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Synthesis of lanthanide(III) complexes of 20-membered octaaza and hexaaza Schiff-base macrocycles†

Shaji James, Dass Suresh Kumar and Vedhamonickom Alexander *

Department of Chemistry, Loyola College, Chennai-6000 034, India

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Mononuclear lanthanide(III) complexes of the 20-membered octaaza Schiff-base macrocycle, 3,9,17,23-tetramethyl-2,10,16,24,29,30,31,32-octaazapentacyclo[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 (L^6), have been synthesized by the condensation of 2,6-diacetylpyridine and 2,6-diaminopyridine in the presence of lanthanide(III) templates. The complexes $[La(L^6)(NO_3)(H_2O)_3][NO_3]_2\cdot 2H_2O$, $[Ln(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot nH_2O$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Y; $n = 2$ or 3), $[Ln(L^6)(ClO_4)_2(H_2O)]ClO_4\cdot 3H_2O$ and $[Ln(L^6)(CH_3CO_2)_3(H_2O)]\cdot 3H_2O$ (Ln = Eu or Tb) have been synthesized by using the lanthanide(III) nitrate, perchlorate or acetate as the metal template. The complexes $[Dy(L^6)(NO_3)(ClO_4)]NO_3\cdot H_2O$ and $[Ln(L^6)(NO_3)(NCS)]NO_3\cdot H_2O$ (Ln = Eu or Tb) have been synthesized by anion metathesis of the respective (nitrato)(aqua) complex with perchlorate or thiocyanate. For the 20-membered hexaaza macrocycle, 6,20-dichloro-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^7), complexes have been synthesized by the condensation of 4-chloro-2,6-diformylphenol and 2,6-diaminopyridine in the presence of lanthanide(III) nitrates yielding $[Ln(HL^7)(NO_3)(H_2O)_2]NO_3\cdot nH_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Y; $n = 3$ or 4). The formation of lanthanide(III) complexes of L^6 and H_2L^7 demonstrates the template potential of the lanthanide(III) cations in the assembly of '2 + 2' symmetric Schiff-base macrocycles having pyridine or phenol head units and pyridine lateral units.

Introduction

Recent years have witnessed a growing interest towards macrocyclic complexes of lanthanides[1] because of their potential applications in biology,[2] in material sciences and in chemical processes.[3] Lanthanide(III) chelates find extensive use in NMR biomedical applications[4] and studies on these complexes have produced technological developments and industrial applications.[3,5] Macrocyclic ligands are also used as therapeutic reagents for the treatment of metal toxicity,[6] functional groups for chelating ion-exchange materials,[7] selective metal extractants in hydrometallurgy[8] and in the separation of lanthanides.[9]

Synthesis of macrocyclic complexes of lanthanide(III) cations in identical ligand frameworks is essential in order to identify the ligand design features required to synthesize robust complexes to harness their potential uses. Symmetric '2 + 2' Schiff-base macrocycles derived from 2,6-diformyl-4-substituted phenols and aromatic diamines would exhibit rigidity due to extended conjugation and consequently their lanthanide complexes would be thermodynamically stable. Furthermore, incorporation of pyridine rings in the macrocyclic framework would increase the stereochemical rigidity and binding ability towards lanthanide(III) cations, a property often associated with an increase in the thermodynamic stability of the complexes. We have therefore undertaken research projects to synthesize lanthanide(III) complexes of macrocycles derived from phenol and pyridine precursors and reported the complexes of the 18-membered tetraaza macrocycle H_2L^1,[10] its chloro and bromo analogues H_2L^2 and H_2L^3,[11] the 18-membered hexaaza macrocycle[12] L^4 and the 20-membered hexaaza macrocycle H_2L^5.[13] In pursuance of our ongoing efforts to synthesize lanthanide(III) complexes of macrocycles we report herein the template synthesis of the complexes of the '2 + 2' symmetric Schiff-base macrocycles L^6 and H_2L^7.

