

Lanthanide Complexes with Compartmental Schiff Bases

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Abstract

Lanthanide complexes have been prepared with acyclic and cyclic compartmental Schiff bases (H_2L) obtained by condensation of 2,6-diformyl-4-chlorophenol and the polyamines $NH_2(CH_2)_2X(CH_2)_2NH_2$ ($X = NH, S$). They can be formulated as $Ln(L)NO_3 \cdot nH_2O$ or $Ln(H_2L)(NO_3)_3 \cdot nH_2O$ ($Ln^{3+} = La, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb; n = 0-5$) and have been obtained by step-by-step reactions, which allow a more appropriate control of the reaction procedure. Template syntheses often produce not well defined complexes.

The Schiff bases act as neutral or dinegative chelating ligands according to the experimental conditions employed. When they coordinate as neutral ligands, one ionic and two bidentate nitrate groups are present in the complexes. A ring contraction, through an internal cyclization, has been observed in the macrocyclic complexes when $X = NH$ (H_2L_C).

The crystal structure of $[Tb(H_2L_C)(NO_3)_2]NO_3$ was determined by X-ray crystallography. The compound is monoclinic, space group $C2/c$, with $a = 23.668(5)$, $b = 14.328(7)$, $c = 19.482(5)$ Å and $\beta = 91.82(5)^\circ$; $D_c = 1.70$ g cm $^{-3}$ for $Z = 8$. The structure was refined to $R = 0.078$.

The terbium ion is nona-coordinated in the usual coordination geometry of a distorted tricapped trigonal prism. Two nitrate groups are chelate in approximately bisphenoidal position, the third nitrate being ionic. The organic macrocycle is coordinated through two oxygen and three nitrogen atoms. Selected bond distances are: Tb–O(nitrate) 2.46 Å (mean), Tb–O(ligand) 2.25 Å (mean), Tb–N(ligand) 2.54 Å (mean).

Introduction

Recently an increasing interest has been directed towards lanthanide chemistry, owing to the possibility of using lanthanide compounds in biological

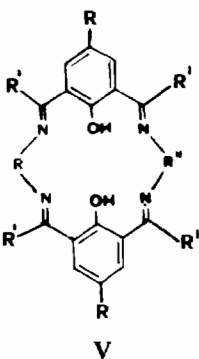
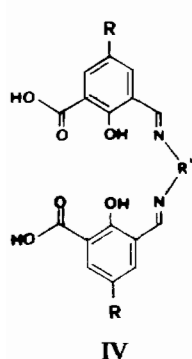
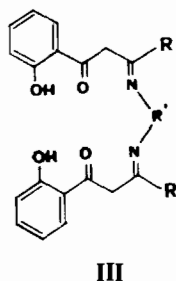
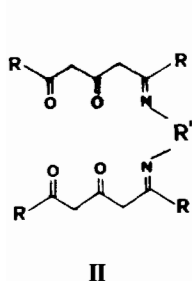
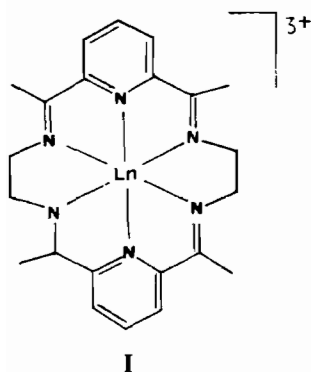
studies, in material science and in chemical processes. These studies have produced technological developments and scientific and industrial applications [1–4].

Lanthanides offer an interesting series of easily available elements with a 3+ stable oxidation state, and other common physico-chemical properties, together with significant differences (*i.e.* the continuously decreasing ionic radius). The high ionic radius allows them to reach high coordination numbers, with consequent unusual coordination geometry in comparison with d elements [5–8]. Their ionic radius being close to biologically essential alkaline or alkaline-earth ions and the paramagnetism present in all the lanthanide ions (except lanthanum(III) and lutetium(III) which are diamagnetic) make them useful biological probes [9–11]. The preparation of ligands especially designed for these ions can thus be very profitable in many fields of chemistry and technology.

Schiff bases offer a versatile and flexible series of ligands capable of binding f-metal ions and to give the resulting complexes the suitable properties to make them candidates for theoretic studies and/or practical applications (*i.e.*, stability in aqueous or non-aqueous solvent, variety of donor atom sets, stabilization of particular coordination geometries or particular oxidation states, etc.).

