Synthesis of lanthanide(III) complexes of a 20-membered hexaaza macrocycle †

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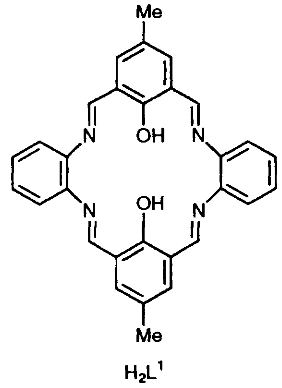
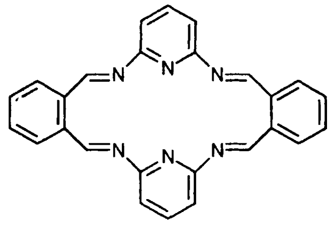
Lanthanide(III) and yttrium(III) complexes of the 20-membered hexaaza Schiff-base macrocycle 6,20-dimethyl-2,10,16,24,29,31-hexaazapentacyclo[23.3.1.1^{4,8}.1^{11,15}.1^{18,22}]dotriaconta-1(29),2,4,6,8(30),9,11,13,15(31),16,18,20,22(32),23,25,27-hexadecaene-30,32-diol (H_2L^3) have been synthesised by metal-template condensation of 2,6-diformyl-4-methylphenol and 2,6-diaminopyridine: $[Pr(H_2L^3)(NO_3)_2(H_2O)_3]NO_3 \cdot 3H_2O$, $[Ln(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$ (Ln = La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} or Tm^{3+}), $[Eu(HL^3)(NO_3)(H_2O)_2]NO_3 \cdot 5H_2O$ and $[Y(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 5H_2O$. The yield of the complexes vary from 93 to 75% (for La^{3+}–Er^{3+} and Y^{3+}) to 50% (for Tm^{3+}). The diminution in the ionic radii of the lanthanide(III) cations does not affect their template potential. The metal ions are bound to the macrocycle and to one bidentate chelating nitrate ion (two for Pr^{3+}) and to two or three water molecules. The complexes are stable in air in the solid state and are inert to release of metal ions in dimethylformamide. The exocyclic ligands are substitution labile and undergo anion metathesis when treated with ClO_4^- or SCN^-. The complexes are thermally stable and the macrocycle remains intact with the metal ions up to 338 °C. The essential requisite for synthesis of the complexes of these metal ions in the same ligand framework seems to be the flexibility of the latter. The template potential of the lanthanide(III) cations of varying sizes in the H_2L^3 assembly is due to the flexibility of the macrocycle to adapt to the geometrical requirements of the metal ions and to the steric demands of the exocyclic ligands.

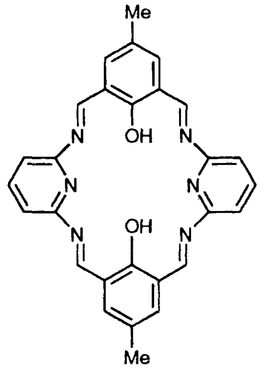
The design and synthesis of macrocyclic complexes of the lanthanides[2–5] continue to receive much attention owing to the ramifying applications of these compounds in fundamental and applied sciences.[2,6,7] Macrocyclic complexes of lanthanides are used as catalysts in the transesterification of RNA,[8] in radioimmunotherapy,[9–11] as radiopharmaceuticals,[9,12] as contrast enhancing agents in magnetic resonance imaging,[13–15] as NMR shift reagents,[16–18] and as fluorescent probes in fluoroimmunoassay.[19–21] They also find use in laser technology,[22] in the separation of lanthanides[23–25] and in material science.[26] The design of ligands capable of forming stable lanthanide complexes would enable chemists to exploit more fully certain important emerging properties of these complexes. The challenge is to design potential macrocycles with appropriate features.



H_2L^1



L^2



H_2L^3

Our research interest in the synthesis of macrocyclic complexes of all lanthanide(III) cations in identical ligand frameworks has two objectives: (*i*) to study the influence of the structure and dynamics of the ligand framework on the physicochemical properties of the rare-earth-metal cations in order to identify the ligand-design features required to form robust lanthanide(III) complexes with specific metal ions and (*ii*) to design flexible macrocycles which can adapt to the geometrical requirements of the lanthanide(III) cations of varying sizes to harness their potential applications in an identical ligand framework. The first macrocycle we have reported is the 18-membered tetraaza macrocycle H_2L^1 derived from phenol head units and aromatic lateral units.[27] It forms complexes with lanthanide(III) cations except lanthanum and cerium. The complexes are stable in the solid state and inert to the release of metal ions in dimethylformamide (dmf) and methanol. However, they are unstable in solution in the presence of precipitating agents and other competing ligands. The second member of the series is the 18-membered hexaaza macrocycle L^2 derived from pyridyl head units and aromatic lateral units.[1] It forms lanthanide(III) complexes of varying stoichiometry under the same experimental conditions due to the different geometrical requirements of these metal ions. The complexes exhibit inertness to the release of metal ions in dmf. Incorporation of the pyridyl unit onto the macrocyclic framework would increase the rigidity and binding ability

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† Macrocyclic complexes of lanthanides in identical ligand frameworks. Part 3.[1]

towards lanthanide(III) cations. In addition, pyridine-containing chelate rings have lower ring strain than the analogous rings formed from alkylamines.[28] Macrocycles incorporating the rigid pyridine ring and flexible 4-substituted 2,6-diformylphenols would form lanthanide(III) complexes having superior properties. We report herein the template synthesis of lanthanide(III) complexes of the 20-membered hexaaza macrocycle 6,20-dimethyl-2,10,16,24,29,31-hexaazapentacyclo[23.3.1.1^{4,8}.1^{11,15}.1^{18,22}]dotriaconta-1(29),2,4,6,8(30),9,11,13,15(31),16,18,20,22(32),23,25,27-hexadecaene-30,32-diol (H_2L^3).

