Yttrium(III) and Lanthanide(III) Metal Complexes of an 18-Membered Hexaaza Tetraimine Macrocycle. Crystal Structure of the Gadolinium(III) Complex†

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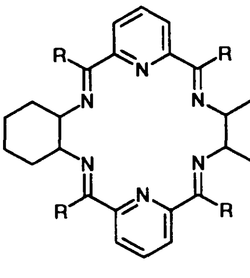
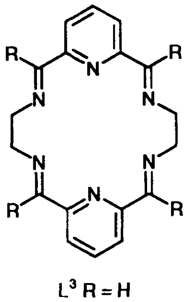
Complexes of Y^{III}, La^{III}, Gd^{III} and Dy^{III} with an 18-membered hexaaza tetraimine macrocyclic ligand (L^1) containing backbone cyclohexyl units have been prepared and characterized. The crystal structure of $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ shows a nine-co-ordinate gadolinium ion bound to three water oxygens and six nitrogen donors from the macrocyclic ligand. Solution studies with radiolabelled ^{90}Y indicated that, in competition with the very strong chelator diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid (H_5dtpa), a $^{90}Y^{III}L^1$ macrocyclic unit is maintained for 1 h. The relaxivity of the gadolinium(III) complex, $[GdL^1(H_2O)_3]^{3+}$, is higher than those of $[Gd(dtpa)(H_2O)]^{2-}$ and $[GdL(H_2O)]^-$ (H_4L = 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid), both of which are currently used as contrast agents in magnetic resonance imaging. A tetramethyl analogue of L^1, *i.e.* L^2, has been synthesized for the first time and a crystal structure determination showed that it adopts a stepped conformation, the direction of folding being dictated by the racemic conformation of the cyclohexane.

Macrocyclic ligand complexes are involved in a number of important biological processes such as photosynthesis and dioxygen transport.[1] The enhanced kinetic and thermodynamic stabilities of macrocycles have led to widespread study of the features which influence their potential applications as metal extractants,[2] and as ligands for radiotherapeutic[3] and medical imaging agents.[4] Macrocycles such as 1,4,7,10-tetraazacyclododecane-*N,N',N'',N'''*-tetraacetic acid and its derivatives have been found to form much more stable complexes and to be better than the linear diethylenetriamine-*N,N,N',N'',N''*-pentaacetic acid (H_5dtpa) and its derivatives for therapeutic and imaging purposes.[5] Gadolinium(III) complexes of macrocyclic ligands have received special attention for their potential applications as NMR imaging agents.[4,6–9]

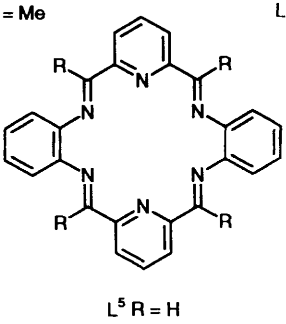
In 1970 Stotz and Stoufer[10] reported the first synthesis of an 18-membered hexadentate macrocycle L^6 by the reaction in dilute solution of 2,6-diacetylpyridine with 1,2-diaminobenzene with, and without, the presence of a copper template ion. Since then the ability of the lanthanide ions to act as metal templates in promoting Schiff-base condensation of 2,6-diformyl- or 2,6-diacetyl-pyridine with either ethane-1,2-diamine or 1,2-diaminobenzene has been well established, and lanthanide complexes of the macrocycles L^{3-6} have been reported.[11–15] Crystal structures of the lanthanide complexes of L^{3-6} show that rigidity of the 18-membered ring is dictated by the four imine bonds,[11–13,15] and is enhanced by the phenyl rings in L^5 and L^6.[12,15] Typically the lanthanide ion co-ordinates to the six nitrogen donor atoms of the macrocycles, leaving the metal ion exposed for potential ligands to co-ordinate on either side of the macrocyclic ligand. The lanthanide complexes of macrocycle L^4 have been shown to be unusually inert to release of metal ions in solution, and this had led to investigation of the magnetic resonance imaging potential of the gadolinium(III) complex.[6]



L^1 R = H
L^2 R = Me



L^3 R = H
L^4 R = Me



L^5 R = H
L^6 R = Me

Despite the extensive work on lanthanide complexes of L^{3-6}, it is only recently that the first reported complexes of the related hexaaza macrocycle L^1, with two cyclohexyl units in the backbone, have been reported.[9,16] Tsubomura *et al.*[16] obtained complexes of L^1 using La^{III}, Eu^{III} and Tb^{III} as template but they were unable to isolate the tetramethyl derivative L^2 or its complexes, which was attributed to electrostatic repulsion between the methyl groups and the hydrogen atom on the cyclohexyl ring preventing cyclization of the diacetylpyridine and the 1,2-diaminocyclohexane. We had independently

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Elemental analysis, effective magnetic moments and yields of complexes

	Analysis[a] (%)				
Complex	C	H	N	μ_{eff}/μ_B	Yield (%)
$YL^1Cl_3(H_2O)_{5.5}$	43.3 (43.3)	5.95 (5.80)	11.6 (11.7)	b	33
$LaL^1(NO_3)_3$	41.6 (41.6)	4.25 (4.05)	16.6 (16.8)	b	56
$GdL^1(NO_3)_3$	39.8 (40.1)	4.45 (3.90)	16.7 (16.4)	7.9	78
$GdL^1Cl_3(H_2O)$	44.0 (44.1)	5.00 (4.55)	11.1 (11.9)	7.4	54
$DyL^1(NO_3)_3$	40.4 (40.3)	3.85 (3.90)	16.3 (16.3)	10.2	57

[a] Calculated values given in parentheses. [b] Diamagnetic.

prepared L^1 using Gd^{III} as a template, and have reported a preliminary structure analysis and results on the potential of the gadolinium complex as a magnetic resonance imaging agent.[9] We now report the synthesis of both L^1 and L^2 by a non-template method and have isolated a series of new complexes of L^1 with Y^{III}, La^{III}, Gd^{III} and Dy^{III}.

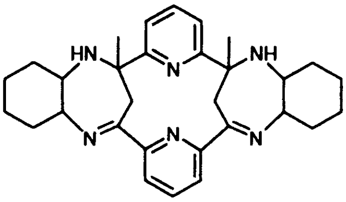
Results and Discussion

Non-template synthesis of L^1 *and* L^2.—The [2 + 2] condensation reaction of 2,6-diformyl- or 2,6-diacetyl-pyridine and (±)-*trans*-1,2-diaminocyclohexane in the absence of a metal, at both low and high dilution, resulted in the isolation of the pure macrocycles L^1 and L^2 respectively. The infrared spectra showed bands at 1639 and 1629 cm^{-1} corresponding to $\nu(C{=}N)_{imine}$ of L^1 and L^2 respectively, and this, together with the absence of any $\nu(C{=}O)$ or $\nu(N{-}H)$ bands, indicated that a Schiff-base macrocycle had been formed. The identities of these macrocyclic products were confirmed by elemental analysis, NMR and mass spectrometry.