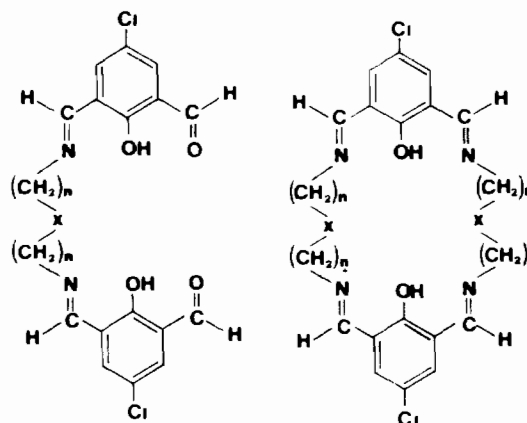
Simple Schiff bases have been used for some time for the synthesis of lanthanide complexes [12–17]. More recently a facile generation of stable macrocyclic Schiff bases by using lanthanide cations as templating agents was found and complexes of the type I have been obtained with most of the 4f elements. The structures of lanthanum(III) [18], samarium(III) [19] and lutetium(III) [20] complexes have also been determined to investigate the role played by the radius of the lanthanide ions on the coordination geometry observed in the complexes.

Homo- and heterobinuclear complexes, containing d- and/or f-metal ions, with the acyclic and macrocyclic ligands II, III, IV, V, have been extensively



studied for their stability and their possible use as mimics for the active site of metallo-enzymes and metallo-proteins [21]. Moreover with 2,6-diformyl-4-chlorophenol, acyclic and macrocyclic compartmental ligands of the type **VI**, **VII**, **VIII** and **IX** can be obtained.

We started some years ago to investigate the physico-chemical, structural and bioinorganic aspects of lanthanide and actinide coordination chemistry [22–24]. In the present paper we report the preparation and characterization of lanthanide complexes with Schiff bases obtained by condensation of 2,6-diformyl-4-chlorophenol with polyamines of the type $\text{NH}_2(\text{CH}_2)_2\text{X}(\text{CH}_2)_2\text{NH}_2$ ($\text{X} = \text{NH}, \text{S}$). The X-ray structure of one of the prepared complexes is also reported. The obtained complexes contain an additional coordination chamber and can thus act as ligands towards a second metal ion. Preliminary results have already been reported [25].



Acyclic ligands

VI H_2L_a : $\text{X} = \text{NH}$

VII H_2L_b : $\text{X} = \text{S}$

Cyclic ligands

VIII H_2L_c : $\text{X} = \text{NH}$

IX H_2L_d : $\text{X} = \text{S}$

Experimental

2,6-Diformyl-4-chlorophenol was prepared according to the literature [26]; 1,5-diamino-3-azapentane and 1,5-diamino-3-thiapentane were commercial products and used without further purification. The acyclic and macrocyclic ligands were prepared and purified according to the literature [27, 28].

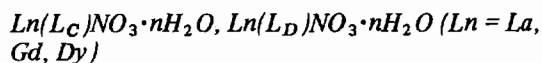
Acyclic Complexes

$\text{Ln}(\text{L}_A)\text{NO}_3 \cdot n\text{H}_2\text{O}$, $\text{Ln}(\text{L}_B)\text{NO}_3 \cdot n\text{H}_2\text{O}$ ($\text{Ln} = \text{La}, \text{Gd}, \text{Dy}$)

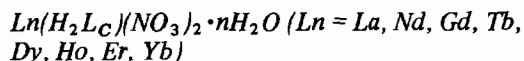
Method A. To a methanolic solution (20 ml) of 2,6-diformyl-4-chlorophenol (1 mmol), $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (0.5 mmol) in methanol (10 ml) was added and after few minutes LiOH (1 mmol) and the appropriate polyamine (0.5 mmol) were added. The volume of the resulting yellow solution was reduced and the yellow–orange precipitate obtained was filtered, washed with diethyl ether and dried *in vacuo*.

Method B. To a suspension of the preformed acyclic Schiff base (1 mmol) in methanol (20 ml), LiOH (2 mmol) and $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (1 mmol) in methanol (20 ml) were added. The solution was refluxed for 1 h. The solvent was partially evaporated and the yellow–orange precipitate obtained was filtered, washed with diethyl ether and dried *in vacuo*.