Experimental

Materials

2,6-Diaminopyridine (Fluka) was used as such. The other chemicals, the methods of purification of the solvents and the details of physical measurements were described elsewhere.[27]

General method of synthesising complexes of H_2L^3

To a solution of 2,6-diformyl-4-methylphenol (0.328 g, 2 mmol) in acetonitrile (40 cm^3) was added a solution of the hydrated lanthanide nitrate (Ln = Y^{3+}, La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} or Tm^{3+}) (1 mmol) in acetonitrile (10 cm^3) and stirred for 5 min using a magnetic stirrer at room temperature (30 °C). A solution of 2,6-diaminopyridine (0.218 26 g, 2 mmol) in acetonitrile (40 cm^3) was added dropwise over a period of 5 min and the reaction mixture stirred for 6 h. The reddish orange microcrystalline compound which separated was filtered off, washed with acetonitrile followed by diethyl ether and dried *in vacuo* over anhydrous calcium chloride.

$[La(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **1**: yield 0.6912 g, 80% (Found: C, 38.60; H, 3.60; N, 13.05. Calc. for $C_{28}H_{35}LaN_8O_{15}$: C, 38.95; H, 4.15; N, 12.95%); Λ_M(MeOH) 154 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 793, $[La(HL^3)(NO_3)_2(H_2O)_3]^+$; 775, $[La(HL^3)(NO_3)_2(H_2O)_2]^+$; 737, $[La(HL^3)(NO_3)_2]^+$; 632, $[La(HL^3)(H_2O)]^+$; and 475, $[H_2L^3 + H]^+$.

$[Pr(H_2L^3)(NO_3)_2(H_2O)_3]NO_3\cdot 3H_2O$ **2**: yield 0.7794 g, 90% (Found: C, 37.30; H, 3.50; N, 13.40. Calc. for $C_{28}H_{34}N_9O_{17}Pr$: C, 36.95; H, 3.75; N, 13.85%); Λ_M(MeOH) 139 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 795, $[Pr(H_2L^3)(NO_3)_2(H_2O)_3]^+$; 759, $[Pr(H_2L^3)(NO_3)_2(H_2O)]^+$; 699, $[Pr(H_2L^3)(NO_3)]^+$; and 477, $[H_4L^3 + H]^+$.

$[Nd(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **3**: yield 0.7039 g, 81% (Found: C, 38.55; H, 4.00; N, 12.45. Calc. for $C_{28}H_{35}N_8NdO_{15}$: C, 38.70; H, 4.15; N, 12.90%); Λ_M(MeOH) 142 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 796, $[Nd(HL^3)(NO_3)_2(H_2O)_3]^+$; 778, $[Nd(HL^3)(NO_3)_2(H_2O)_2]^+$; 716, $[Nd(HL^3)(NO_3)(H_2O)_2]^+$; 654, $[Nd(HL^3)(H_2O)_2]^+$; and 475, $[H_2L^3 + H]^+$.

$[Sm(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **4**: yield 0.70 g, 80% (Found: C, 38.10; H, 3.80; N, 12.40. Calc. for $C_{28}H_{35}N_8O_{15}Sm$: C, 38.45; H, 4.10; N, 12.80%); Λ_M(MeOH) 151 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 806, $[Sm(HL^3)(NO_3)_2(H_2O)_3]^+$; 788, $[Sm(HL^3)(NO_3)_2(H_2O)_2]^+$; 725, $[^{154}Sm(HL^3)(NO_3)(H_2O)_2]^+$; 723, $[^{152}Sm(HL^3)(NO_3)(H_2O)_2]^+$; 660, $[Sm(HL^3)(H_2O)_2]^+$; 625, $[Sm(HL^3)]^+$; and 479, $[H_6L^3 + H]^+$.

$[Eu(HL^3)(NO_3)(H_2O)_2]NO_3\cdot 5H_2O$ **5**: yield 0.6665 g, 76% (Found: C, 39.20; H, 4.20; N, 12.45. Calc. for $C_{28}H_{35}EuN_8O_{15}$: C, 38.35; H, 4.10; N, 12.80%); Λ_M(MeOH) 124 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 808, $[Eu(HL^3)(NO_3)_2(H_2O)_2]^+$; 806, $[Eu(HL^3)(NO_3)_2(H_2O)_2]^+$; 724, $[Eu(HL^3)(NO_3)(H_2O)_2]^+$; 664, $[Eu(HL^3)(H_2O)_2]^+$; 662, $[Eu(HL^3)(H_2O)_2]^+$; and 475, $[H_2L^3 + H]^+$.

