

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 (L⁶), have been synthesized by the condensation of 2,6-diacetylpyridine and 2,6-diaminopyridine in the presence of lanthanide(III) templates. The complexes [La(L⁶)(NO₃)(H₂O)₃][NO₃]₂·2H₂O, [Ln(L⁶)(NO₃)(H₂O)₂][NO₃]₂·nH₂O (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Y; n = 2 or 3), [Ln(L⁶)(ClO₄)₂(H₂O)]ClO₄·3H₂O and [Ln(L⁶)(CH₃CO₂)₃(H₂O)]·3H₂O (Ln = Eu or Tb) have been synthesized by using the lanthanide(III) nitrate, perchlorate or acetate as the metal template. The complexes [Dy(L⁶)(NO₃)(ClO₄)]NO₃·H₂O and [Ln(L⁶)(NO₃)(NCS)]NO₃·H₂O (Ln = Eu or Tb) have been synthesized by anion metathesis of the respective (nitrate)(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 (H₂L⁷), 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(HL⁷)(NO₃)(H₂O)₂][NO₃]₂·nH₂O (Ln = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Y; n = 3 or 4). The formation of lanthanide(III) complexes of L⁶ and H₂L⁷ 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 lanthanides¹ 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 applications⁴ 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 hydrometallurgy⁸ 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 H₂L¹,¹⁰ its chloro and bromo analogues H₂L² and H₂L³,¹¹ the 18-membered hexaaza macrocycle¹² L⁴ and the 20-membered hexaaza macrocycle H₂L⁵.¹³ In pursuance of our ongoing efforts to synthesize lanthanide(III) complexes of macrocycles we report herein the template syn-

thesis of the complexes of the '2 + 2' symmetric Schiff-base macrocycles L⁶ and H₂L⁷.

Experimental

Materials and physical methods

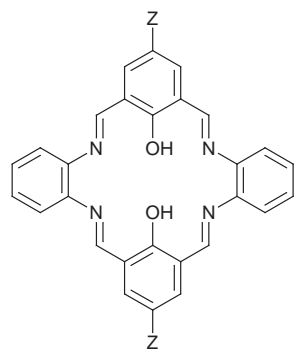
Lanthanide(III) perchlorates and acetates were prepared by the reaction of the corresponding metal carbonate with perchloric and acetic acid. 2,6-Diaminopyridine and 2,6-diacetylpyridine (Fluka) were used as received. 4-Chloro-2,6-diformylphenol was synthesized by the procedure described by Gagne *et 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 L⁶

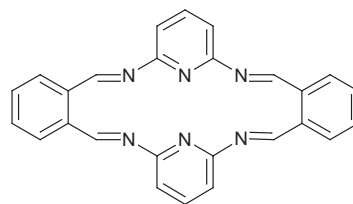
(a) (Nitrate)(aqua) complexes: [La(L⁶)(NO₃)(H₂O)₃][NO₃]₂·2H₂O **1**, [Ln(L⁶)(NO₃)(H₂O)₂][NO₃]₂·nH₂O (Ln = Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er or Y 2–10; n = 2 for Nd, Sm, Eu, Tb, Ho and Er and n = 3 for Gd, Dy and Y). To a solution of 2,6-diacetylpyridine (0.163 g, 1 mmol) in acetonitrile (10 cm³) was added 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 CaCl₂. 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(L⁶)(ClO₄)₂(H₂O)]ClO₄·3H₂O **11** and [Tb(L⁶)(ClO₄)₂(H₂O)]ClO₄·3H₂O **12**. To a solution of 2,6-diacetylpyridine (0.163 g, 1 mmol) in aceto-

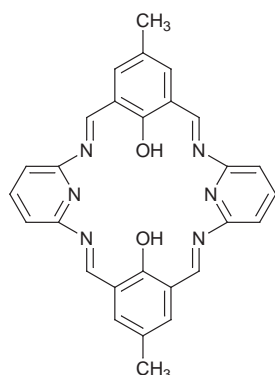
† Supplementary data available: physicochemical characterization and infrared data and mass spectra for the complexes. Available from BLDSC (No. SUP 57541, 10 pp.). See Instructions for Authors, 1999, Issue 1 (<http://www.rsc.org/dalton>).