Cyclic Complexes



These can be obtained by procedures similar to those of the acyclic complexes. A 2,6-diformyl-4-chlorophenol/polyamine ratio of 1:1 must be used.



To a solution of 2,6-diformyl-4-chlorophenol (1 mmol) in chloroform (20 ml), the appropriate polyamine (1 mmol) in chloroform (10 ml) was added. To the yellow solution, $\text{Ln}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ (0.5 mmol) was added and the yellow–orange precipitate obtained was filtered, washed with diethyl ether and dried *in vacuo*.

Crystals, suitable for X-ray determinations, were obtained by dissolving the complex $[\text{Tb}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_2]\text{NO}_3$ in warm dimethylformamide and maintaining the solution, after the addition of a few drops of methanol, in an atmosphere saturated by diethyl ether.

Physical Measurements

The IR spectra were carried out as KBr pellets or nujol mulls by using a Perkin-Elmer 580B model infrared spectrophotometer.

Metal, sulphur and chlorine ratios were conveniently determined by the integral counting of back-scattered X-ray fluorescence radiation from a Philips SEM 505 Model scanning electron microscope equipped with an EDAX model data station.

Samples suitable for SEM analysis were prepared by suspending the microcrystalline powders in petroleum ether. Some drops of the resulting sus-

pension were placed on a graphite plate and after evaporation of the solvent the samples were metalized with gold or graphite by using an Edward's S150B model sputter coater.

Elemental analysis and infrared data for the prepared complexes are reported in Tables I and II, respectively.

X-ray Data

Crystal and intensity data for $[\text{Tb}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_2]\text{NO}_3$ are reported in Table III. Space group $C2/c$ was determined from the systematic absences: hkl for the $h+k$ odd, $h0l$ for h or l odd, $0k0$ for k odd. The hydrogen atoms were introduced in calculated positions ($\text{C}-\text{H} = 1.08 \text{ \AA}$) with fixed temperature factors ($\mu_{180} = 0.06 \text{ \AA}^2$). A final Fourier difference map showed no significant features, the maximum residual of electronic density being 2.3 e/\AA^3 . At convergence, the maximum shift on the refined parameters was 0.3σ . The carbon atoms of the two phenylene rings were refined as rigid bodies assuming a C–C distance of 1.395 \AA .

Final atomic parameters are listed in Table IV. Bond distances and angles are given in Tables V and VI.

Results and Discussion

The reactions of 2,6-diformyl-4-chlorophenol, polyamines and the appropriate lanthanide nitrate give the acyclic and cyclic complexes shown in Scheme 1. According to this Scheme, the template synthesis does not often form the foreseen complex; it is thus better to use step-by-step reactions, which

TABLE I. Elemental Analysis for the Prepared Complexes

Complexes	Calculated (%)			Found (%)		
	C	H	N	C	H	N
$\text{La}(\text{L}_\text{A})(\text{NO}_3) \cdot \text{H}_2\text{O}$	36.75	2.91	8.57	36.83	2.98	8.92
$\text{Dy}(\text{L}_\text{A})(\text{NO}_3) \cdot 2\text{H}_2\text{O}$	34.56	3.02	8.06	34.69	2.91	8.34
$\text{Gd}(\text{L}_\text{A})(\text{NO}_3) \cdot \text{H}_2\text{O}$	35.76	2.83	8.35	35.24	2.87	8.79
$\text{La}(\text{L}_\text{B})(\text{NO}_3) \cdot 3\text{H}_2\text{O}$	33.91	3.39	6.00	33.27	3.26	6.52
$\text{Dy}(\text{L}_\text{B})(\text{NO}_3) \cdot 2\text{H}_2\text{O}$	33.75	2.81	5.90	33.48	2.32	6.53
$\text{Dy}(\text{L}_\text{C})(\text{NO}_3) \cdot 3\text{H}_2\text{O}$	36.94	4.10	12.57	36.25	3.39	12.83
$\text{Gd}(\text{L}_\text{C})(\text{NO}_3) \cdot 4\text{H}_2\text{O}$	36.36	4.29	12.37	36.10	3.42	13.11
$\text{La}(\text{L}_\text{D})(\text{NO}_3) \cdot 4\text{H}_2\text{O}$	35.66	3.99	8.66	35.93	3.53	8.95
$\text{Dy}(\text{L}_\text{D})(\text{NO}_3) \cdot 2\text{H}_2\text{O}$	36.20	3.52	8.80	36.24	3.38	8.05
$\text{La}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	32.67	3.88	14.29	32.35	3.28	14.44
$\text{Nd}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	32.47	3.86	14.20	32.16	3.14	13.51
$\text{Gd}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_3^{\text{a}}$	34.05	3.33	14.89	33.90	3.39	14.51
$\text{Tb}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_3^{\text{a}}$	33.97	3.30	14.86	33.34	3.52	14.29
$\text{Ho}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$	31.73	3.77	13.88	31.68	3.01	13.42
$\text{Er}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	30.45	4.05	13.31	29.84	3.80	12.40
$\text{Yb}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_3^{\text{a}}$	33.41	3.25	14.61	33.30	3.26	13.98