$[Gd(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **6**: yield 0.679 14 g, 77% (Found: C, 38.80; H, 4.10; N, 12.40. Calc. for $C_{28}H_{35}GdN_8O_{15}$: C, 38.15; H, 4.10; N, 12.70%); Λ_M(MeOH) 129 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 810, $[Gd(HL^3)(NO_3)_2(H_2O)_3]^+$; 792, $[Gd(HL^3)(NO_3)_2(H_2O)_2]^+$; 728, $[Gd(HL^3)(NO_3)(H_2O)]^+$; 668, $[Gd(HL^3)(H_2O)_2]^+$; and 475, $[H_2L^3 + H]^+$.

$[Tb(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **7**: yield 0.769 g, 87% (Found: C, 37.50; H, 3.45; N, 12.65. Calc. for $C_{28}H_{35}N_8O_{15}Tb$: C, 38.05; H, 4.05, N, 12.70%); Λ_M(MeOH) 119 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 812, $[Tb(HL^3)(NO_3)_2(H_2O)_3]^+$; 731, $[Tb(HL^3)(NO_3)(H_2O)_2]^+$; 668, $[Tb(HL^3)(H_2O)_2]^+$; 650, $[Tb(HL^3)(H_2O)]^+$; and 475, $[H_2L^3 + H]^+$.

$[Dy(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **8**: yield 0.665 25 g, 75% (Found: C, 38.00; H, 4.05; N, 12.80. Calc. for $C_{28}H_{35}DyN_8O_{15}$: C, 37.90; H, 4.05; N, 12.60%); Λ_M(MeOH) 123 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 818, $[Dy(HL^3)(NO_3)_2(H_2O)_3]^+$; 755, $[Dy(HL^3)(NO_3)(H_2O)_3]^+$; and 477, $[H_4L^3 + H]^+$.

$[Ho(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **9**: yield 0.801 g, 90% (Found: C, 37.20; H, 3.95; N, 12.20. Calc. for $C_{28}H_{35}HoN_8O_{15}$: C, 37.80; H, 4.05; N, 12.60%); Λ_M(MeOH) 129 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 819, $[Ho(HL^3)(NO_3)_2(H_2O)_3]^+$; 799, $[Ho(HL^3)(NO_3)_2(H_2O)_2]^+$; 735, $[Ho(HL^3)(NO_3)(H_2O)_2]^+$; 673, $[Ho(HL^3)(H_2O)_2]^+$; and 481, $[H_8L^3 + H]^+$.

$[Er(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **10**: yield 0.7938 g, 89% (Found: C, 37.55; H, 3.90; N, 12.15. Calc. for $C_{28}H_{35}ErN_8O_{15}$: C, 37.70; H, 4.05; N, 12.55%); Λ_M(MeOH) 126 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 764, $[Er(HL^3)(NO_3)_2]^+$; 643, $[Er(HL^3)]^+$; and 475, $[H_2L^3 + H]^+$.

$[Tm(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 4H_2O$ **11**: yield 0.447 g, 50% (Found: C, 38.60; H, 4.00; N, 12.00. Calc. for $C_{28}H_{35}N_8O_{15}Tm$: C, 37.60; H, 4.05; N, 12.55%); Λ_M(MeOH) 107 ohm^{-1} cm^2 mol^{-1}; FAB mass spectrum, *m/z* 823, $[Tm(HL^3)(NO_3)_2(H_2O)_3]^+$; 804, $[Tm(HL^3)(NO_3)_2(H_2O)_2]^+$; 742, $[Tm(HL^3)(NO_3)(H_2O)_2]^+$; 706, $[Tm(HL^3)(NO_3)]^+$; 680, $[Tm(HL^3)(H_2O)_2]^+$; 662, $[Tm(HL^3)(H_2O)]^+$; 644, $[Tm(HL^3)]^+$; and 475, $[H_2L^3 + H]^+$.

$[Y(HL^3)(NO_3)(H_2O)_3]NO_3\cdot 5H_2O$ **12**: yield 0.757 02 g, 93% (Found: C, 40.15; H, 4.50; N, 12.85. Calc. for $C_{28}H_{37}N_8O_{16}Y$: C, 40.45; H, 4.55; N, 13.45%); Λ_M(MeOH) 138 ohm^{-1} cm^2 mol^{-1}.

$[Dy(HL^3)(ClO_4)(H_2O)_2]NO_3\cdot 3H_2O$ 13

This complex was synthesised by anion metathesis of **8** with ClO_4^-. To a solution of **8** (0.887 g, 1 mmol) in methanol (20 cm^3) was added solid $LiClO_4\cdot 3H_2O$ (0.4813 g, 3 mmol) and the mixture was allowed to stand at room temperature for 2 d in a stoppered flask. The resulting solution was poured into diethyl ether when a deep red microcrystalline compound separated. It was filtered off, washed with methanol–ether (1:5 v/v) and dried over anhydrous calcium chloride. Yield 0.3932 g, 44% (Found: C, 38.05; H, 3.60; N, 11.25. Calc. for $C_{28}H_{32}ClDyN_7O_{14}$: C, 37.85; H, 3.65; N, 11.05%). Λ_M(dmf) 91 ohm^{-1} cm^2 mol^{-1}.