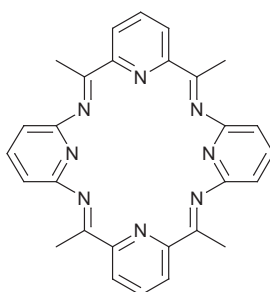
H_2L^1 , Z = CH_3
 H_2L^2 , Z = Cl
 H_2L^3 , Z = Br



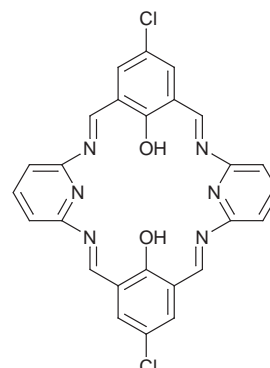
L^4



H_2L^5



L^6



H_2L^7

nitrile (10 cm^3) was added $\text{Ln}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}$ 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: $[\text{Eu}(\text{L}^6)(\text{CH}_3\text{CO}_2)_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ **13** and $[\text{Tb}(\text{L}^6)(\text{CH}_3\text{CO}_2)_3(\text{H}_2\text{O})] \cdot 3\text{H}_2\text{O}$ **14**. To a solution of 2,6-diacetylpyridine (0.163 g , 1 mmol) in acetonitrile (10 cm^3) was added $\text{Ln}(\text{CH}_3\text{CO}_2)_3 \cdot \text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}$ 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) (Nitrate)(perchlorato) complex: $[\text{Dy}(\text{L}^6)(\text{NO}_3)(\text{ClO}_4)]\text{NO}_3 \cdot \text{H}_2\text{O}$ **15**. To a suspension of $[\text{Dy}(\text{L}^6)(\text{NO}_3)(\text{H}_2\text{O})_2][\text{NO}_3]_2 \cdot 3\text{H}_2\text{O}$ (1 mmol) in methanol (20 cm^3) was added $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (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) (Nitrate)(isothiocyanato) complexes: $[\text{Eu}(\text{L}^6)(\text{NO}_3)(\text{NCS})]\text{NO}_3 \cdot \text{H}_2\text{O}$ **16** and $[\text{Tb}(\text{L}^6)(\text{NO}_3)(\text{NCS})]\text{NO}_3 \cdot \text{H}_2\text{O}$ **17**. To a suspension of $[\text{Eu}(\text{L}^6)(\text{NO}_3)(\text{H}_2\text{O})_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ or $[\text{Tb}(\text{L}^6)(\text{NO}_3)(\text{H}_2\text{O})_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$ (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) (Nitrate)(aqua) complexes: $[\text{Ln}(\text{HL}^7)(\text{NO}_3)(\text{H}_2\text{O})_2]\text{NO}_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La}$, 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: $[\text{Eu}(\text{L}^7)(\text{H}_2\text{O})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ **29** and $[\text{Tb}(\text{L}^7)(\text{H}_2\text{O})_2]\text{ClO}_4 \cdot \text{H}_2\text{O}$ **30**. Synthesized by the above procedure using $\text{Ln}(\text{ClO}_4)_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{Eu}$ or Tb) as the metal template.