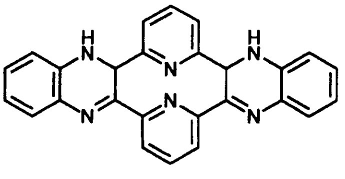
Template Synthesis of L^1 *and* L^2 *in the Presence of Metal Salts*.—Metal chloride and nitrate salts were used for the template synthesis of L^1, and satisfactory elemental analyses were obtained for the resultant white amorphous solids (see Table 1). The metal complexes of L^1 with nitrate as counter ions were isolated in better yields, but the chloride complexes were more soluble in water and methanol. Recrystallization from methanol yielded a crystalline product in all cases, the crystal of $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ being suitable for X-ray diffraction studies. The observed magnetic moments indicate there are seven unpaired electrons in the complexes of Gd^{III} and five unpaired electrons in that of Dy^{III}. Comparison of the IR spectra of free L^1 with those of the metal complexes showed that on complexation the $\nu(C{=}N)$ band of the imine at 1639 cm^{-1} shifts to higher wavenumbers, 1640–1660 cm^{-1}, for the metal complexes. Similarly on co-ordination $\nu(C{=}N)$ of pyridine shifted from 1585 cm^{-1} for L^1 to 1590–1594 cm^{-1} for the complexes. In each of the nitrate complexes one of the nitrate anions was not co-ordinated, giving characteristic sharp bands at 1384 and 813–817 cm^{-1}.

Attempts to synthesize L^2, using (±)-*trans*-1,2-diaminocyclohexane and 2,6-diacetylpyridine in the presence of lanthanide salts at low dilution, gave only lanthanide diaminocyclohexane complexes, but at high dilution a mixture of products was obtained. However, when the lanthanide salts were replaced by those of Ba^{II} a white solid was first formed during the reflux and is formulated as a tricyclic (7 + 12 + 7) compound, L^{2a}, on the basis of its IR and NMR spectra. On filtering whilst hot and allowing the filtrate to stand a white solid having the same composition as L^{2a}, but different IR and NMR spectra, was isolated and assigned as the Ba^{II}-free macrocycle L^2. Both L^2 and L^{2a} were insoluble in common solvents with partial solubility in hot dimethyl sulfoxide, chloroform and pyridine. Of the earlier hexaaza macrocycles the only one so far reported free is L^5,[17] obtained from a potassium complex.

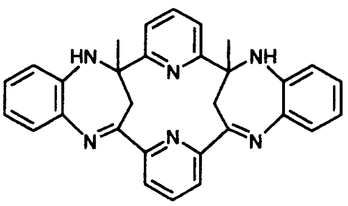
Interestingly, unusual 18-membered macrocyclic rearrangements have also been observed during the preparation of L^5 and L^6 giving the tricyclic (6 + 10 + 6) and (7 + 12 + 7) compounds L^{5a} and L^{6a} respectively.[14,18] In the present work the main difference in the IR spectra observed for the tricyclic compound L^{2a} and the 18-membered macrocycle L^2 were two strong, sharp bands at 3540 and 3399 cm^{-1} for L^{2a}, assigned to $\nu(NH)$ stretching modes of a secondary amine. An IR band in this region was also observed for L^{6a}, the tricyclic structure of which has been confirmed by X-ray crystallography.[18]



L^{2a}



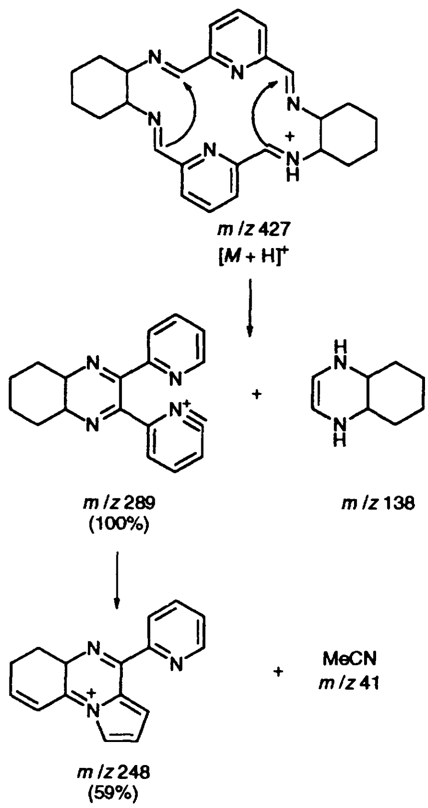
L^{5a}



L^{6a}

Mass Spectra.—The liquid secondary ion mass spectrum of the macrocycle L^1 has a parent ion at *m/z* 427 corresponding to $[M + H]^+$ and the fragmentation pattern is presented in Scheme 1, the base peak observed at *m/z* 289 indicating that the conformation of L^1 is twisted in a similar manner to that of the reported[17] structure of L^5 before fragmentation begins. The base peaks of both L^2 and L^{2a} are similar, each having a molecular ion of $[M + H]^+$ at *m/z* 483 consistent with the formulation of both as $C_{30}H_{38}N_6$. The spectra of the metal complexes of L^1 corresponded to the formation of a [2 + 2] macrocycle. In all the metal complexes the parent ion contains no water and is $[ML^1X_2]^+$ (X = Cl or NO_3); subsequent peaks correspond to loss of the remaining two anions consecutively. All the yttrium and lanthanide metal complexes showed the correct isotopic pattern for each metal except for the chlorides which are difficult to interpret.