$[Sm(HL^3)(NCS)(H_2O)]NO_3\cdot 4H_2O$ 14

This complex was synthesised by anion metathesis of **4** with SCN^-. To a solution of **4** (0.875 g, 1 mmol) in methanol (20 cm^3) was added KSCN (0.291 g, 3 mmol) and the mixture was allowed to stand at room temperature for 2 d in a stoppered flask. The resulting solution was poured into diethyl ether when an orange-red microcrystalline compound separated. It was filtered off, washed with methanol–ether (1:5 v/v) and dried over anhydrous calcium chloride. Yield 0.2052 g, 30% (Found: C, 43.40; H, 3.95; N, 13.10. Calc. for $C_{29}H_{32}N_8O_{10}SSm$: C, 43.70; H, 3.85; N, 13.45%). Λ_M(dmf) 89 ohm^{-1} cm^2 mol^{-1}.

$[Cu_2(H_2L^3)(ClO_4)(NO_3)_2]ClO_4{\cdot}3H_2O$ 15

This complex was synthesised by transmetallation of **1** with $Cu(ClO_4)_2{\cdot}6H_2O$. To a solution of **1** (0.08 g, 0.1 mmol) in acetonitrile (20 cm^3) was added $Cu(ClO_4)_2{\cdot}6H_2O$ (0.0741 g, 0.2 mmol) in acetonitrile (20 cm^3) and stirred for 6 h at room temperature. The resulting solution was cooled, diethyl ether added and kept at 0 °C for 15 h. The brown amorphous solid which separated was filtered off and dried *in vacuo* over anhydrous calcium chloride. Yield 0.019 56 g, 20% (Found: C, 34.30; H, 3.05; N, 11.45. Calc. for $C_{28}H_{28}Cl_2Cu_2N_8O_{19}$: C, 34.35; H, 2.85; N, 11.45%). Λ_M(dmf) 102 ohm^{-1} cm^2 mol^{-1}.

CAUTION: reactions involving perchlorate salts were carried out on small quantities (100–200 mg) owing to their explosive nature.

Results

Synthesis of complexes

Lanthanide(III) (except Ce^{3+}, Pm^{3+}, Yb^{3+} and Lu^{3+}) and Y^{3+} cations promote Schiff-base condensation of 2,6-diaminopyridine and 2,6-diformyl-4-methylphenol leading to the formation of complexes of the '2 + 2' symmetric macrocycle H_2L^3. Discrete mononuclear complexes $[Pr(H_2L^3)(NO_3)_2(H_2O)_3]NO_3{\cdot}3H_2O$, $[Ln(HL^3)(NO_3)(H_2O)_3]NO_3{\cdot}4H_2O$ (Ln = La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} or Tm^{3+}), $[Eu(HL^3)(NO_3)(H_2O)_2]NO_3{\cdot}5H_2O$ and $[Y(HL^3)(NO_3)(H_2O)_3]NO_3{\cdot}5H_2O$ have been synthesised by using the respective hydrated metal nitrate as the template. The yields are quite high (75–93%) for the lanthanides La^{3+}–Er^{3+} and Y^{3+} and 50% for Tm^{3+}. These complexes are best synthesised in acetonitrile. When the Schiff-base condensation is carried out in super-dry ethanol or methanol in the presence of hydrated lanthanide(III) nitrate, compounds of undefined composition are obtained.

Infrared spectra of the complexes

The infrared spectra of the complexes are devoid of absorptions characteristic of NH_2 and >C=O functions. A strong band at *ca.* 1630 cm^{-1} is assigned to ν(C=N) vibration.[27,29] The broad band of medium intensity occurring in the 3400–3300 cm^{-1} region is due to the symmetric and antisymmetric O–H stretching vibrations of the lattice water.[30] Those at *ca.* 3200 and 840 cm^{-1} are characteristic of co-ordinated water.[31] The medium-intensity band in the region 498–505 cm^{-1} is characteristic of ν(Ln–O) vibration of the phenolic oxygen and the co-ordinated water molecules.[32] In the far-infrared spectrum of $[Sm(HL^3)(NO_3)(H_2O)_3]NO_3{\cdot}4H_2O$ bands at 206 and 283m cm^{-1} can be assigned to ν(Sm–N) vibration.[32] The weak band of medium intensity at *ca.* 1000 cm^{-1} is due to the pyridine-ring vibrations.[1,33] The infrared spectra of the nitrato complexes contain bands characteristic of both co-ordinated and ionic nitrates. The bands at *ca.* 1465 and *ca.* 1320 cm^{-1} are due to ν(N=O) (ν_1) and $\nu_{asym}(NO_2)$ (ν_5), respectively, of the co-ordinated nitrate. The $\nu_{sym}(NO_2)$ vibration (ν_2) at *ca.* 1030 cm^{-1} is characteristic of bidentate chelating nitrate. The separation (Δν) of the nitrate stretching fundamentals ($\nu_1 - \nu_5$) has been used as a criterion to distinguish between mono- and bi-dentate chelating nitrates,[1,27] increasing as the co-ordination changes from *mono-* to bi-dentate and/or bridging. The magnitude of this separation (Δν 130, 145, 150, 134, 145, 140, 150, 133, 150, 140, 130 and 155 cm^{-1} for the La^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+} and Y^{3+} complexes, respectively) is indicative of bidentate co-ordination of the nitrate ion. The strong and sharp band at 1380 cm^{-1} is characteristic of ionic nitrate.[30] The samarium thiocyanato complex $[Sm(HL^3)(NCS)(H_2O)]NO_3{\cdot}4H_2O$ exhibits absorptions at 2050, 815 and 490 cm^{-1} assignable to ν(CN), ν(C–S) and δ(NCS) vibrations, respectively, of the co-ordinated thiocyanate. These values are consistent with that reported for *N*-bonded thiocyanate.[31]