(c) (Isothiocyanato)(aqua) complex: $[\text{Eu}(\text{L}^7)(\text{NCS})(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$ **31**. To a suspension of $[\text{Eu}(\text{HL}^7)(\text{NO}_3)(\text{H}_2\text{O})_2]\text{NO}_3 \cdot 4\text{H}_2\text{O}$ (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 $[\text{La}(\text{L}^6)(\text{NO}_3)(\text{H}_2\text{O})_3][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$, $[\text{Ln}(\text{L}^6)(\text{NO}_3)(\text{H}_2\text{O})_2][\text{NO}_3]_2 \cdot 2\text{H}_2\text{O}$

Table 1 FAB Mass spectral data of the complexes of L⁶ and H₂L⁷

Complex	Species	<i>m/z</i>
[La(L ⁶)(NO ₃)(H ₂ O) ₃][NO ₃] ₂ ·2H ₂ O	[La(L ⁶)(NO ₃) ₂ (H ₂ O) ₃ + H] ⁺	789
[Nd(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	[Nd(L ⁶)(NO ₃) ₂ (H ₂ O) ₂ + H] ⁺	776
[Sm(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	[Sm(L ⁶)(NO ₃) ₃ + H] ⁺	811
[Eu(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	[Eu(L ⁶)(NO ₃) ₃ + H] ⁺	813
[Gd(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·3H ₂ O	[Gd(L ⁶)(NO ₃) ₃ (H ₂ O) + H] ⁺	837
[Tb(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	[Tb(L ⁶)(NO ₃) ₂ + H] ⁺	828
[Dy(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·3H ₂ O	[Dy(L ⁶)(NO ₃) ₃ (H ₂ O) + H] ⁺	835
[Ho(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	[Ho(L ⁶)(NO ₃) ₃ (H ₂ O) ₂ + H] ⁺	840
[Er(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	[Er(L ⁶)(NO ₃) ₃ (H ₂ O) ₂ + H] ⁺	872
[Y(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·3H ₂ O	[Y(L ⁶)(NO ₃) ₃ + H] ⁺	751
[La(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·3H ₂ O	[La(HL ⁷)(NO ₃) ₂ (H ₂ O) ₂ + H] ⁺	812
[Nd(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·3H ₂ O	[Nd(HL ⁷)(NO ₃) ₂ (H ₂ O) ₂ + H] ⁺	779
[Sm(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·4H ₂ O	[Sm(HL ⁷)(NO ₃) ₂ (H ₂ O) ₂ + H] ⁺	764
[Eu(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·4H ₂ O	[Eu(HL ⁷)(NO ₃) ₂ + H] ⁺	791
[Ho(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·3H ₂ O	[Ho(HL ⁷)(NO ₃) ₂ + H] ⁺	798
[Er(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·3H ₂ O	[Er(HL ⁷)(NO ₃) ₂ + H] ⁺	810
[Y(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·3H ₂ O	[Y(HL ⁷)(NO ₃) ₂ (H ₂ O) ₂ + H] ⁺	766
[Tb(L ⁷)(H ₂ O) ₂][ClO ₄ ·H ₂ O	[Tb(L ⁷)(H ₂ O) ₂ (ClO ₄) + H] ⁺	808

(Ln = Nd, Sm, Eu, Tb, Ho or Er) and [Ln(L⁶)(NO₃)(H₂O)₂][NO₃]₂·3H₂O (Ln = Gd, Dy or Y). The perchlorato complexes [Ln(L⁶)(ClO₄)₂(H₂O)]ClO₄·3H₂O (Ln = Eu or Tb) and the acetato complexes [Ln(L⁶)(CH₃CO₂)₃(H₂O)]·3H₂O (Ln = Eu or Tb) are synthesized by using the corresponding lanthanide(III) perchlorate or acetate as the metal template. The (perchlorato)-(nitrate) complex [Dy(L⁶)(NO₃)(ClO₄)]NO₃·H₂O is synthesized by the anion metathesis reaction of [Dy(L⁶)(NO₃)(H₂O)₂][NO₃]₂·3H₂O with NaClO₄. The (nitrate)(isothiocyanato) complexes [Ln(L⁶)(NO₃)(NCS)]NO₃·H₂O (Ln = Eu or Tb) are synthesized by the anion metathesis reaction of the corresponding (nitrate)(aqua) complexes with KSCN. The formation of lanthanide(III) complexes of L⁶ demonstrates the template potential of these metal ions in the assembly of Schiff-base macrocycles having pyridine head and lateral units. In the (nitrate)(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 H₂L⁷