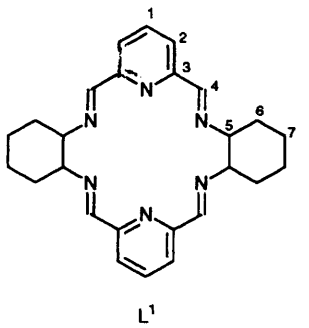
NMR Spectra and Relaxation Studies.—The proton and carbon-13 NMR spectra for the complexes of Y^{III} and La^{III} (^{13}C of this complex cannot be obtained due to insolubility) with L^1, and for the compounds L^2 and L^{2a} (Table 2), are consistent with the formulations proposed. Free L^1 was insoluble in most deuteriated solvents and the NMR spectrum cannot be measured for comparative studies with its metal complexes. Assignments were achieved with the aid of heteronuclear correlation spectroscopy (^1H–^{13}C COSY), and distortionless enhancements by polarization transfer (DEPT-135) spectroscopy. The NMR spectra of L^2 and the complexes of L^1 gave signals corresponding to a quarter of the macrocycle which indicate the solution structures of these compounds have D_2 symmetry. One important feature of the ^1H NMR spectra of L^2 and L^{2a} compared to the complexes of L^1 is the downfield shift of the γ-pyridine proton H^1 of the complexes. This indicates the decrease in electron density of the pyridine ring upon complexation of the macrocycle. A similar observation has also been reported for the macrocycle L^5 and its complex.[17] The striking differences in structure between L^2 and L^{2a} are the methylene and NH groups present in the seven-membered ring of L^{2a} which should theoretically be easily identified by ^1H NMR spectroscopy. However, the signal for the NH proton was not observed. The methylene group, $CH^9{}_2$, of which the carbon atom is prochiral, and the methylene protons are thus expected to show chemical shift non-equivalence in a chiral environment and generate an AB sub-spectrum. Indeed an AB sub-spectrum centred at δ 2.44 and 2.77 corresponding to the methylene protons were observed. Furthermore the number of different carbon atom environments is ten in L^{2a} as opposed to the expected eight for L^2 and similarly the number of quaternary carbon atoms in L^{2a} is three (C^3, C^4 and C^{10}) as opposed to two (C^3 and C^4) for L^2. Therefore carbon-13 NMR studies would be able to confirm the structure of L^{2a}. Ten signals were observed in the ^{13}C off-resonance broad-band proton-decoupled NMR spectrum of L^{2a} (Table 2). DEPT-135 Spectroscopy identified three methylene carbon atoms in different environments and also three quaternary carbon atoms as expected for the proposed (7 + 12 + 7) tricyclic structure.



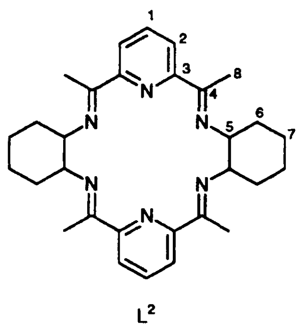
Scheme 1 Fragmentation pattern of L^1

Relaxivity measurements R_1 in water (pH 6, 20 MHz, 37 °C) on $[GdL^1(H_2O)_3]Cl_3$ gave a value of 11.0 $dm^3\ mmol^{-1}\ s^{-1}$ which is very much greater than that of 4.4 $dm^3\ mmol^{-1}\ s^{-1}$ for $[Gd(dtpa)(H_2O)]^{2-}$ which is in current clinical use. The

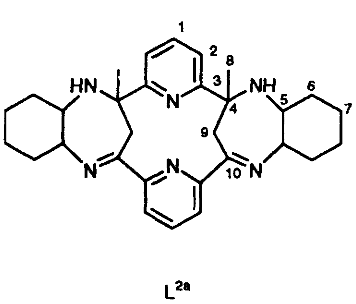
Table 2 Proton and carbon-13 NMR data for complexes of Y^{III} and La^{III} with L^1 and for L^2 and L^{2a}



L^1



L^2



L^{2a}

Assignment	δ_H[a]				δ_C[a]		
	$[YL^1]^{3+}$	$[LaL^1]^{3+}$	L^2	L^{2a}	$[YL^1]^{3+}$	L^2	L^{2a}
1	8.63 (t)	8.61 (t)	7.60 (t)	7.60 (t)	145.9	135.8	135.8
2	8.31 (d)	8.32 (d)	7.81 (d)	7.82 (d)	132.5	119.7	119.7
3	—	—	—	—	154.6	156.6	156.6
4	9.12 (s)	9.02 (s)	—	—	165.8	166.5	77.2
5	3.98 (m)	4.01 (m)	3.74 (m)	3.73 (m)	70.7	66.6	67.9
6	1.9, 2.6 (m)	1.5–2.5 (m)	1.92 (m)	1.92 (m)	32.9	32.1	31.1
7	1.7, 2.2 (m)	1.5–2.5 (m)	1.92 (m)	1.92 (m)	26.9	24.7	24.7
8	—	—	1.86 (s)	1.85 (s)	—	15.0	15.0
9	—	—	—	2.44, 2.77 (d)[b]	—	—	67.9
10	—	—	—	—	—	—	166.5
$J(H^1$-$H^2)$/Hz	7.72	7.75	7.48	7.15			
Solvent	D_2O	D_2O	$CDCl_3$	$CDCl_3$	D_2O	$CDCl_3$	$CDCl_3$

[a] Values in ppm relative to $SiMe_4$ for $CDCl_3$ and to sodium 3-trimethylsilyl[$^2H_4$]propionate for D_2O. [b] $J(H^9$–$H^9)$ = 14.5 Hz.