Experimental

Materials and physical methods

Lanthanide(III) perchlorates and acetates were prepared by the reaction of the corresponding metal carbonate with perchloric and acetic acid. 2,6-Diaminopyridine and 2,6-diacetylpyridine (Fluka) were used as received. 4-Chloro-2,6-diformylphenol was synthesized by the procedure described by Gagne *et al.*[14] The other chemicals used and the details of physical measurements were described elsewhere.[11]

General procedure for the synthesis of lanthanide(III) complexes of L^6

(a) (Nitrato)(aqua) complexes: $[La(L^6)(NO_3)(H_2O)_3][NO_3]_2\cdot 2H_2O$ 1, $[Ln(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot nH_2O$ (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Y 2–10; $n = 2$ for Nd, Sm, Eu, Tb, Ho and Er and $n = 3$ for Gd, Dy and Y). To a solution of 2,6-diacetylpyridine (0.163 g, 1 mmol) in acetonitrile (10 cm³) was added lanthanide(III) nitrate (0.5 mmol) and the solution stirred on a magnetic stirrer at room temperature (30 °C). A solution of 2,6-diaminopyridine (0.109 g, 1 mmol) in acetonitrile (10 cm³) was added slowly over a period of 5 min. The solution turned yellow and became turbid after 5–10 min and pale yellow particles started depositing on the walls of the container. Stirring was continued for 3 h and the solid compound that separated was filtered off, washed with acetonitrile and dried *in vacuo* over anhydrous $CaCl_2$. In the case of the lanthanum(III) complex the product was isolated from the reaction medium after keeping it for a day at room temperature.

(b) (Perchlorato)(aqua) complexes: $[Eu(L^6)(ClO_4)_2(H_2O)]ClO_4\cdot 3H_2O$ 11 and $[Tb(L^6)(ClO_4)_2(H_2O)]ClO_4\cdot 3H_2O$ 12. To a solution of 2,6-diacetylpyridine (0.163 g, 1 mmol) in aceto-

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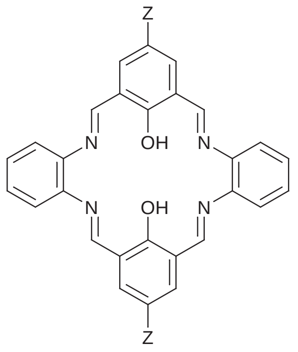
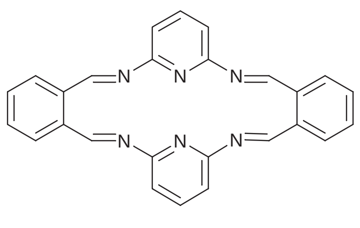
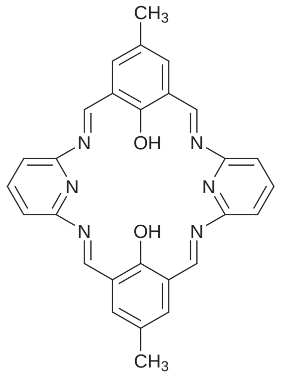
† *Supplementary data available*: physicochemical characterization and infrared data and mass spectra for the complexes. Available from BLDSC (No. SUP 57541, 10 pp.). See Instructions for Authors, 1999, Issue 1 (http://www.rsc.org/dalton).



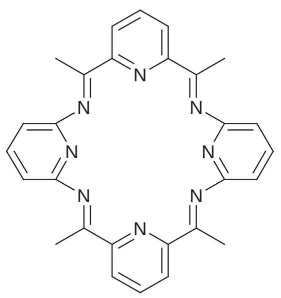
H_2L^1, Z = CH_3
H_2L^2, Z = Cl
H_2L^3, Z = Br



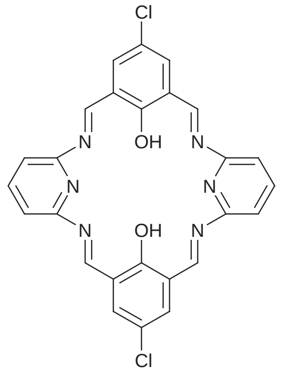
L^4



H_2L^5



L^6



H_2L^7

nitrile (10 cm^3) was added $Ln(ClO_4)_3 \cdot nH_2O$ (Ln = Eu or Tb, 0.5 mmol) and the solution stirred on a magnetic stirrer. A solution of 2,6-diaminopyridine (0.109 g, 1 mmol) in acetonitrile (5 cm^3) was added slowly whereupon the solution turned yellow. After stirring for 2 h, diethyl ether (10 cm^3) was added and stirred for another hour when yellow particles separated. The product was filtered off, washed with acetonitrile and dried *in vacuo* over anhydrous $CaCl_2$.