^aAfter recrystallization from DMF.

TABLE II. Infrared Spectroscopic Data for the Prepared Complexes (cm⁻¹)

Complexes	Bands attributable to			N-H	NO ₃ ⁻ Ionic	Bands attributable to coordinated nitrates			
	C=N	C=C	C=O						
La(L _A)(NO ₃)·H ₂ O	1665s	1644s	1538s	^b	1386vs				
Dy(L _A)(NO ₃)·2H ₂ O	1662s	1640s	1542s	3270	1386vs				
Gd(L _A)(NO ₃)·H ₂ O	1652s	1638s	1540s	3270sh	1386vs				
La(L _B)(NO ₃)·3H ₂ O	1655s	1634s	1537s		1386vs				
Dy(L _B)(NO ₃)·2H ₂ O	1650b	1535s			1386vs				
Dy(L _C)(NO ₃)·3H ₂ O	1660s	1638s	1543s	3277b	1386vs				
Gd(L _C)(NO ₃)·4H ₂ O	1658s	1640s	1540s	3268sh	1386vs				
La(L _D)(NO ₃)·4H ₂ O	1655s	1634s	1538s		1386vs				
Dy(L _D)(NO ₃)·2H ₂ O	1650s	1629s	1542s		1386vs				
La(H ₂ L _C)(NO ₃) ₃ ·3H ₂ O	1662s	1640s	1539s	3272sh	1386vs	1460s	1266b	1038m	820m
Nd(H ₂ L _C)(NO ₃) ₃ ·3H ₂ O	1661s	1638s	1541s	3261	1387vs	1461s	1294s	1032m	819m
Gd(H ₂ L _C)(NO ₃) ₃ ^a	1661s	1637s	1542s	3278	1386vs	1462s	1291s	1027m	818m
Tb(H ₂ L _C)(NO ₃) ₃ ^a	1662s	1637s	1542s	3224b	1386vs	1465s	1294m	1033m	817m
Ho(H ₂ L _C)(NO ₃) ₃ ·3H ₂ O	1663s	1639s	1543s	3272	1386vs	1466s	1298s	1032m	817m
Er(H ₂ L _C)(NO ₃) ₃ ·5H ₂ O	1663s	1639s	1542s	3270	1386vs	1467s	1298s	1034m	817m
Yb(H ₂ L _C)(NO ₃) ₃ ^a	1665s	1638s	1545s	3269	1386vs	1466s	1301s	1034m	817m

^aAfter recrystallization from DMF. ^bThe N-H is not always observed.