Table 3 Selected bond lengths (Å) and angles (°) for $[GdL^1(H_2O)_3]^{3+}$

Gd–N(2a)	2.632(11)	N(1e)–C(3a)	1.338(17)	N(1e)–C(3b)	1.363(17)		
Gd–N(2b)	2.583(12)	N(1f)–C(3c)	1.340(16)	N(1f)–C(3d)	1.327(16)		
Gd–N(2c)	2.571(11)	N(2a)–C(4a)	1.264(15)	N(2b)–C(4b)	1.294(17)		
Gd–N(2d)	2.692(11)	N(2c)–C(4c)	1.281(17)	N(2d)–C(4d)	1.270(15)		
Gd–N(1e)	2.618(11)	N(2a)–C(5a)	1.496(16)	N(2b)–C(5b)	1.448(17)		
Gd–N(1f)	2.638(10)	N(2c)–C(5c)	1.479(17)	N(2d)–C(5d)	1.483(16)		
Gd–O(1w)	2.385(9)	C(3a)–C(4a)	1.468(18)	C(3b)–C(4b)	1.425(19)		
Gd–O(2w)	2.330(9)	C(3c)–C(4c)	1.473(19)	C(3d)–C(4d)	1.489(18)		
Gd–O(3w)	2.319(10)	C(5a)–C(5c)	1.540(19)	C(5b)–C(5d)	1.556(18)		
N(1e)–Gd–N(2a)	61.2(3)	N(1e)–Gd–N(2b)	62.3(4)	N(2b)–Gd–O(1w)	86.9(3)	N(2b)–Gd–O(2w)	82.3(4)
N(1f)–Gd–N(2c)	62.0(3)	N(1f)–Gd–N(2d)	60.4(3)	N(2a)–Gd–O(1w)	72.1(3)	N(2a)–Gd–O(2w)	132.5(3)
N(1e)–Gd–N(2c)	122.2(4)	N(1e)–Gd–N(2d)	112.0(3)	N(2b)–Gd–O(3w)	96.4(4)	N(2a)–Gd–O(3w)	76.8(3)
N(2a)–Gd–N(2b)	123.2(3)	N(2d)–Gd–N(2c)	122.0(3)	N(1e)–Gd–O(1w)	74.2(3)	N(1e)–Gd–O(2w)	130.4(4)
N(2a)–Gd–N(2c)	61.3(3)	N(2b)–Gd–N(2d)	60.3(3)	N(1e)–Gd–O(3w)	76.2(4)	N(2c)–Gd–O(1w)	83.3(3)
N(1f)–Gd–N(2a)	112.7(3)	N(1f)–Gd–N(2b)	120.4(3)	N(2c)–Gd–O(2w)	86.5(3)	N(2c)–Gd–O(3w)	96.5(4)
N(2b)–Gd–N(2c)	167.1(4)	N(2a)–Gd–N(2d)	153.7(3)	N(2d)–Gd–O(1w)	132.8(3)	N(2d)–Gd–O(2w)	72.4(3)
C(5a)–N(2a)–Gd	122.0(8)	C(5b)–N(2b)–Gd	117.5(9)	N(2d)–Gd–O(3w)	76.9(3)	N(1f)–Gd–O(1w)	131.3(3)
C(5c)–N(2c)–Gd	116.5(9)	C(5d)–N(2d)–Gd	121.2(8)	N(1f)–Gd–O(2w)	74.5(3)	N(1f)–Gd–O(3w)	76.6(3)
C(4a)–N(2a)–Gd	121.5(9)	C(4b)–N(2b)–Gd	121(1)	O(2w)–Gd–O(1w)	70.1(3)	O(3w)–Gd–O(1w)	144.5(3)
C(3a)–N(1e)–Gd	121.1(9)	C(3b)–N(1e)–Gd	119.7(9)	O(3w)–Gd–O(2w)	145.4(3)	N(1f)–Gd–N(1e)	152.9(3)
C(3c)–N(1f)–Gd	119.7(9)	C(3d)–N(1f)–Gd	124.1(9)				
C(4c)–N(2c)–Gd	123.2(9)	C(4d)–N(2d)–Gd	120.3(9)				

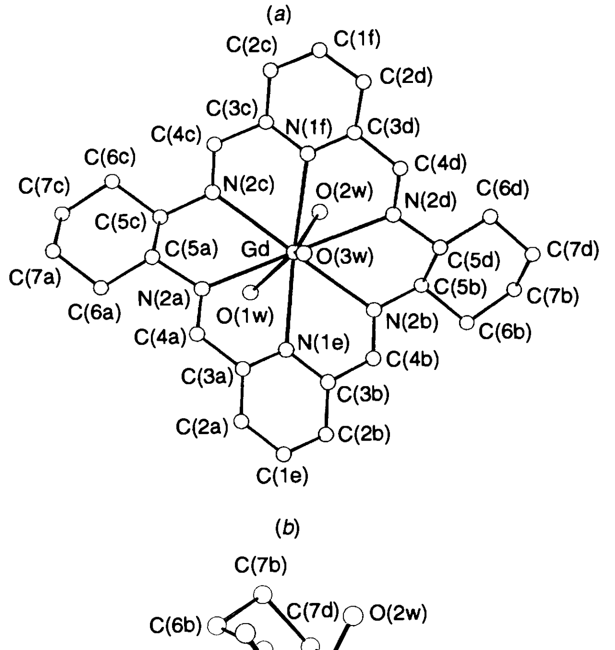


Fig. 1 Two views of the structure of *R,R,R,R* form of $[GdL^1(H_2O)_3]^{3+}$ (the *S,S,S,S* is present in the centrosymmetric crystal in equal amounts) (*a*) onto the best plane through N_6 donor set and (*b*) showing the twist and fold of the macrocycle and the chair conformation of the cyclohexyl rings

L^1 complex has also significantly greater relaxivity than that of the complex $[GdL^4(O_2CMe)_2]^+$ (9.7 dm^3 $mmol^{-1}$ s^{-1}, 20 MHz, 30 °C). This appears to be related to the number of water molecules co-ordinated, but surprisingly luminescence studies of an analogous L^4 complex, $[EuL^4(O_2CMe)_2]^+$, show ready replacement of the acetate ligands by water in aqueous solution. Even in phosphate buffer (pH 6) the relaxivity of $[GdL^1(H_2O)_3]Cl_3$ (4.7 dm^3 $mmol^{-1}$ s^{-1}) is still comparable to that of the dtpa complex in water. These results demonstrate the potential of $[GdL^1(H_2O)_3]Cl_3$ as a contrast agent in magnetic resonance imaging.

Crystal Structure of $[GdL^1(H_2O)_3]Cl_3\cdot3H_2O$.—The asymmetric unit of the crystal consists of the complex cation, three chloride counter ions, and three molecules of water of crystallization. Selected bond lengths and angles for $[GdL^1(H_2O)_3]^{3+}$ are listed in Table 3. The gadolinium ion has a characteristic nine-co-ordinate geometry (Fig. 1), the donor atoms being six nitrogens from the macrocycle [Gd–N 2.571(11)–2.692(11) Å] and three oxygen atoms from co-ordinated water molecules [Gd–O 2.319(10)–2.385(9) Å].