The infrared spectrum of $[Dy(HL^3)(ClO_4)(H_2O)_2]NO_3{\cdot}3H_2O$ contains three well resolved bands at 1030, 1060 and 1110 cm^{-1} due to the co-ordinated ClO_4^-. The splitting of the ν_3 band of ionic perchlorate at 1100 cm^{-1} is due to the lowering of symmetry upon co-ordination. A similar triple splitting of the ν_{asym}(Cl–O) vibration has been observed for $[Ni(en)_2(ClO_4)_2]$ (en = ethane-1,2-diamine) containing bidentate chelating ClO_4^- and in lanthanide[34] and alkaline-earth-metal[35] complexes containing co-ordinated ClO_4^-. The ν_4 band at *ca.* 620 cm^{-1}, characteristic of ionic ClO_4^-, is also split for this complex indicating the co-ordination of ClO_4^-. The characteristic infrared bands of the complexes are presented in Table 1.

Molar conductivities

The molar conductivities of the complexes were measured in dmf and in methanol for freshly prepared solutions and after standing for 2 weeks. They do not vary with time in dmf. However, they increase with time in methanol for the complexes of Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+} and Tm^{3+}. This may be due to slow replacement of the co-ordinated nitrate by the solvent molecules. The molar conductivities of these complexes are in the range 107–154 ohm^{-1} cm^2 mol^{-1} in methanol. Even though the Λ_M values of the complexes of La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+} are higher than the expected value for a 1:1 electrolyte, reported[36] for transition-metal complexes, all these complexes are 1:1 electrolytes as inferred from spectral and analytical data.

Electronic absorption spectra

The electronic absorption spectra of the complexes were recorded for freshly prepared solutions in dmf and in methanol at 25 °C. The spectra are virtually identical in dmf and consist of a fairly symmetrical band at *ca.* 415 nm (ε = *ca.* 15 000 dm^3 mol^{-1} cm^{-1}) and shoulders at *ca.* 389 and 310 nm. The shoulder at 310 nm is well resolved as a symmetrical band after leaving the solution to stand for 2 weeks, whereas that at 389 nm remains unaffected. In methanol the complexes exhibit similar spectral features, symmetrical bands at *ca.* 333 (ε = *ca.* 10 000) and at *ca.* 405 nm (ε = *ca.* 9000 dm^3 mol^{-1} cm^{-1}) and shoulders at *ca.* 270 and 470 nm. After standing for 1 week the shoulder at *ca.* 470 nm disappears and the band at around 333 nm increases in intensity. The spectra of $[Ho(HL^3)(NO_3)(H_2O)_3]NO_3{\cdot}4H_2O$ and $[Eu(HL^3)(NO_3)(H_2O)_2]NO_3{\cdot}5H_2O$ are presented in Fig. 1(*a*) and (*b*), respectively. The spectrum of $[Tb(HL^3)(NO_3)(H_2O)_3]NO_3{\cdot}4H_2O$ in dmf [Fig. 2(*a*)] consists of bands at 315 and 419 nm. After treating the complex with $NaBH_4$ the band at 419 nm disappears [Fig. 2(*b*)] and therefore must be associated with the >C=N chromophore of H_2L^3. The intense band at *ca.* 315 nm has been assigned to a transition localised either on the ligand or to a charge-transfer transition. The electronic spectral data for the complexes are presented in Table 2.

Magnetic moments

The μ_{eff} values of the lanthanide(III) complexes show that these are paramagnetic in nature. The observed values for the complexes of Nd^{3+}, Eu^{3+}, Tb^{3+} and Dy^{3+} are 3.03, 3.63, 9.72 and 10.56 μ_B respectively ($\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}). These values are very similar to the Van Vleck values[37] for the free metal ions, suggesting that the 4f electrons do not take part in bonding.

Thermogravimetric analysis

Thermogravimetric analysis shows that the lanthanide(III) complexes of H_2L^3 have very high thermal stability. The

Table 1 Characteristic infrared absorption bands (cm^{-1}) of the complexes[a]