TABLE III. Crystal and Intensity Data for [Tb(H₂L_C)(NO₃)₂]NO₃

Compound	[Tb(C ₂₄ H ₂₆ Cl ₂ N ₆ O ₂)(NO ₃) ₂]NO ₃
Formula	C ₂₄ H ₂₆ Cl ₂ N ₉ O ₁₁ Tb
Formula weight	846
System	Monoclinic
Space group	C2/c
General positions	(0, 0, 0; 1/2, 1/2, 0); ±(x, y, z); -x, y, 1/2 - z)
a (Å)	23.668(5)
b (Å)	14.328(7)
c (Å)	19.482(5)
β (°)	91.82(5)
V (Å ³)	6603
Z	8
D _c (g cm ⁻³)	1.70
Max crystal size (mm)	0.2
Radiation	Mo Kα
μ(Mo Kα) (cm ⁻¹)	31.4
Technique and geometry	Four-circle diffractometer (Philips PW 1100) with graphite monochromated radiation; θ/2θ scan mode; scan rate 2° min ⁻¹
θ _{max} (°)	25
Stability	No significant variation
Number of recorded intensities	10185
Criterion for observed intensities	I > 3σ(I)
Number of observed intensities	3848
Corrections applied	Lorentz polarization, adsorption [38]
Atomic scattering factors	Tb: ref. 42; C, H, N, O, Cl: ref. 39
Corrections for anomalous dispersion (Tb)	ΔF' = -0.591, ΔF'' = 4.151
Solution of the structure	Patterson and Fourier methods
Refinement of parameters	Full-matrix least-squares
Weighting scheme	w = 1
Conventional R factor	0.078
Programs used	SHELX [39], PARST [40], PLUTO [41]

TABLE IV. Atomic Parameters for $[\text{Tb}(\text{H}_2\text{L}_\text{C})(\text{NO}_3)_2]\text{NO}_3$

Atom	x/a	y/b	z/c			
Atomic coordinates						
Tb1	0.63268(3)	0.00542(6)	0.11317(5)			
O1	0.59169(48)	0.03875(86)	-0.00259(70)			
O2	0.67160(37)	0.10746(83)	0.02105(65)			
O3	0.61273(49)	0.16600(107)	-0.05591(78)			
O4	0.63029(52)	0.04080(118)	0.23426(102)			
O5	0.64055(60)	-0.09962(129)	0.21093(130)			
O6	0.64348(74)	-0.05049(175)	0.31399(121)			
O7	0.59891(40)	0.15220(74)	0.12027(65)			
O8	0.72022(34)	0.04244(83)	0.15141(62)			
O9	0.59580(80)	0.41090(154)	0.59605(117)			
O10	0.66051(80)	0.45071(137)	0.66162(126)			
O11	0.64327(89)	0.31178(158)	0.65167(136)			
N1	0.62482(57)	0.10563(121)	-0.01571(85)			
N2	0.63790(74)	-0.03430(247)	0.25359(109)			
N3	0.52830(48)	-0.00648(107)	0.14075(77)			
N4	0.59250(58)	-0.15044(108)	0.07700(101)			
N5	0.70087(54)	-0.09926(107)	0.04994(96)			
N6	0.75834(52)	0.15461(130)	0.25608(78)			
N7	0.74203(44)	0.25729(103)	0.16829(73)			
N8	0.64963(44)	0.30511(97)	0.09193(70)			
N9	0.63367(72)	0.39240(148)	0.63734(115)			
C1	0.55231(33)	0.20121(64)	0.13395(54)			
C2	0.55508(33)	0.29836(64)	0.13078(54)			
C3	0.50807(33)	0.35192(64)	0.14682(54)			
C4	0.45830(33)	0.30831(64)	0.16602(54)			
C5	0.45553(33)	0.21116(64)	0.16919(54)			
C6	0.50253(33)	0.15761(64)	0.15315(54)			
C7	0.49290(69)	0.05680(116)	0.15193(86)			
C8	0.50910(79)	-0.10396(127)	0.13841(100)			
C9	0.52815(82)	-0.15021(154)	0.07469(109)			
C10	0.61147(87)	-0.17648(167)	0.00973(116)			
C11	0.67939(86)	-0.18382(153)	0.01792(118)			
C12	0.75398(85)	-0.08750(146)	0.04095(107)			
C13	0.78931(38)	-0.01363(65)	0.07344(54)			
C14	0.84408(38)	-0.00759(65)	0.04938(54)			
C15	0.88011(38)	0.06339(65)	0.07285(54)			
C16	0.86137(38)	0.12835(65)	0.12037(54)			
C17	0.80660(38)	0.12231(65)	0.14443(54)			
C18	0.77057(38)	0.05133(65)	0.12096(54)			
C19	0.78704(74)	0.19801(129)	0.19408(98)			
C20	0.72452(98)	0.23805(160)	0.28603(121)			
C21	0.72647(79)	0.30937(130)	0.22850(97)			
C22	0.75344(70)	0.30584(125)	0.10607(92)			
C23	0.70189(65)	0.35843(116)	0.07742(92)			
C24	0.60622(72)	0.34898(133)	0.11041(94)			
Cl1	0.40198(19)	0.37635(44)	0.19130(37)			
Cl2	0.94920(16)	0.07039(48)	0.04716(31)			
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Thermal parameters ^a $U_{ij} \times 10^{-4}$						
Tb1	289(3)	559(4)	817(5)	90(6)	16(3)	16(4)
O1	574(67)	721(79)	1045(104)	85(74)	-94(68)	-146(60)
O2	232(43)	868(82)	940(92)	27(72)	66(51)	90(49)
O3	504(68)	1115(114)	1085(119)	420(99)	56(71)	10(72)
O4	350(63)	1132(119)	1751(185)	603(121)	-10(84)	25(69)