The inner great ring of the macrocyclic ligand may be divided into two almost planar sections; the first consists of the nine atoms from C(5a) through N(1e) to C(5b) [maximum deviation from the least-squares mean plane, 0.137 Å for C(5a)] and the second contains the nine atoms from C(5c) through N(1f) to C(5d) [maximum deviation from the least-squares mean plane, 0.126 Å for C(5d)]. These sections correspond to two regions of extended conjugation, linked by the cyclohexane rings. The dihedral angle between the two sections is 42.8°, which arises from the two components, a twist due to the *R,R*-chair conformation of both cyclohexane rings and an overall folding away from two co-ordinated water molecules, O(1w) and O(2w), towards the third, O(3w). A similar combination of twisting and folding has been discussed for the related hexaaza tetraimine macrocycle in $[GdL^4(O_2CMe)_2]Cl\cdot4H_2O$, with ethylene instead of cyclohexyl bridges, where a dihedral angle of 48.8° occurs. Very similar dihedral angles are observed in $[NdL^4(O_2CMe)_2]^+$ (48.1°) and the monochloride of $[EuL^4(O_2CMe)_2]^+$ (47.6°) (Table 4); however when the $[EuL^4(O_2CMe)_2]^+$ complex crystallizes with an acetate counter ion the dihedral angle is much larger (57.5°). This indicates a strong influence of external factors, a conclusion further supported by the observation that two independent molecules of $[EuL^4(NCS)_3]$, in one solvent-free crystal, have very different dihedral angles of 68.7 and 77.9° (Table 4). The difficulty in rationalizing the large variation of the dihedral angles observed in complexes of this type illustrates an unusual flexibility in the ligands which appear to be susceptible to conformational changes introduced not only by the non-macrocyclic ligand set, but also by factors such as solvent, counter ions and crystal-packing interactions between the

Table 4 Dihedral angles of complexes of L^1, L^{4-6}

Complex	Co-ordination number	Dihedral angle/°	Ref.
$[GdL^1(H_2O)_3]Cl_3 \cdot 3H_2O$	9	42.8	9
$[LaL^4(NO_3)_3]$	12	26.7	19
$[CeL^4(NO_3)_2(H_2O)][NO_3] \cdot H_2O$	11	59.0	19
$[NdL^4(NO_3)(H_2O)_2]_2[NO_3][ClO_4]_3 \cdot 4H_2O$[a]	10	61.6, 62.9	19
$[NdL^4(O_2CMe)_2]Cl \cdot 4H_2O$	10	48.1[b]	20
$[EuL^4(O_2CMe)_2]Cl \cdot 4H_2O$	10	47.6	20
$[EuL^4(O_2CMe)_2][O_2CMe] \cdot 9H_2O$	10	57.5	21
$[EuL^4(NCS)_3]$[c]	9	68.7, 77.9	22
$[GdL^4(O_2CMe)_2]Cl \cdot 4H_2O$	10	48.8[b]	6
$[LuL^4(O_2CMe)(H_2O)][OH][ClO_4] \cdot MeOH$	9	65.6	23
$[LaL^5(NCS)_2(O_2CMe)]$	10	32.6	24
$[PrL^6(NO_3)_2(MeOH)][ClO_4]$	11	69.7	12

[a] Although the complex was formulated[19] as $[\{NdL^4(NO_3)(H_2O)_2\}_2][NO_3][ClO_4]_3 \cdot 4H_2O$, it is not a dimer but contains two independent molecules. [b] Recalculated value. [c] Two independent molecules observed.

Table 5 Bond lengths (Å) and angles (°) for L^2

N(1e)–C(3a)	1.330(7)	N(1e)–C(3c)	1.334(7)
N(2a)–C(4a)	1.278(7)	N(2a)–C(5a)	1.446(7)
N(2c)–C(4c)	1.263(8)	N(2c)–C(5c)	1.452(7)
C(1e)–C(2a)	1.371(8)	C(1e)–C(2c)	1.382(8)
C(2a)–C(3a)	1.386(8)	C(3a)–C(4a)	1.483(8)
C(4a)–C(8a)	1.509(9)	C(5a)–C(6a)	1.511(8)
C(5a)–C(5c)	1.556(8)	C(6a)–C(7a)	1.517(8)
C(7a)–C(7c)	1.533(9)	C(2c)–C(3c)	1.385(8)
C(4c)–C(8c)	1.521(9)	C(5c)–C(6c)	1.530(8)
C(6c)–C(7c)	1.520(9)	C(3c)–C(4c)	1.481(8)
C(3c)–N(1e)–C(3a)	118.8(5)	C(5a)–N(2a)–C(4a)	121.0(6)
C(5c)–N(2c)–C(4c)	119.7(6)	C(2c)–C(1e)–C(2a)	120.0(7)
C(3a)–C(2a)–C(1e)	118.2(7)	C(2a)–C(3a)–N(1e)	122.6(6)
C(4a)–C(3a)–N(1e)	116.7(6)	C(4a)–C(3a)–C(2a)	120.7(6)
C(3a)–C(4a)–N(2a)	116.5(6)	C(8a)–C(4a)–N(2a)	126.5(6)
C(8a)–C(4a)–C(3a)	116.9(6)	C(6a)–C(5a)–N(2a)	109.4(5)
C(5c)–C(5a)–N(2a)	108.8(5)	C(5c)–C(5a)–C(6a)	109.5(5)
C(7a)–C(6a)–C(5a)	111.7(6)	C(7c)–C(7a)–C(6a)	111.6(6)
C(3c)–C(2c)–C(1e)	118.1(7)	C(2c)–C(3c)–N(1e)	122.3(6)
C(8c)–C(4c)–N(2c)	127.8(6)	C(5a)–C(5c)–N(2c)	107.3(5)
C(6c)–C(5c)–N(2c)	110.2(5)	C(6c)–C(5c)–C(5a)	109.1(5)
C(7c)–C(6c)–C(5c)	110.7(6)	C(6c)–C(7c)–C(7a)	111.4(6)
C(8c)–C(4c)–C(3c)	114.0(6)	C(3c)–C(4c)–N(2c)	117.7(6)

complex species themselves. It seems probable that this inherent adaptability of the macrocycle would be favourable in allowing easy access and maximum co-ordination of water in aqueous solution, both factors which will tend to optimize relaxivity and provide a possible explanation of the enhanced relaxivity of the complexes of both L^1 and L^4 compared to dtpa.

The two *cis* water ligands, O(1w) and O(2w), are in sufficiently close contact to allow hydrogen-bonding interaction, O(1w) ··· O(2w) 2.71 Å. All three chloride counter ions are involved in hydrogen bonding with surrounding water molecules (Cl ··· O 2.96–3.16 Å) and there are further hydrogen-bonding interactions between pairs of water molecules (O ··· O 2.65–2.71 Å). The closest contact distance between the water molecules of crystallization and the gadolinium metal atom is Gd ··· O(5w) 4.49 Å.

Crystal Structure of L^2.—X-Ray analysis shows that the macrocycle L^2 is centrosymmetric (Fig. 2) and selected bond lengths and angles are given in Table 5. The symmetry-related cyclohexyl rings adopt chair conformations of opposite hand, *S,S* at C(5a), C(5c) and *R,R* at C(5a′) and C(5c′).