						Exocyclic ligands							
	Macrocycle					Nitrate			Water			Lattice water	Ionic nitrate
Complex	ν(C–H)[b]	ν(C=N)[c]	ν(C–C)[d]	ν(C–O)[d]	Pyridine ring vibrations[b]	ν(N=O)[c] (ν_1)	$\nu_{asym}(NO_2)$[b] (ν_5)	$\nu_{sym}(NO_2)$[b] (ν_2)	ν(OH)[e]	δ(OH)[f]	ν(Ln–O)[g]	ν(OH)[e]	ν(NO)[c] (ν_3)
$[La(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2920	1650	1540	1340	990	1450	1320	1050	3220	820	498	3380	1390
$[Pr(H_2L^3)(NO_3)_2(H_2O)_3]NO_3 \cdot 3H_2O$	2930	1650	1540	1340	1000	1455	1310	1055	3220	830	498	3380	1385
$[Nd(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2940	1650	1530	1330	1000	1450	1300	1060	3220	820	500	3370	1390
$[Sm(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2919	1632	1532	1329	994	1444	1310	1038	3220	830	501	3350	1384
$[Eu(HL^3)(NO_3)(H_2O)_2]NO_3 \cdot 5H_2O$	2940	1645	1540	1340	1000	1455	1310	1060	3220		501	3380	1390
$[Gd(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2945	1650	1538	1350	1000	1460	1320	1040	3200		502	3400	1395
$[Tb(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2938	1640	1540	1335	990	1450	1300	1060	3200	825	503	3380	1390
$[Dy(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2918	1635	1535	1330	994	1443	1310	1059	3200	831	503	3357	1384
$[Ho(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2940	1640	1540	1332	1000	1450	1300	1060	3200	825	504	3380	1380
$[Er(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2940	1635	1530	1330	1000	1440	1300	1050	3200	830	504	3380	1380
$[Tm(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	2940	1640	1540	1330	990	1450	1320	1030	3200		505	3380	1390
$[Y(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 5H_2O$	2945	1650	1534	1328	1000	1455	1300	1040	3210	820		3400	1385

[a] Spectra recorded in the solid state using KBr pellets. For assignments see the text. [b] Weak bands. [c] Very strong bands. [d] Medium bands. [e] Broad bands. [f] Strong bands. [g] The Ln–O stretching vibration of the co-ordinated water or phenolic oxygen.

Table 2 Electronic spectral data for the complexes in methanol[a]

Complex	Freshly prepared solution					After 10 d			
$[La(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	239 (4.2)	270 (3.8)	333 (3.7)	410 (3.7)	470 (3.6)	239 (4.2)	334 (3.7)	408 (3.7)	
$[Pr(H_2L^3)(NO_3)_2(H_2O)_3]NO_3 \cdot 3H_2O$	239 (4.3)	270 (3.9)	334 (3.8)	409 (3.8)	470 (3.6)	240 (4.4)	270 (4.0)	335 (3.9)	395 (3.8)
$[Nd(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	239 (4.5)	270 (4.1)	334 (3.9)	410 (3.9)	470 (3.7)	240 (4.5)	270 (4.1)	333 (3.9)	395 (3.9)
$[Sm(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	270 (4.4)	333 (4.1)	406 (4.1)	470 (4.0)		270 (4.3)	333 (4.2)	395 (4.1)	
$[Sm(HL^3)(NCS)(H_2O)]NO_3 \cdot 4H_2O$[b]	311 (4.4)	389 (4.3)	404 (4.3)						
$[Eu(HL^3)(NO_3)(H_2O)_2]NO_3 \cdot 5H_2O$	238 (4.2)	274 (3.9)	328 (3.7)	403 (3.7)	470 (3.4)	239 (4.2)	273 (3.8)	329 (3.7)	395 (4.0)
$[Gd(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	270 (4.4)	332 (4.1)	405 (4.1)	470 (3.9)		273 (4.2)	333 (4.1)	395 (4.0)	
$[Tb(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	270 (4.3)	333 (4.1)	403 (3.9)	470 (3.8)		273 (4.1)	334 (4.1)	395 (3.9)	
$[Dy(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	238 (4.3)	273 (4.0)	333 (3.7)	409 (3.8)		242 (4.0)	274 (3.7)	317 (3.6)	395 (3.5)
$[Dy(HL^3)(ClO_4)(H_2O)_2]NO_3 \cdot 3H_2O$[b]	311 (4.4)	389 (4.3)	403 (4.3)						
$[Ho(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	272 (4.3)	333 (4.1)	403 (3.2)			334 (4.1)	795 (4.0)		
$[Er(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	272 (4.1)	333 (4.0)	400 (3.9)	481 (3.7)		272 (4.1)	334 (4.1)	393 (3.9)	
$[Tm(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$	272 (3.9)	332 (3.8)	400 (3.7)	483 (3.5)		333 (3.9)	394 (3.7)		
$[Y(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 5H_2O$	272 (4.3)	331 (4.1)	399 (4.1)	483 (3.8)		272 (4.2)	333 (4.2)	393 (4.1)	
$[Cu_2(H_2L^3)(ClO_4)(NO_3)_2]ClO_4 \cdot 3H_2O$[b]	388 (4.2)	401 (4.2)	491 (3.9)	532 (3.7)		388 (4.2)	401 (4.2)	491 (3.8)	532 (3.7)

[a] Spectra recorded using $\approx 10^{-4}$ mol dm^{-3} solution; λ/nm with log ε in parentheses. [b] Spectra recorded using $\approx 10^{-4}$ mol dm^{-3} solution in dmf.