(c) (Acetato)(aqua) complexes: $[Eu(L^6)(CH_3CO_2)_3(H_2O)] \cdot 3H_2O$ 13 and $[Tb(L^6)(CH_3CO_2)_3(H_2O)] \cdot 3H_2O$ 14. To a solution of 2,6-diacetylpyridine (0.163 g, 1 mmol) in acetonitrile (10 cm^3) was added $Ln(CH_3CO_2)_3 \cdot H_2O$ (Ln = Eu or Tb, 0.5 mmol) in methanol (10 cm^3) and the solution stirred on a magnetic stirrer. A solution of 2,6-diaminopyridine (0.109 g, 1 mmol) in acetonitrile (10 cm^3) was added and the solution turned yellow. Stirring was continued for 4 h and ether (15 cm^3) added whereupon yellow particles separated. The product was filtered off, washed with acetonitrile and ether and dried *in vacuo* over anhydrous $CaCl_2$.

(d) (Nitrato)(perchlorato) complex: $[Dy(L^6)(NO_3)(ClO_4)]NO_3 \cdot H_2O$ 15. To a suspension of $[Dy(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 3H_2O$ (1 mmol) in methanol (20 cm^3) was added $NaClO_4 \cdot H_2O$ (5 mmol) and the mixture stirred on a magnetic stirrer for 6 h. It was kept for 4 d in a stoppered conical flask. The solid product was filtered off, washed with methanol and ether and dried *in vacuo*.

(e) (Nitrato)(isothiocyanato) complexes: $[Eu(L^6)(NO_3)(NCS)]NO_3 \cdot H_2O$ 16 and $[Tb(L^6)(NO_3)(NCS)]NO_3 \cdot H_2O$ 17. To a suspension of $[Eu(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 2H_2O$ or $[Tb(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 2H_2O$ (1 mmol) in methanol (20 cm^3) was added KSCN (5 mmol) and the mixture stirred on a magnetic stirrer for 5 h. It was kept for 2 d in a stoppered conical flask at ambient temperature. The product was filtered off, washed with methanol and ether and dried *in vacuo*.

General procedure for the synthesis of lanthanide(III) complexes of H_2L^7

(a) (Nitrato)(aqua) complexes: $[Ln(HL^7)(NO_3)(H_2O)_2]NO_3 \cdot nH_2O$ (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Y 18–28; $n = 3$ for La, Pr, Nd, Gd, Dy, Ho, Er or Y and $n = 4$ for Sm, Eu or Tb). To a solution of 4-chloro-2,6-diformylphenol (0.1845 g, 1 mmol) in acetonitrile (15 cm^3) was added hydrated lanthanide(III) nitrate (0.5 mmol) and the solution stirred on a magnetic stirrer. A solution of 2,6-diaminopyridine (0.109 g, 1 mmol) in acetonitrile (15 cm^3) was added dropwise over a period of 15 min upon which the solution turned wine red and after 15 min red particles started depositing on the sides of the container. Stirring was continued for 3 h and the solid product was filtered off, washed with acetonitrile and chloroform, and dried *in vacuo* over anhydrous $CaCl_2$.

(b) Diaqua complexes: $[Eu(L^7)(H_2O)_2]ClO_4 \cdot H_2O$ 29 and $[Tb(L^7)(H_2O)_2]ClO_4 \cdot H_2O$ 30. Synthesized by the above procedure using $Ln(ClO_4)_3 \cdot nH_2O$ (Ln = Eu or Tb) as the metal template.

(c) (Isothiocyanato)(aqua) complex: $[Eu(L^7)(NCS)(H_2O)] \cdot 2H_2O$ 31. To a suspension of $[Eu(HL^7)(NO_3)(H_2O)_2]NO_3 \cdot 4H_2O$ (1 mmol) in methanol (20 cm^3) was added KSCN (0.485 g, 5 mmol) and the mixture stirred on a magnetic stirrer for 5 h. It was kept for 4 d in a stoppered conical flask and the solid compound was filtered off, washed with methanol and dried *in vacuo* over anhydrous $CaCl_2$.

