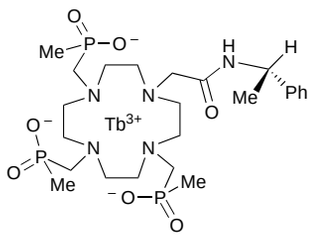
[GdL^{1a}].



This compound was prepared following a method similar to that for complex [EuL^2] using gadolinium(III) acetate (0.049 g, 0.15 mmol) and compound L^{1a} (0.07 g, 0.1 mmol) in water

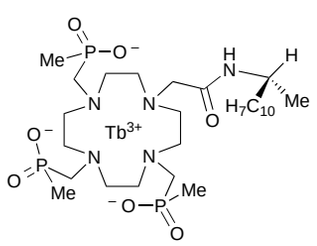
(3 cm^3) to yield a colourless solid (0.02 g, 25%), m.p. >250 °C; R_f (Al_2O_3; 15% CH_3OH–CH_2Cl_2; I_2 detection) 0.42 (br); *m*/*z* (ES^-) 812 (100%, *M*). (A satisfactory accurate mass spectrum could not be obtained for this product.)

[TbL^2].



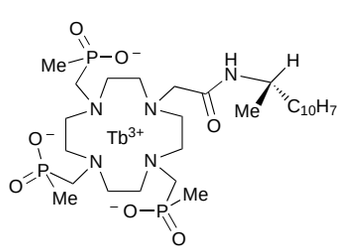
This compound was prepared following a method similar to that of complex [EuL^2] using terbium(III) acetate (0.05 g, 0.14 mmol) and compound **2** (0.06 g, 0.1 mmol) in water (3 cm^3) to yield a pale yellow solid (0.03 g, 40%); m.p. >250 °C; R_f (Al_2O_3; 15% CH_3OH–CH_2Cl_2; I_2 detection) 0.4 (br); ν_{max}(solid)/cm^{-1} 3333 (br) (N–H), 1620 (C=O); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 631 (br), 607 (br), 599 (br), 495 (br), 455 (br); *m*/*z* (ES^-) 764 (100%, *M*) (Found: MH^+, 766.1707. $C_{24}H_{44}N_5O_7P_3Tb$ requires MH^+, 766.1707).

[TbL^{1a}].



This compound was prepared following a method similar to that for complex [EuL^2] using terbium(III) acetate (0.043 g, 0.13 mmol) and compound L^{1a} (0.06 g, 0.09 mmol) in water (3 cm^3) to yield a pale yellow solid (0.03 g, 40%); m.p. >250 °C; R_f (Al_2O_3; 15% CH_3OH–CH_2Cl_2; I_2 detection) 0.51 (br); ν_{max}(solid)/cm^{-1} 3333 (br) (N–H), 1614 (C=O); $\delta_P\{^1H\}$ (101.3 MHz; D_2O) 663 (br), 619 (br), 609 (br), 487 (br), 450 (br); *m*/*z* (ES^-) 814 (100%, *M*) (Found: MH^+, 816.1862. $C_{28}H_{46}N_5O_7P_3Tb$ requires MH^+, 816.1863).

[TbL^{1b}].



This compound was prepared following a method similar to that for complex [EuL^2] using terbium(III) acetate (0.071 g, 0.21 mmol) and compound L^{1b} (0.1 g, 0.15 mmol) in water (3 cm^3) to yield a yellow solid (0.08 g, 65%). Characterisation data are the same as those reported for [TbL^{1a}] (Found: MH^+, 816.1880. $C_{28}H_{46}N_5O_7P_3Tb$ requires MH^+, 816.1863).

Acknowledgements

We thank Durham University, the Royal Society and EPSRC for grant support.