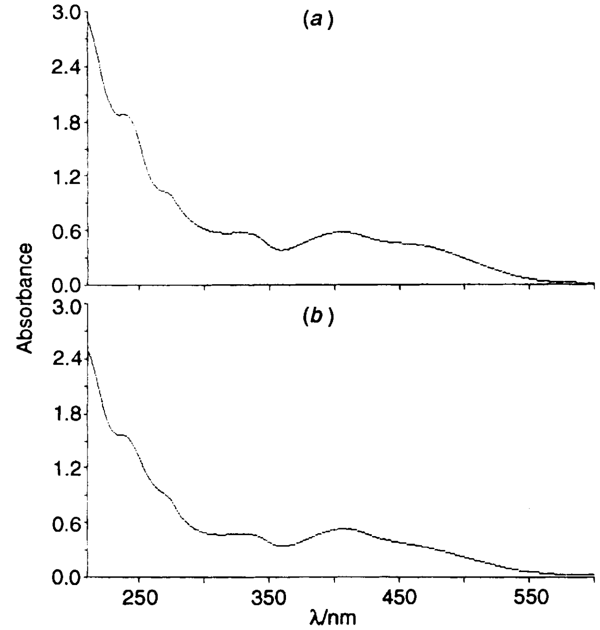

Fig. 1 Electronic absorption spectra of (*a*) $[Ho(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$ and (*b*) $[Eu(HL^3)(NO_3)(H_2O)_2]NO_3 \cdot 5H_2O$ in methanol

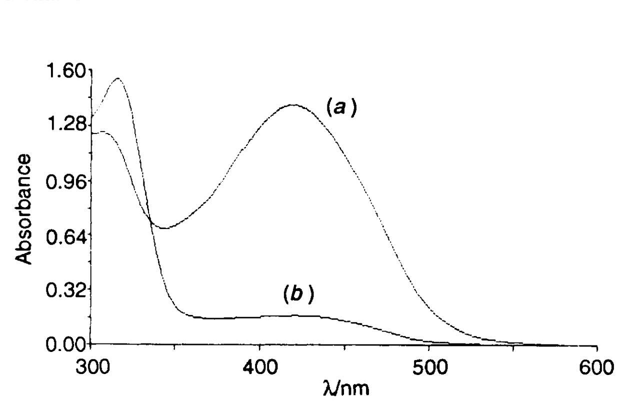

Fig. 2 Electronic spectra of (*a*) $[Tb(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$ and (*b*) upon reduction with $NaBH_4$ in dmf

hydrated complexes readily lose lattice water in the first step at *ca.* 75 °C. The macrocycles remain intact with the metal ions up to 338 °C. The thermogram of $[Er(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$ is presented in Fig. 3.

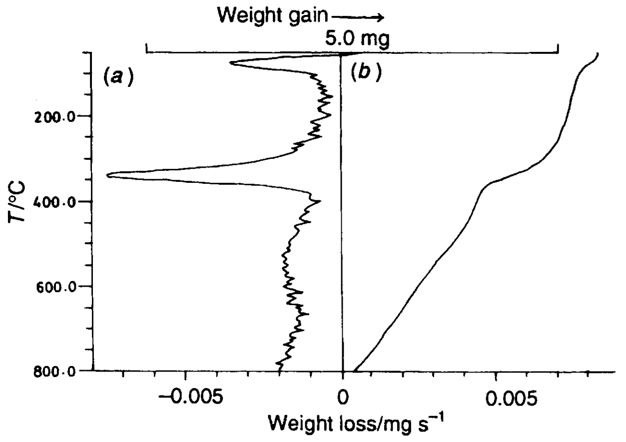

Fig. 3 Thermogram of $[Er(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$: (*a*) percentage mass loss *vs.* temperature; (*b*) first derivative

FAB mass spectra

The FAB mass spectra of the complexes consist of peaks due to the species $[Ln(HL^3)(NO_3)_2(H_2O)_3 + H]^+$ ($Ln = La^{3+}$, Pr^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+} or Tm^{3+}). This undergoes fragmentation to give species such as $[Ln(HL^3)(NO_3)(H_2O)_2 + H]^+$ ($Ln = La^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}$, Ho^{3+} or Tm^{3+}), $[Pr(HL^3)(NO_3)_2(H_2O) + H]^+$, $[Ln(HL^3)(NO_3)(H_2O)_2 + H]^+$ ($Ln = Nd^{3+}, Sm^{3+}, Eu^{3+}, Tb^{3+}, Ho^{3+}$ or Tm^{3+}), $[Ln(HL^3)(NO_3)_2 + H]^+$ ($Ln = La^{3+}$ or Er^{3+}), $[Ln(HL^3)(NO_3)(H_2O) + H]^+$ ($Ln = Pr^{3+}$ or Gd^{3+}) and $[Ln(HL^3)(H_2O)_2 + H]^+$ ($Ln = Nd^{3+}$, Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+} or Ho^{3+}). These fragments lose the exocyclic ligands to give the species $[Ln(HL^3) + H]^+$ ($Ln = Sm^{3+}$, Er^{3+} or Tm^{3+}). A peak due to the species $[H_2L^3 + H]^+$ has been observed at *m*/*z* 475 for the complexes of La^{3+}, Nd^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Er^{3+} and Tm^{3+}. The free macrocycle, formed by demetallation of the complex, undergoes reduction under FAB conditions to give species such as $[H_4L^3 + H]^+$ (for Pr^{3+} and Dy^{3+}), $[H_6L^3 + H]^+$ (for Sm^{3+}) and $[H_8L^3 + H]^+$ (for Ho^{3+}) probably due to reaction with the matrix compound. In the FAB mass spectra of the complexes of Sm^{3+} and Eu^{3+}, which are polyisotropic, clusters of peaks are obtained. For example, in the spectrum of $[Sm(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$ the peaks at *m*/*z* 725 and 723 for the species $[Sm(HL^3)(NO_3)(H_2O)_2]^+$ are due to the natural isotopes of ^{152}Sm and ^{154}Sm, respectively. The spectra of $[Pr(H_2L^3)(NO_3)_2(H_2O)_3]NO_3 \cdot 3H_2O$ and $[Ho(HL^3)(NO_3)(H_2O)_3]NO_3 \cdot 4H_2O$ are given in Fig. 4(*a*) and (*b*) respectively.