Results and discussion

Synthesis of lanthanide(III) complexes of L^6

Schiff-base condensation of 2,6-diacetylpyridine and 2,6-diaminopyridine in the presence of hydrated lanthanide(III) nitrate in 2:2:1 mole ratio yields the complexes $[La(L^6)(NO_3)(H_2O)_3][NO_3]_2 \cdot 2H_2O$, $[Ln(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 2H_2O$

Table 1 FAB Mass spectral data of the complexes of L^6 and H_2L^7

Complex	Species	*m*/*z*
$[La(L^6)(NO_3)(H_2O)_3][NO_3]_2\cdot 2H_2O$	$[La(L^6)(NO_3)_2(H_2O)_3 + H]^+$	789
$[Nd(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 2H_2O$	$[Nd(L^6)(NO_3)_2(H_2O)_2 + H]^+$	776
$[Sm(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 2H_2O$	$[Sm(L^6)(NO_3)_3 + H]^+$	811
$[Eu(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 2H_2O$	$[Eu(L^6)(NO_3)_3 + H]^+$	813
$[Gd(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 3H_2O$	$[Gd(L^6)(NO_3)_3(H_2O) + H]^+$	837
$[Tb(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 2H_2O$	$[Tb(L^6)(NO_3)_2 + H]^+$	828
$[Dy(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 3H_2O$	$[Dy(L^6)(NO_3)_3(H_2O) + H]^+$	835
$[Ho(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 2H_2O$	$[Ho(L^6)(NO_3)_3(H_2O)_2 + H]^+$	840
$[Er(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 2H_2O$	$[Er(L^6)(NO_3)_3(H_2O)_2 + H]^+$	872
$[Y(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 3H_2O$	$[Y(L^6)(NO_3)_3 + H]^+$	751
$[La(HL^7)(NO_3)(H_2O)_2]NO_3\cdot 3H_2O$	$[La(HL^7)(NO_3)_2(H_2O)_2 + H]^+$	812
$[Nd(HL^7)(NO_3)(H_2O)_2]NO_3\cdot 3H_2O$	$[Nd(HL^7)(NO_3)_2(H_2O) + H]^+$	779
$[Sm(HL^7)(NO_3)(H_2O)_2]NO_3\cdot 4H_2O$	$[Sm(HL^7)(NO_3)_2(H_2O)_2 + H]^+$	764
$[Eu(HL^7)(NO_3)(H_2O)_2]NO_3\cdot 4H_2O$	$[Eu(HL^7)(NO_3)_2 + H]^+$	791
$[Ho(HL^7)(NO_3)(H_2O)_2]NO_3\cdot 3H_2O$	$[Ho(HL^7)(NO_3)_2 + H]^+$	798
$[Er(HL^7)(NO_3)(H_2O)_2]NO_3\cdot 3H_2O$	$[Er(HL^7)(NO_3)_2 + H]^+$	810
$[Y(HL^7)(NO_3)(H_2O)_2]NO_3\cdot 3H_2O$	$[Y(HL^7)(NO_3)_2(H_2O)_2 + H]^+$	766
$[Tb(L^7)(H_2O)_2]ClO_4\cdot H_2O$	$[Tb(L^7)(H_2O)_2(ClO_4) + H]^+$	808

(Ln = Nd, Sm, Eu, Tb, Ho or Er) and $[Ln(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 3H_2O$ (Ln = Gd, Dy or Y). The perchlorato complexes $[Ln(L^6)(ClO_4)_2(H_2O)]ClO_4\cdot 3H_2O$ (Ln = Eu or Tb) and the acetato complexes $[Ln(L^6)(CH_3CO_2)_3(H_2O)]\cdot 3H_2O$ (Ln = Eu or Tb) are synthesized by using the corresponding lanthanide(III) perchlorate or acetate as the metal template. The (perchlorato)(nitrato) complex $[Dy(L^6)(NO_3)(ClO_4)]NO_3\cdot H_2O$ is synthesized by the anion metathesis reaction of $[Dy(L^6)(NO_3)(H_2O)_2][NO_3]_2\cdot 3H_2O$ with $NaClO_4$. The (nitrato)(isothiocyanato) complexes $[Ln(L^6)(NO_3)(NCS)]NO_3\cdot H_2O$ (Ln = Eu or Tb) are synthesized by the anion metathesis reaction of the corresponding (nitrato)(aqua) complexes with KSCN. The formation of lanthanide(III) complexes of L^6 demonstrates the template potential of these metal ions in the assembly of Schiff-base macrocycles having pyridine head and lateral units. In the (nitrato)(aqua) complexes the metal ion is co-ordinated to the macrocycle, to one bidentate nitrate and to two water molecules. In the (perchlorato)(aqua) and (acetato)(aqua) complexes, the metal ion is co-ordinated to the macrocycle, to two perchlorates or three acetates and to one water molecule.