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(HL⁷)-(NO₃)₂(H₂O)₂]NO₃·3H₂O (Ln = La, Pr, Nd, Gd, Dy, Ho, Er or Y) and [Ln(HL⁷)(NO₃)₂(H₂O)₂]NO₃·4H₂O (Ln = Sm, Eu or Tb). The diaqua complexes [Ln(L⁷)(H₂O)₂][ClO₄·H₂O] (Ln = Eu or Tb) are synthesized by using the corresponding lanthanide(III) perchlorate as the template. The complex [Eu(L⁷)-(NCS)(H₂O)]·2H₂O is synthesized by the anion metathesis of the (nitrate)(aqua) complex with KSCN. The formation of lanthanide(III) complexes of H₂L⁷ 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 L⁶ and H₂L⁷ exhibit the ν(C=N) vibration¹⁵ 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 H₂L⁷ 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 nitrate complexes of L⁶ are assignable to the ν(N=O) (ν₁), ν_{asym}(NO₂) (ν₅) and ν_{sym}(NO₂) (ν₂), vibrations, respectively,¹⁸ of the bidentate chelating nitrate. The corresponding vibrations of the nitrate complexes of H₂L⁷ occur at lower

energy region (1410–1430, 1308–1320 and 1010–1030 cm⁻¹, respectively). The separation between the ν₅ and ν₁ vibrations (Δν) 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) (ν₃) 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)(nitrate) 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

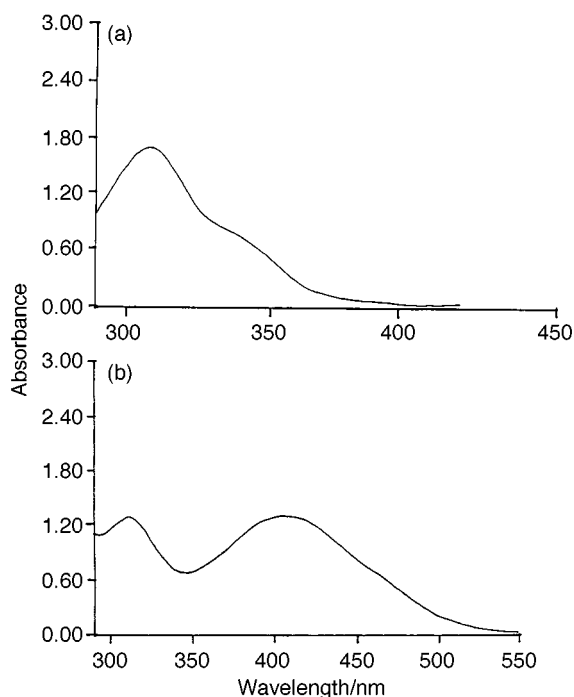
FAB Mass spectra of the complexes of L⁶ contain peaks due to the molecular ions [Ln(L⁶)(NO₃)₃(H₂O)₂ + H]⁺ (Ln = Sm, Eu, Gd, Tb, Dy, Ho, Er or Y). These species undergo fragmentation to give fragments such as [Ln(L⁶)(NO₃)₂(H₂O)₂]⁺ (Ln = Dy or Ho), [Ln(L⁶)(NO₃)₂]⁺ (Ln = Eu or Tb), [Ln(L⁶)(NO₃)]⁺ (Ln = Sm, Eu, Tb or Dy), [Ln(L⁶)(H₂O)]⁺ (Ln = Nd or Er) and [Ln(L⁶)]⁺ (Ln = Sm, Eu, Gd, Tb, Er or Y). For the complexes of H₂L⁷ peaks due to the molecular ions [Ln(HL⁷)(NO₃)₂-(H₂O)₂ + H]⁺ (Ln = La, Ho or Y) and fragments such as [Nd(HL⁷)(NO₃)₂(H₂O)₂ + H]⁺, [Ln(HL⁷)(NO₃)₂ + H]⁺ (Ln = Eu or Er), [Ln(HL⁷)(NO₃)(H₂O)₂]⁺ (Ln = Sm or Tb), [Ln(HL⁷)(NO₃)]⁺ (Ln = Nd or Y), [Ln(HL⁷)(H₂O)]⁺ (Ln = La, Nd, Ho or Er) and [Ln(HL⁷)]⁺ (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 L⁶ and of Sm, Eu and Ho with H₂L⁷. The imine nitrogens of the macrocycle undergo reduction under FAB conditions in some complexes. The FAB mass spectral data of the complexes of L⁶ and H₂L⁷ are given in Table 1.