The isolation of the centrosymmetric *R,R,S,S* macrocycle L^2 from the reaction of (±)-*trans*-1,2-diaminocyclohexane and 2,6-diacetylpyridine throws some light on the lack of success reported[16] in attempting to synthesize the *R,R,R,R* isomer from the optically pure *R,R* precursor; in the present work even using the racemic precursor we were unable to isolate the macrocycle L^2 with a lanthanide template. Significantly all the complexes of the related ethylene-bridged L^4 so far reported (Table 4) have shown the same folded conformation which arises from *R,R,R,R* (or *S,S,S,S*) configuration of the two cyclohexyl rings in L^1, observed in $[GdL^1(H_2O)_3]^{3+}$. Introduction of four methyl groups in calculated positions to the observed structure of the L^1 complex, illustrated in Fig. 3, confirms that they give rise to impossibly short contacts (H ··· H 1.14–1.27 Å) between hydrogen atoms of the methyl groups and the cyclohexyl rings; whether or not the *R,R,R,R* isomer of the tetramethyl macrocycle is ever isolated, it seems probable that it could never function as a hexadentate ligand. Examination of the structure of L^2 shows the macrocycle has no twist between the pyridine rings which are exactly parallel and the two halves of the macrocycle fold in opposite directions to give a step

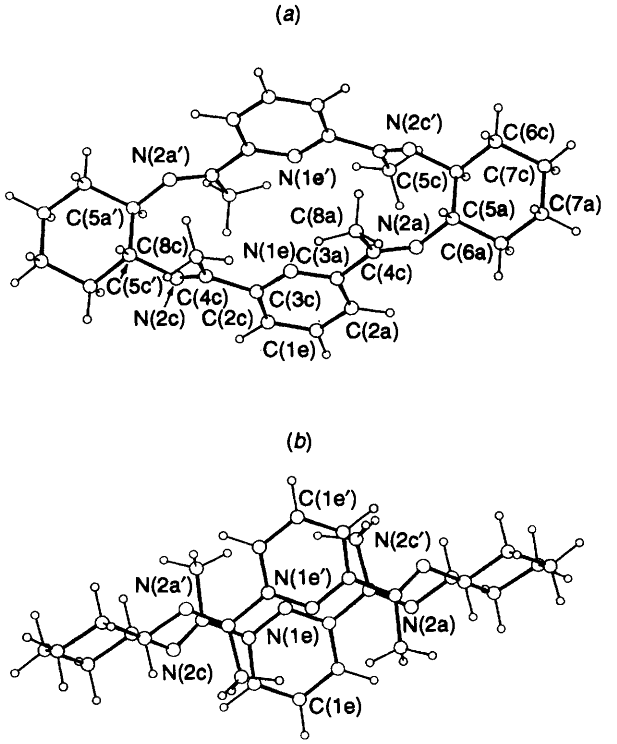


Fig. 2 Views of the structure of the centrosymmetric tetramethyl hexaaza macrocycle L^2 showing (*a*) the *S,S* configuration at C(5a), C(5c) and *R,R* at C(5a′), C(5c′) and (*b*) the step conformation and the parallel pyridine-ring arrangement

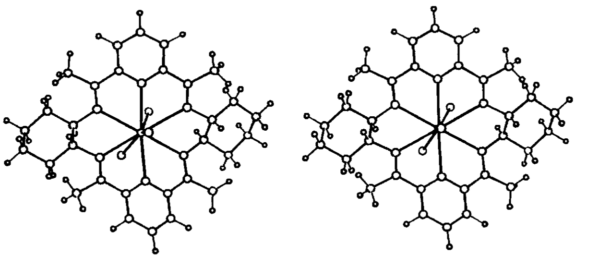


Fig. 3 Stereoview of the simulated structure of the hypothetical gadolinium complex of the *R,R,R,R* isomer of L^2 showing the prohibitively short H ··· H contacts between the methyl and cyclohexyl groups

conformation arising from the *R,R,S,S* configuration of the cyclohexyl rings. This unfavourable conformation (Fig. 2) may well rule out any potential for hexadentate complex formation for this tetramethyl isomer.

Radiolabelling Studies.—Instant thin-layer chromatography (ITLC) was used to monitor the template synthesis of $[^{90}YL^1]^{3+}$ with radioactive yttrium-90, a pure β^- emitter, and a competition study of the labelled yttrium complex with H_5dtpa. The insolubility of the 'cold' complexes of $[YL^1Cl_2(H_2O)]Cl{\cdot}3.5H_2O$ and $[YL^1(NO_3)_2][NO_3]$ in common solvents at room temperature prevented their 'spiking'. Various individual complexes that might be present during the synthesis of the $[^{90}YL^1]^{3+}$ were also prepared to assist the assignment of the species present. The R_f values of these complexes, the yttrium macrocyclic complex and results of the competition study are listed in Table 6. The good separation observed for the R_f values indicates that methanol is a good solvent system for monitoring the template synthesis and the ligand competition study. The R_f values of the yttrium macrocyclic complex remain constant after 1 and 24 h showing that the complex is stable in methanol solution. When a 10-fold excess of H_5dtpa at pH 7 was added to the above solution, R_f values of 0.73 and 0.63 were obtained after 1 and 24 h respectively. The former value is assigned to a ternary complex of yttrium(III), the macrocycle and H_5dtpa. The latter R_f value matched that of the $[^{90}Y(dtpa)]^{2-}$ complex suggesting that after 24 h H_5dtpa had scavenged the metal from the macrocycle. The 100% loss of a metal ion of a hexaaza tetraimine complex in the presence of H_5dtpa after 20 h or more has been reported before, for example both lanthanum(III) and lutetium(III) complexes of L^4 lost their metal ions in the presence of a two-fold excess of H_5dtpa after 20.5 h at pH 7.[25]

Experimental

Materials.—All reagents and solvents were generally of GPR grade, obtained from Aldrich Chemical Company and used without further purification. 2,6-Diformylpyridine was prepared in 87% yield by following a literature method.[26] The compound $^{90}YCl_3$ was obtained from Amersham International plc as a solution in 0.04 mol dm^{-3} HCl.