Synthesis of lanthanide(III) complexes of H_2L^7

Schiff-base condensation of 4-chloro-2,6-diformylphenol and 2,6-diaminopyridine in the presence of hydrated lanthanide(III) nitrate in 2 : 2 : 1 mole ratio yields the complexes $[Ln(HL^7)(NO_3)_2(H_2O)_2]NO_3\cdot 3H_2O$ (Ln = La, Pr, Nd, Gd, Dy, Ho, Er or Y) and $[Ln(HL^7)(NO_3)_2(H_2O)_2]NO_3\cdot 4H_2O$ (Ln = Sm, Eu or Tb). The diaqua complexes $[Ln(L^7)(H_2O)_2]ClO_4\cdot H_2O$ (Ln = Eu or Tb) are synthesized by using the corresponding lanthanide(III) perchlorate as the template. The complex $[Eu(L^7)(NCS)(H_2O)]\cdot 2H_2O$ is synthesized by the anion metathesis of the (nitrato)(aqua) complex with KSCN. The formation of lanthanide(III) complexes of H_2L^7 shows the template potential of lanthanide(III) cations in the formation of symmetric '2 + 2' Schiff-base macrocycles having phenol head and pyridine lateral units.

Infrared spectra

The complexes of L^6 and H_2L^7 exhibit the ν(C=N) vibration[15] in the region 1630–1650 cm^{-1} and the pyridine ring vibrations in the regions 1570–1600 and 970–1000 cm^{-1}.[16] The strong band at *ca.* 1520 cm^{-1} in the complexes of H_2L^7 is assignable to the phenolic ν(C–O) vibration.[17] The absorption bands occurring in the regions 1430–1455, 1300–1328 and 1020–1040 cm^{-1} for the nitrato complexes of L^6 are assignable to the ν(N=O) (ν_1), $\nu_{asym}(NO_2)$ (ν_5) and $\nu_{sym}(NO_2)$ (ν_2), vibrations, respectively,[18] of the bidentate chelating nitrate. The corresponding vibrations of the nitrato complexes of H_2L^7 occur at lower energy region (1410–1430, 1308–1320 and 1010–1030 cm^{-1}, respectively). The separation between the ν_5 and ν_1 vibrations ($\Delta\nu$) of the co-ordinated nitrate is above 130 cm^{-1} indicating its bidentate mode of co-ordination.[18b,19] Complexes containing nitrate as the counter ion exhibit the ν(N=O) (ν_3) absorption at *ca.* 1370 cm^{-1}.[19] The (perchlorato)(aqua) complexes exhibit well resolved peaks at 1130, 1100 and 1070 cm^{-1} characteristic of co-ordinated perchlorate.[20] Complexes containing perchlorate as the counter anion exhibit intense unsplit absorption bands at 630 and 1100 cm^{-1}.[21] The (acetato)(aqua) complexes exhibit the ν_{asym}(COO) and ν_{sym}(COO) vibrations at *ca.* 1560 and 1430 cm^{-1}, respectively. The difference between them is 130 cm^{-1}, characteristic of bidentate chelating acetate.[22] The (isothiocyanato)(nitrato) complexes exhibit a very strong peak at *ca.* 2050 cm^{-1} and a weak band at 800 cm^{-1}, assignable to the ν(CN) and ν(CS) vibrations, respectively, typical of N-bonded thiocyanate.[23] The broad bands occurring at *ca.* 3200 and 3400 cm^{-1} are due to the co-ordinated[18a] and lattice water,[23c] respectively.