References

1 D. Parker and J. A. G. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 3613.
2 S. Aime, M. Botta, D. Parker and J. A. G. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1995, 2259.
3 K. P. Pulukkody, T. J. Norman, D. Parker, L. Royle and C. J. Broan, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 605.
4 A. Harrison, T. J. Norman, D. Parker, L. Royle, K. A. Pereira, K. P. Pulukkody and C. A. Walker, *Magn. Reson. Imaging*, 1993, **11**, 761.
5 S. Aime, M. Botta, D. Parker and J. A. G. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1996, 17.
6 R. S. Dickins, J. A. K. Howard, C. W. Lehmann,. J. Moloney, D. Parker and R. D. Peacock, *Angew. Chem.*, *Int. Ed. Engl.*, 1997, 521.
7 R. S. Dickins, J. A. K. Howard, J. Moloney, D. Parker, R. D. Peacock and G. Siligardi, *Chem. Commun.*, 1997, 1747.
8 J.-J. Yaouanc, N. Le Bris, G. Le Gall, J.-C. Clement, H. Handel and H. des Abbayes, *J. Chem. Soc.*, *Chem. Commun.*, 1991, 206.
9 E. Cole, C. J. Broan, K. J. Jankowski, P. K. Pulukkody, D. Parker, A. T. Millican, N. R. A. Beeley, K. Millar and B. A. Boyce, *Synthesis*, 1992, 67.
10 I. Bertini and C. Luchinat, *NMR of Paramagnetic Molecules in Biological Systems*, Benjamin-Cummings, Boston, MA, 1986.
11 T. J. Swift, in *NMR of Paramagnetic Molecules: Principles and Applications*, eds. G. N. LaMar, W. De W. Horrocks and R. H. Holm, Academic Press, London, 1973.
12 S. Aime, A. S. Batsanov, M. Botta, R. S. Dickins, S. Faulkner, C. E. Foster, A. Harrison, J. A. K. Howard, J. M. Moloney, T. J. Norman, D. Parker, L. Royle and J. A. G. Williams, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3623.
13 S. Aime, A. S. Batsanov, M. Botta, J. A. K. Howard, D. Parker, P. K. Senanayake and J. A. G. Williams, *Inorg. Chem.*, 1994, **33**, 4696.
14 S. Aime, M. Botta and G. Ermondi, *Inorg. Chem.*, 1992, **32**, 4296.
15 S. Aime, M. Botta, M. Fasano and E. Terreno, *Chem. Soc. Rev.*, 1998, **27**, 19; R. B. Lauffer, *Chem. Rev.*, 1987, **87**, 901.
16 J. F. Desreux, *Inorg. Chem.*, 1980, **19**, 1319; X. Wang, T. Jin, V. Comblin, A. Lopez-Mut, E. Merciny and J. F. Desreux, *Inorg. Chem.*, 1992, **31**, 1095.
17 J.-P. Dubost, M. Leger, M. H. Langlois, D. Meyer and M. C. Schaefer, *C. R. Acad. Sci.*, *Ser. 2*, 1991, **312**, 349.
18 J. A. Peters, J. Huskens and D. J. Raber, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1996, **18**, 283.
19 S. Aime, M. Botta, M. Grandi, M. Panero and F. Uggeri, *Magn. Reson. Chem.*, 1991, **29**, 293.
20 K. A. Connors, in *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle and J.-M. Lehn, Pergamon, Oxford, 1996, vol. 3, ch. 6.
21 A. Beeby, D. Parker and J. A. G. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1165; D. Parker and J. A. G. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 1581.
22 D. Parker and J. A. G. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, 1995, 1305.
23 R. S. Dickins, D. Parker, A. S. deSousa and J. A. G. Williams, *Chem. Commun.*, 1996, 697.
24 D. T. Richens, *The Chemistry of Aqua Ions*, Wiley, Chichester, 1997, ch. 3.
25 J. P. Riehl and F. S. Richardson, *Methods Enzymol.*, 1993, **226**, 539.
26 D. H. Metcalf, S. W. Snyder, J. N. DeMar and F. S. Richardson, *J. Am. Chem. Soc.*, 1990, **112**, 469.
27 E. Huskowska, C. L. Maupin, D. Parker, J. P. Riehl and J. A. G. Williams, *Enantiomer*, 1998, in the press.
28 Y. Haas and G. Stein, *J. Chem. Phys.*, 1971, **75**, 3668.
29 K. Nakamura, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697.
30 S. R. Meech and D. Phillips, *J. Photochem.*, 1983, **23**, 193.

Received 2*nd December* 1997; *Paper* 7/08667I