(continued)

TABLE IV. (continued)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O5	390(71)	1215(149)	2085(237)	607(148)	46(115)	130(82)
O6	1080(134)	2599(270)	1510(180)	499(186)	291(127)	934(153)
O7	413(54)	529(63)	906(96)	-7(64)	172(57)	-84(48)
O8	168(39)	942(84)	900(87)	-33(70)	66(47)	-18(46)
O9	1082(137)	1747(200)	1881(211)	445(167)	-622(142)	3(134)
O10	1117(139)	1188(150)	2321(249)	582(157)	-570(152)	-415(121)
O11	1443(174)	1320(172)	2555(283)	-310(184)	-1113(182)	381(146)
N1	445(75)	890(117)	785(119)	57(97)	60(75)	8(78)
N2	411(83)	2516(379)	602(118)	756(173)	254(82)	284(155)
N3	456(62)	559(79)	1083(111)	148(102)	10(66)	-144(74)
N4	508(82)	690(101)	1321(169)	-65(107)	145(94)	-65(74)
N5	376(69)	697(98)	1414(162)	-206(104)	118(85)	65(67)
N6	385(68)	1277(145)	565(97)	-22(99)	132(64)	35(82)
N7	248(51)	873(100)	631(93)	-31(81)	35(56)	61(59)
N8	233(50)	752(90)	689(93)	26(77)	53(55)	10(55)
N9	485(86)	889(132)	1311(183)	191(131)	-178(105)	38(97)
C1	523(38)					
C2	484(36)					
C3	582(41)					
C4	671(48)					
C5	644(46)					
C6	520(37)					
C7	576(41)					
C8	715(50)					
C9	862(60)					
C10	917(65)					
C11	889(63)					
C12	811(57)					
C13	643(42)					
C14	652(40)					
C15	647(45)					
C16	606(44)					
C17	537(38)					
C18	518(37)					
C19	651(46)					
C20	922(68)					
C21	672(49)					
C22	639(45)					
C23	601(43)					
C24	674(48)					
Cl1	496(24)	1173(46)	1696(62)	401(44)	486(32)	380(28)
Cl2	275(18)	1551(53)	1169(45)	153(41)	263(22)	167(25)

^aAnisotropic thermal parameters are in the form: $T = \exp[-2\pi^2(U_{ij}h_i h_j a_i^* a_j^*)]$.

allow a more appropriate control of the reaction procedure.

It must be noted also that the reaction with the preformed ligands causes some problems owing to their low solubility in alcoholic solution; dimethylformamide can be added to increase their solubility. The best way to synthesize the complexes is to prepare the appropriate fresh ligand in solution and add to it the desired lanthanide salt without prior separation and purification.

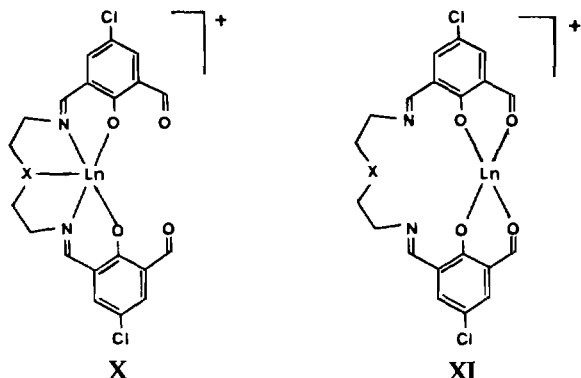
The Schiff bases behave as neutral or dianionic ligands according to the synthesis procedure em-

ployed. The presence of a base (LiOH, NaOH, etc.) promotes the formation of complexes containing only one nitrate group and dianionic Schiff base, whereas, in the absence of a base and in aprotic solvents (*i.e.* chloroform), complexes containing three nitrate groups have been obtained. Two nitrates coordinate as bidentate, the third is ionic, while the Schiff base coordinates as a neutral ligand.