FAB Mass spectra

FAB Mass spectra of the complexes of L^6 contain peaks due to the molecular ions $[Ln(L^6)(NO_3)_3(H_2O)_2 + H]^+$ (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er or Y). These species undergo fragmentation to give fragments such as $[Ln(L^6)(NO_3)_2(H_2O)_2]^+$ (Ln = Dy or Ho), $[Ln(L^6)(NO_3)_2]^+$ (Ln = Eu or Tb), $[Ln(L^6)(NO_3)]^+$ (Ln = Sm, Eu, Tb or Dy), $[Ln(L^6)(H_2O)]^+$ (Ln = Nd or Er) and $[Ln(L^6)]^+$ (Ln = Sm, Eu, Gd, Tb, Er or Y). For the complexes of H_2L^7 peaks due to the molecular ions $[Ln(HL^7)(NO_3)_2(H_2O)_2 + H]^+$ (Ln = La, Ho or Y) and fragments such as $[Nd(HL^7)(NO_3)_2(H_2O)_2 + H]^+$, $[Ln(HL^7)(NO_3)_2 + H]^+$ (Ln = Eu or Er), $[Ln(HL^7)(NO_3)(H_2O)_2]^+$ (Ln = Sm or Tb), $[Ln(HL^7)(NO_3)]^+$ (Ln = Nd or Y), $[Ln(HL^7)(H_2O)]^+$ (Ln = La, Nd, Ho or Er) and $[Ln(HL^7)]^+$ (Ln = La, Nd, Ho, Er or Y) are observed. The peak due to the macrocycle, formed after demetallation under the FAB condition, is observed for the complexes of La, Nd, Eu, Gd, Tb and Ho with L^6 and of Sm, Eu and Ho with H_2L^7. The imine nitrogens of the macrocycle undergo reduction under FAB conditions in some complexes. The FAB mass spectral data of the complexes of L^6 and H_2L^7 are given in Table 1.

Molar conductivity

The ionic nature of the complexes is ascertained from the molar conductivities which are well within the reported[24] range of values for the 1 : 1 and 1 : 2 electrolytes. There is no appreciable change in the Λ_M values after a period of one week which shows the inertness of these complexes towards demetallation and removal of exocyclic ligands by the solvent molecules.

Table 2 Thermal data of the lanthanide(III) complexes of L^6 and H_2L^7

Complex	Temperature range/°C	Species lost	Mass loss (%) found	Mass loss (%) calc.
$[Sm(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 2H_2O$	50–160	Lattice and co-ordinated H_2O	8.2	9.5
	200–250	NO_3^-	21.3	21.5
	>300	Macrocycle	53.6	52.1
$[Ho(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 2H_2O$	50–160	Lattice and co-ordinated H_2O	8.0	8.7
	200–250	NO_3^-	20.8	20.0
	>300	Macrocycle		
$[Er(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 2H_2O$	50–160	Lattice and co-ordinated H_2O	8.0	9.0
	200–250	NO_3^-	20.7	19.0
	>300	Macrocycle	52.6	50.0
$[Sm(HL^7)(NO_3)(H_2O)_2]NO_3 \cdot 4H_2O$	50–100	Lattice H_2O	8.0	7.0
	100–320	Co-ordinated H_2O and NO_3^-	17.8	16.0
	>320	Macrocycle		
$[Ho(HL^7)(NO_3)(H_2O)_2]NO_3 \cdot 3H_2O$	50–100	Lattice H_2O	6.0	5.1
	100–320	Co-ordinated H_2O and NO_3^-	17.9	16.1
	>300	Macrocycle		

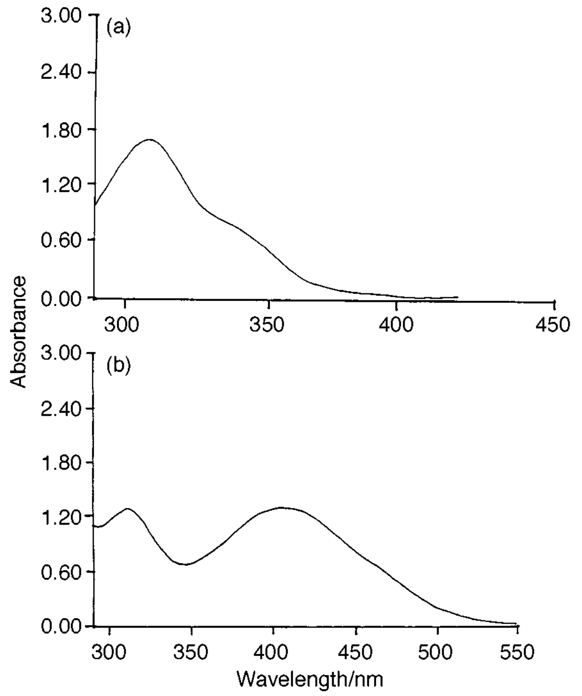


Fig. 1 Electronic absorption spectra of (*a*) $[Eu(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 2H_2O$ and (*b*) $[Ho(HL^7)(NO_3)(H_2O)_2]NO_3 \cdot 3H_2O$.