Molar conductivity

The ionic nature of the complexes is ascertained from the molar conductivities which are well within the reported²⁴ 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 L⁶ and H₂L⁷

Complex	Temperature range/°C	Species lost	Mass loss (%)	
			found	calc.
[Sm(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	50–160	Lattice and co-ordinated H ₂ O	8.2	9.5
	200–250	NO ₃ ⁻	21.3	21.5
	>300	Macrocycle	53.6	52.1
[Ho(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	50–160	Lattice and co-ordinated H ₂ O	8.0	8.7
	200–250	NO ₃ ⁻	20.8	20.0
	>300	Macrocycle		
[Er(L ⁶)(NO ₃)(H ₂ O) ₂][NO ₃] ₂ ·2H ₂ O	50–160	Lattice and co-ordinated H ₂ O	8.0	9.0
	200–250	NO ₃ ⁻	20.7	19.0
	>300	Macrocycle	52.6	50.0
[Sm(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·4H ₂ O	50–100	Lattice H ₂ O	8.0	7.0
	100–320	Co-ordinated H ₂ O and NO ₃ ⁻	17.8	16.0
	>320	Macrocycle		
[Ho(HL ⁷)(NO ₃)(H ₂ O) ₂ NO ₃ ·3H ₂ O	50–100	Lattice H ₂ O	6.0	5.1
	100–320	Co-ordinated H ₂ O and NO ₃ ⁻	17.9	16.1
	>300	Macrocycle		

**Fig. 1** Electronic absorption spectra of (a) [Eu(L⁶)(NO₃)(H₂O)₂][NO₃]₂·2H₂O and (b) [Ho(HL⁷)(NO₃)(H₂O)₂NO₃·3H₂O.

Electronic absorption spectra

The (nitrate)(aqua) complexes of L⁶ exhibit two absorption bands at *ca.* 310 ($\epsilon \approx 19\,000$) and *ca.* 340 nm ($\epsilon \approx 8000$ dm³ mol⁻¹ cm⁻¹) except for the lanthanum(III) complex which exhibits one absorption at 335 nm ($\epsilon = 3304$ dm³ 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 H₂L⁷ exhibit absorption bands at *ca.* 310 ($\epsilon = ca. 11\,000$) and *ca.* 405 nm ($\epsilon = ca. 13\,000$ dm³ 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(L⁶)(NO₃)(H₂O)₂][NO₃]₂·2H₂O and [Ho(HL⁷)(NO₃)(H₂O)₂NO₃·3H₂O] are shown in Fig. 1.

Thermal study

The complexes exhibit high thermal stability. The thermograms of the complexes of Sm, Ho and Er with L⁶ 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 (nitrate)(aqua) complexes of Sm and Er with H₂L⁷ 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 L⁶ (2.62, 6.64 and 9.04 μ_{B} , respectively) and of Nd^{III}, Gd^{III} and Dy^{III} with H₂L⁷ (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 L⁶ and H₂L⁷. 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 L⁶ and H₂L⁷ 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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