With the acyclic ligands it is feasible to obtain positional isomers of the type X and XI, as already observed for copper(II) and uranyl(VI) complexes with similar systems [29, 30].

TABLE V. Bond Distances (Å) for [Tb(H₂L_C)(NO₃)₂]₂NO₃

Coordination sphere			
Tb–O(1)	2.47(1)	Tb–O(7)	2.26(1)
Tb–O(2)	2.51(1)	Tb–O(8)	2.24(1)
Tb–O(4)	2.42(2)	Tb–N(3)	2.55(1)
Tb–O(5)	2.43(2)	Tb–N(4)	2.52(2)
		Tb–N(5)	2.55(2)
Multidentate ligand			
C(1)–O(7)	1.34(1)	C(19)–N(6)	1.54(2)
C(6)–C(7)	1.46(2)	C(19)–N(7)	1.44(2)
C(7)–N(3)	1.26(2)	N(6)–C(20)	1.56(3)
N(3)–C(8)	1.47(2)	C(20)–C(21)	1.52(3)
C(8)–C(9)	1.49(3)	C(21)–N(7)	1.45(2)
C(9)–N(4)	1.52(2)	N(7)–C(22)	1.43(2)
N(4)–C(10)	1.45(3)	C(22)–C(23)	1.52(2)
C(10)–C(11)	1.61(3)	C(23)–N(8)	1.49(2)
C(11)–N(5)	1.45(3)	N(8)–C(24)	1.27(2)
N(5)–C(12)	1.29(2)	C(24)–C(2)	1.48(2)
C(12)–C(13)	1.48(2)	C(4)–Cl(1)	1.74(1)
C(18)–O(8)	1.35(1)	C(15)–Cl(2)	1.73(1)
C(17)–C(19)	1.53(2)		
Chelate nitrates			
N(1)–O(1)	1.27(2)	N(2)–O(4)	1.15(4)
N(1)–O(2)	1.30(2)	N(2)–O(5)	1.26(4)
N(1)–O(3)	1.20(2)	N(2)–O(6)	1.20(3)
Ionic nitrate			
N(9)–O(9)	1.22(3)	N(9)–O(11)	1.21(3)
N(9)–O(10)	1.14(3)		



Generally, useful information about the inner or outer site occupancy was gained by IR data; the coordination of the metal ion in the outer site lowers the $\nu(\text{C}=\text{O})$ with respect to the free ligand, while inner coordination produces small shifts.

In the complexes with H₂L_A and H₂L_B there is not a linear trend; a lowering in the $\nu(\text{C}=\text{O}) = 1643\text{--}1635\text{ cm}^{-1}$ has been observed for NiL_B and NiL_E where an inner occupancy was demonstrated by an X-ray structural determination [31] (H₂L_E is the Schiff base obtained by condensation of 2,6-diformyl-4-chlorophenol and 3,3'-diamino-*N*-methyl-