Electronic absorption spectra

The (nitrato)(aqua) complexes of L^6 exhibit two absorption bands at *ca.* 310 ($\varepsilon \approx 19\,000$) and *ca.* 340 nm ($\varepsilon \approx 8000$ dm^3 mol^{-1} cm^{-1}) except for the lanthanum(III) complex which exhibits one absorption at 335 nm ($\varepsilon = 3304$ dm^3 mol^{-1} cm^{-1}). The other complexes exhibit one absorption band in the 315–325 nm region, characteristic of the ligand. The shift in the absorption maxima in these complexes may be due to the presence of different exocyclic ligands. When the spectra are recorded after a period of one week the intensity of the absorption band at 340 nm is reduced. This may be due to the replacement of co-ordinated water molecules by the solvent molecules (dmf). The complexes of H_2L^7 exhibit absorption bands at *ca.* 310 ($\varepsilon =$ *ca.* 11 000) and *ca.* 405 nm ($\varepsilon =$ *ca.* 13 000 dm^3 mol^{-1} cm^{-1}). The diaqua complex of Sm and (isothiocyanato)(aqua) complexes of Eu and Tb exhibit three absorption bands at *ca.* 310, 400 and 485 nm. There is no appreciable change in the absorption spectra recorded after one week indicating the stability of the complexes in solution. The electronic absorption spectra of $[Eu(L^6)(NO_3)(H_2O)_2][NO_3]_2 \cdot 2H_2O$ and $[Ho(HL^7)(NO_3)(H_2O)_2]NO_3 \cdot 3H_2O$ are shown in Fig. 1.

Thermal study

The complexes exhibit high thermal stability. The thermograms of the complexes of Sm, Ho and Er with L^6 show that the lattice and co-ordinated water molecules are removed between 50 and 160 °C and the co-ordinated nitrate between 200 and 250 °C. The macrocycle is lost at *ca.* 300 °C. Thermogravimetric analysis of the (nitrato)(aqua) complexes of Sm and Er with H_2L^7 indicates that the lattice water is removed between 50 and 100 °C. The co-ordinated water and nitrates are lost in the temperature range 100–320 °C and the macrocycle is lost above 400 °C. The thermogravimetric data of the complexes are given in Table 2.

Magnetic moments

The calculated μ_{eff} values of the complexes of Nd^{III}, Gd^{III} and Er^{III} with L^6 (2.62, 6.64 and 9.04 μ_B, respectively) and of Nd^{III}, Gd^{III} and Dy^{III} with H_2L^7 (3.64, 6.39 and 9.75 μ_B respectively) show that they are paramagnetic in nature and the values are close to what is predicted in the free ion approximation.[25]

Conclusion

Our study demonstrates the template potential of lanthanide(III) cations in the assembly of '2 + 2' symmetric Schiff-base macrocycles having pyridine head and lateral units and phenol head and pyridine lateral units. The difference in the size of the lanthanide(III) cations does not affect their template potential in the formation of the complexes of L^6 and H_2L^7. This indicates the adaptability of these macrocycles to folding according to the geometric requirements of the metal ions. The formation of complexes of these macrocycles along with co-ordinated nitrate, perchlorate or acetate and water shows the ability of oxygen donor ligands in stabilising the lanthanide(III) ions in the macrocyclic frameworks. The complexes undergo anion exchange reaction with perchlorate and thiocyanate to give the perchlorato and isothiocyanato complexes. The complexes of L^6 and H_2L^7 could be used to study the co-ordination properties of the lanthanide(III) cations in an identical ligand framework and the effect of varying the exocyclic ligands on the properties of the metal ions within the same ligand framework.

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