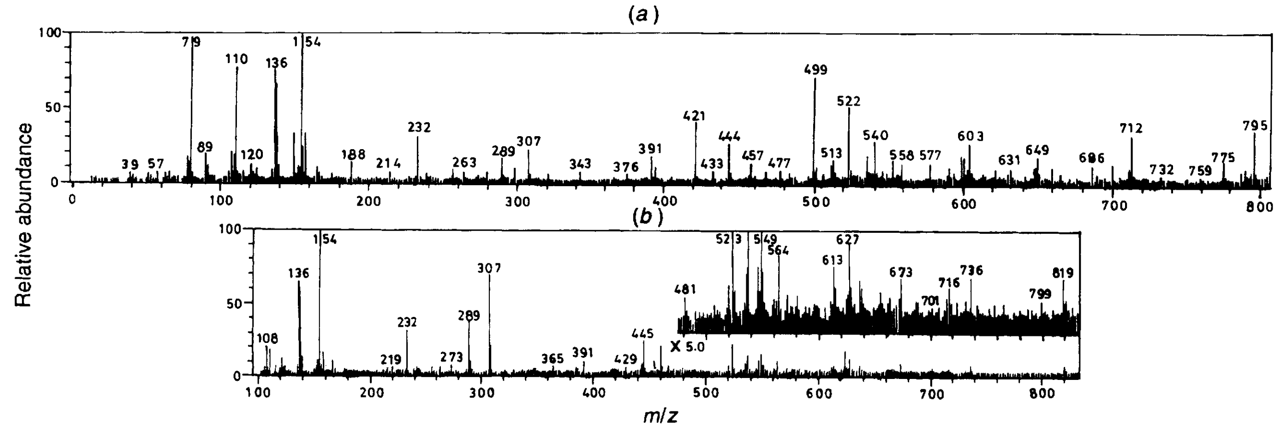

Fig. 4 The FAB mass spectra of (*a*) $[Pr(H_2L^3)(NO_3)_2(H_2O)_3]NO_3{\cdot}3H_2O$; (*b*) $[Ho(HL^3)(NO_3)(H_2O)_3]NO_3{\cdot}4H_2O$

Discussion

Lanthanide(III) complexes of H_2L^3 have been synthesised by the Schiff-base condensation of 2,6-diformyl-4-methylphenol and 2,6-diaminopyridine in the presence of the hydrated metal nitrates (except for Ce^{3+}, Pm^{3+}, Yb^{3+} and Lu^{3+}), under the same experimental conditions. The size of the lanthanide(III) ions decreases along the series and consequently they adopt different geometries in the complexes. Thus the change in stoichiometry most likely results from the different geometrical requirements of the metal ions. The yields of the complexes decrease with decreasing ionic radii of the metal ions. This diminution in the ionic radii does not affect the template potential of the metal ions but it affects the yields of the complexes of the heavier lanthanides. The higher yields of the complexes of the larger lanthanide(III) cations are probably due to the 'best fit' between the sizes of these metal ions and the macrocyclic cavity. In each complex the metal ion is co-ordinated to the macrocycle and to one chelating bidentate nitrate ion (two for Pr^{3+}) and to two or three water molecules. This illustrates the influence of oxygen-donor ligands in stabilizing the lanthanide(III) cations in macrocyclic frameworks. The role of the exocyclic ligands appears to fulfil the geometrical requirements of the metal ions due to their ability to expand the inner co-ordination sphere. Each complex (except that of Pr^{3+}) is monocationic with one co-ordinated bidentate chelating NO_3^- ion. Thus one of the macrocycle OH protons is lost during complexation. In the case of H_2L^1 the macrocycle behaves as a neutral ligand and the phenolic OH groups are not deprotonated. This difference may be due to the basicity of the pyridine analogue H_2L^3. The complexes undergo anion metathesis when treated with ClO_4^- and SCN^-.

The formation of complexes of both the lighter and heavier lanthanide(III) cations by H_2L^1 and H_2L^3 by metal template synthesis under the same experimental conditions reflects the ability of these macrocycles to adapt to the geometrical requirements of the metal ions. Nevertheless, in the case of the 18-membered tetraaza macrocycle H_2L^1 there is a gradual increase in the yield of the complexes along the lanthanide series, whereas the yield decreases for H_2L^3. Our results suggest that the 20-membered macrocycle H_2L^3 is more suitable to synthesise complexes of the larger lanthanides and the 18-membered macrocycle H_2L^1 is more suitable for the smaller lanthanides. The lower denticity of H_2L^1 makes it more suitable for smaller lanthanides as the co-ordination number of the lanthanides decreases as their size decreases.[2,3] The higher denticity and moderate flexibility of H_2L^3 make it a suitable ligand system for lanthanide(III) cations.

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