Physical Measurements.—Microanalyses were performed by the Microanalysis Laboratory and mass spectrometry was carried out by the Mass Spectrometry Service of University of North London; liquid secondary ion mass spectra were recorded on a Kratos Profile spectrometer with *m*-nitrobenzyl alcohol as matrix. Fourier-transform IR spectra were recorded as potassium bromide discs for solid samples on a Bio-rad FTS-40 spectrometer, ^1H and ^{13}C NMR spectra on a Bruker AM 250 MHz spectrometer. Water relaxation measurements were obtained using a Bruker 20 MHz multispec. A room-temperature magnetic susceptibility balance were used with $Hg[Co(SCN)_4]$ as the standard. Corrections for diamagnetism were made using Pascal's constants.[27]

Table 6 The R_f values obtained for various complexes of yttrium-90 at 1 and 24 h

Complex *	R_f	Complex	R_f
$YCl_3{\cdot}nH_2O$	0.0	$[YL^1]^{3+}$	0.41
$[Y(dtpa)]^{2-}$	0.62	$[YL^1]^{3+}$ and H_5dtpa, 1 h	0.73
$[Y(chxn)_3]^{3+}$	0.0	$[YL^1]^{3+}$ and H_5dtpa, 24 h	0.63

* chxn = 1,2-Diaminocyclohexane.

Preparation of Macrocycles.—L^1. A solution of (±)-*trans*-1,2-diaminocyclohexane (1.70 g, 15.0 × 10^{-3} mol) in methanol (10 cm^3) was added dropwise to a refluxing solution of 2,6-diformylpyridine (2.04 g, 15.1 × 10^{-3} mol) in methanol (80 cm^3). The white solid of L^1 (2.22 g, 68%) precipitated during the 3 h reflux and was filtered off whilst hot, washed with methanol (2 × 10 cm^3) and diethyl ether (1 × 10 cm^3) and dried under vacuum, m.p. 349–352 °C (Found: C, 73.3; H, 7.10; N, 19.9. $C_{26}H_{30}N_6$ requires C, 73.2; H, 7.10; N, 19.7%). IR (cm^{-1}): ν(C=N) 1639, (imine) and 1585 (pyridine). Liquid secondary ion (LSI) mass spectrum: *m*/*z* 427 (25%), parent ion.

L^2. A solution of (±)-*trans*-1,2-diaminocyclohexane (3.50 g, 31.0 × 10^{-3} mol) in acetonitrile or methanol (150 cm^3) was added dropwise over 2 h to a refluxing solution of 2,6-diacetylpyridine (5.04 g, 15.1 × 10^{-3} mol) in acetonitrile or methanol (150 cm^3). Reflux was continued for 4 h during which the white solid of L^2 (4.26 g, 57%) precipitated and was filtered off whilst hot, washed with acetonitrile (3 × 15 cm^3) and diethyl ether (1 × 10 cm^3) and dried under vacuum, m.p. 304–315 °C (Found: C, 74.8; H, 7.90; N, 17.4. $C_{30}H_{38}N_6$ requires C, 74.7; H, 7.95; N, 17.4%). IR (cm^{-1}): ν(C=N) 1629 (imine) and 1567 (pyridine). LSI mass spectrum: *m*/*z* 483 (100%), parent ion.

L^2 *and* L^{2a} *in the presence of* Ba^{II}. Dropwise addition of a solution of (±)-*trans*-1,2-diaminocyclohexane (2.1 g, 18.4 mmol) in methanol (20 cm^3) to a refluxing solution of 2,6-diacetylpyridine (3.05 g, 18.7 mmol) and barium(II) chloride dihydrate (2.24 g, 9.2 mmol) in methanol (100 cm^3) resulted in the precipitation of the white solid of L^{2a} (1.26 g, 28%) which was filtered off whilst hot under suction, m.p. 291–299 °C (decomp.) (Found: C, 74.9; H, 8.15; N, 17.6. $C_{30}H_{38}N_6$ requires C, 74.7; H, 7.95; N, 17.4%). The filtrate was allowed to stand at room temperature overnight, resulting in the precipitation of the white compound L^2 (0.93 g, 21%).

Preparation of Metal Complexes of L^1.—A general procedure was used to prepare the complexes of Y^{III}, La^{III}, Gd^{III} and Dy^{III} with L^1. A solution of (±)-*trans*-1,2-diaminocyclohexane (1.7 g, 15.0 mmol) in methanol (10 cm^3) was added dropwise over 30 min to a solution of the metal salt (0.5 mol equivalent) and 2,6-diformylpyridine (1 mol equivalent) in methanol (100 cm^3) and heated for 3–4 h. Where the metal salt was the nitrate a white precipitate formed during reflux, analysing for the appropriate metal complex of L^1. For the metal chloride salts the volume of the reaction mixture was reduced by half and allowed to stand at room temperature resulting in the precipitation of the metal complex over several weeks. The complexes were filtered off under suction, washed with cold methanol and diethyl ether and dried under vacuum. Elemental analysis, yields and magnetic moments are shown in Table 1. LSI mass spectra (parent ion only): $[YL^1Cl_2]^+$, *m*/*z* 587 (7); $[LaL^1(NO_3)_2]^+$, 690 (100); $[GdL^1Cl_2]^+$, 654 (12); $[GdL^1(NO_3)_2]^+$, 707 (80%); $[DyL^1(NO_3)_2]^+$ 714 (100%).

X-Ray Structural Analyses of $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ *and* L^2.—*Crystal data.* $C_{26}H_{38}Cl_3GdN_6O_6$, *M* = 794.23, monoclinic, space group $P2_1/c$ (no. 14), *a* = 16.842(3), *b* 12.189(3), *c* = 17.741(3) Å, β = 115.61(2)°, *U* = 3284.2 Å^3, *Z* = 4, *F*(000) = 1516, D_c = 1.46 g cm^{-3}, μ(Mo-Kα) = 21.78 cm^{-1}, λ = 0.710 69 Å.

Table 7 Fractional atomic coordinates for $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$

Atom	*x*	*y*	*z*
Gd	0.249 26(5)	0.156 80(6)	−0.008 96(4)
Cl(1)	0.216 4(3)	−0.093 0(3)	0.196 1(3)
Cl(2)	0.200 8(3)	0.298 7(4)	0.205 4(3)
Cl(3)	0.713 4(3)	0.061 9(3)	0.471 0(3)
O(1w)	0.260 9(6)	0.322 0(8)	0.067 1(6)
O(2w)	0.239 9(6)	0.117 6(8)	0.115 5(6)
O(3w)	0.249 0(7)	0.083 6(9)	−0.129 7(6)
N(2a)	0.186 3(7)	0.317 8(9)	−0.117 6(6)
N(1e)	0.359 6(7)	0.281 8(10)	−0.037 7(7)
N(2b)	0.415 4(8)	0.129 5(9)	0.084 2(7)
N(2c)	0.083 5(8)	0.198 5(9)	−0.070 8(7)
N(1f)	0.139 5(7)	−0.010 2(9)	−0.043 2(6)
N(2d)	0.313 2(7)	−0.046 9(9)	0.038 2(7)
C(7a)	−0.025 9(10)	0.495 4(13)	−0.206 4(10)
C(6a)	0.072 9(10)	0.469 2(13)	−0.177 6(10)
C(5a)	0.091 0(9)	0.349 2(12)	−0.154 9(8)
C(4a)	0.235 6(8)	0.374 6(10)	−0.139 5(8)
C(3a)	0.330 9(9)	0.355 1(12)	−0.099 9(8)
C(2a)	0.389 8(10)	0.414 3(13)	−0.118 5(10)
C(1e)	0.479 3(11)	0.399 8(14)	−0.074 3(10)
C(2b)	0.506 5(10)	0.328 4(13)	−0.010 2(9)
C(3b)	0.448 0(10)	0.268 2(12)	0.008 4(9)
C(4b)	0.473 5(10)	0.187 0(12)	0.072 3(9)
C(5b)	0.440 8(9)	0.041 0(12)	0.144 6(9)
C(6b)	0.541 8(10)	0.033 6(14)	0.203 1(10)
C(7b)	0.556 5(12)	−0.067 7(14)	0.260 7(11)
C(7c)	−0.055 2(12)	0.463 3(14)	−0.139 3(11)
C(6c)	−0.040 4(10)	0.339 8(14)	−0.122 4(10)
C(5c)	0.057 5(10)	0.314 8(12)	−0.090 2(9)
C(4c)	0.024 3(10)	0.123 7(12)	−0.092 6(9)
C(3c)	0.052 5(9)	0.008 1(12)	−0.079 2(9)
C(2c)	−0.008 8(10)	−0.075 1(12)	−0.099 8(9)
C(1f)	0.020 1(9)	−0.182 9(12)	−0.086 6(9)
C(2d)	0.108 8(9)	−0.204 3(12)	−0.048 6(9)
C(3d)	0.164 6(9)	−0.114 2(11)	−0.028 3(8)
C(4d)	0.261 7(9)	−0.128 9(10)	0.017 9(8)
C(5d)	0.408 1(9)	−0.065 7(11)	0.092 0(9)
C(6d)	0.430 0(9)	−0.168 8(13)	0.149 2(9)
C(7d)	0.526 2(10)	−0.170 6(14)	0.207 7(10)
O(4w)	0.269 6(8)	−0.161 0(11)	−0.314 3(7)
O(5w)	0.293 2(9)	−0.116 5(11)	−0.156 0(8)
O(6w)	0.753 0(10)	0.309 7(13)	0.131 8(10)

Table 8 Fractional atomic coordinates for L^2

Atom	*x*	*y*	*z*
N(1e)	0.3934(4)	0.1385(6)	0.0159(2)
N(2a)	0.3263(4)	0.0249(6)	−0.1163(2)
N(2c)	0.5346(4)	−0.0643(6)	−0.1494(2)
C(1e)	0.2227(5)	−0.0533(8)	0.0406(3)
C(2a)	0.2451(6)	−0.0178(8)	−0.0123(3)
C(3a)	0.3322(5)	0.0786(8)	−0.0230(3)
C(4a)	0.3631(5)	0.1159(8)	−0.0795(3)
C(5a)	0.3598(5)	0.0411(8)	−0.1720(2)
C(6a)	0.2636(6)	0.0220(9)	−0.2086(2)
C(7a)	0.2948(5)	0.0301(9)	−0.2679(3)
C(8a)	0.4384(5)	0.2529(9)	−0.0877(3)
C(2c)	0.2878(5)	0.0037(8)	0.0814(3)
C(3c)	0.3735(5)	0.0987(8)	0.0671(2)
C(4c)	0.5450(5)	−0.1479(8)	−0.1075(3)
C(5c)	0.4436(5)	−0.0892(8)	−0.1850(2)
C(6c)	0.4783(5)	−0.0741(8)	−0.2441(3)
C(7c)	0.3824(5)	−0.0899(9)	−0.2817(3)
C(8c)	0.4790(5)	−0.2905(8)	−0.0910(3)

$C_{30}H_{38}N_6$, $M = 482.67$, orthorhombic, space group *Pccn* (no. 56), $a = 12.473(3)$, $b = 8.494(2)$, $c = 24.722(3)$ Å, $U = 2619.19$ Å^3, $Z = 4$, $F(000) = 1040$, $D_c = 1.224$ g cm^{-3}, μ(Mo-Kα) = 0.7 cm^{-1}.

Data collection. Intensity data were collected on a Philips four-circle diffractometer using Mo-Kα radiation from a graphite monochromator, in the range θ 3–25° with a scan width of 0.90°, using the method described previously.[28] Both crystals used were colourless with dimensions 0.25 × 0.35 × 0.25 and 0.32 × 0.30 × 0.08 mm for $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ and L^2 respectively. In each case three reference reflections were measured every 5 h which showed no significant variation in intensities. Lorentz and polarization corrections were applied to the data and equivalent reflections were merged to give 2726 and 730 unique reflections with $I/\sigma(I) \geqslant 3$ for $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ and L^2 respectively.

Structure solution and refinement.[29] For $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ the coordinates of the metal and one chlorine atom were deduced from a Patterson synthesis and those of the nitrogen and nine carbon atoms for L^2 were obtained by direct methods.[30] For each structure the remaining non-hydrogen atoms were located from subsequent Fourier-difference syntheses. After several cycles of refinement with isotropic thermal parameters the hydrogen atoms were included at calculated positions (C–H 1.08 Å) with fixed isotropic thermal parameters of 0.08 Å^2. Absorption corrections[31] (maximum 1.117, minimum 0.883) were applied to the data of $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ at this stage. In the final cycles of full-matrix least-squares refinement anisotropic thermal parameters were assigned to the gadolinium, the co-ordinated oxygen and nitrogen atoms and the chlorine atoms in $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$, and to the three nitrogen atoms in L^2; refinement converged at $R = 0.0588$ ($R' = 0.0572$) and 0.0605 (0.0602) for $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ and L^2 respectively with weights of $1/\sigma^2(F)$ assigned to individual reflections for both structures. Final atomic coordinates for $[GdL^1(H_2O)_3]Cl_3{\cdot}3H_2O$ and L^2 are listed in Tables 7 and 8 respectively.

Additional material available for both structures from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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