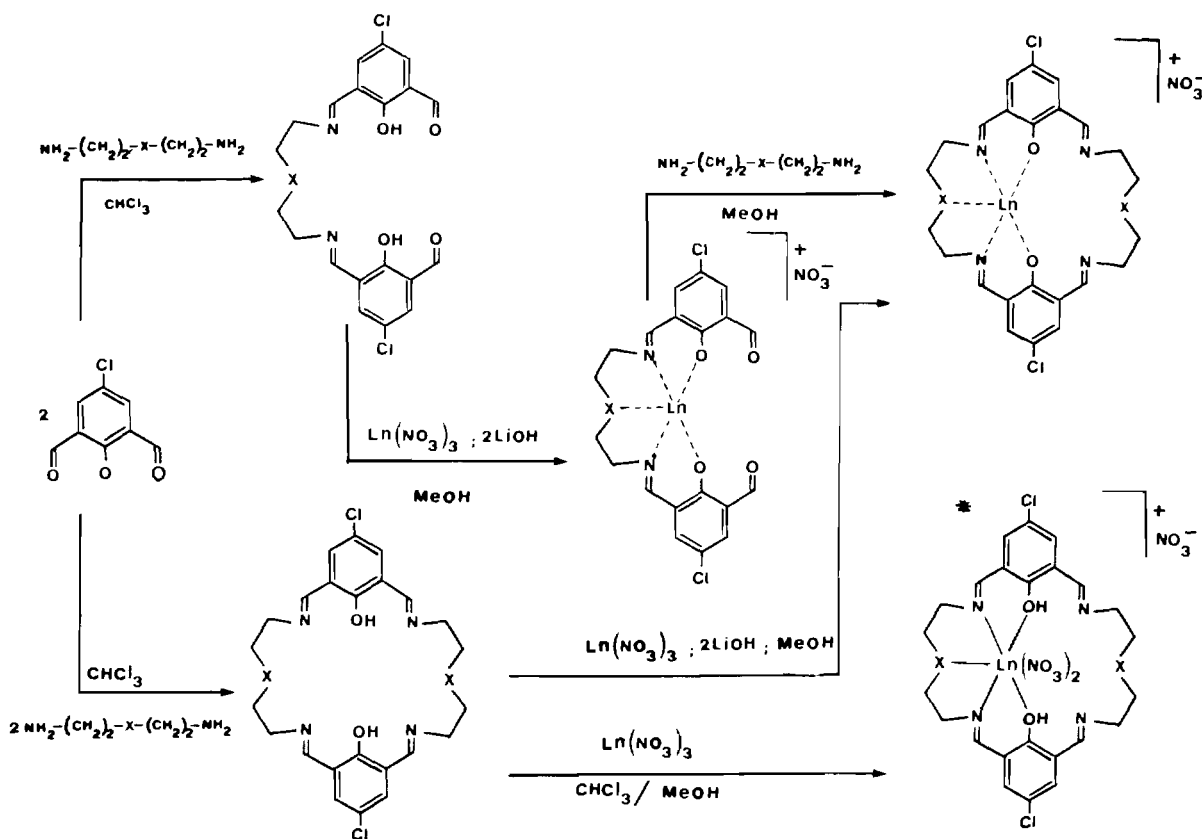
TABLE VI. Selected Bond Angles (deg) for [Tb(H₂L_C)(NO₃)₂]₂NO₃ e.s.d.s Refer to the Last Significant Digit.

Coordination sphere			
O(1)–Tb–O(2)	51.6(4)	N(3)–Tb–N(4)	68.9(5)
O(4)–Tb–O(5)	50.8(6)	N(4)–Tb–N(5)	65.3(5)
O(7)–Tb–N(3)	72.7(4)	O(7)–Tb–O(8)	94.8(4)
O(8)–Tb–N(5)	73.0(4)		
Terbium with ligands			
Tb–O(1)–N(1)	96(1)	Tb–N(3)–C(7)	130(1)
Tb–O(2)–N(1)	93(1)	Tb–N(3)–C(8)	119(1)
Tb–O(4)–N(2)	97(2)	Tb–N(4)–C(9)	112(1)
Tb–O(5)–N(2)	93(2)	Tb–N(4)–C(10)	111(1)
Tb–O(7)–C(1)	143(1)	Tb–N(5)–C(11)	119(1)
Tb–O(8)–C(18)	134(1)	Tb–N(5)–C(12)	129(1)
Multidentate ligand			
C(6)–C(7)–N(3)	128(1)	N(6)–C(19)–N(7)	100(1)
C(7)–N(3)–C(8)	119(1)	C(19)–N(6)–C(20)	103(1)
N(3)–C(8)–C(9)	110(1)	N(6)–C(20)–C(21)	102(2)
C(8)–C(9)–N(4)	108(2)	C(20)–C(21)–N(7)	105(2)
C(9)–N(4)–C(10)	108(2)	C(19)–N(7)–C(21)	103(1)
N(4)–C(10)–C(11)	105(2)	C(19)–N(7)–C(22)	115(1)
C(10)–C(11)–N(5)	109(2)	C(21)–N(7)–C(22)	120(2)
C(11)–N(5)–C(12)	112(2)	N(7)–C(22)–C(23)	112(1)
N(5)–C(12)–C(13)	125(2)	C(22)–C(23)–N(8)	110(1)
C(17)–C(19)–N(6)	111(1)	C(23)–N(8)–C(24)	119(2)
C(17)–C(19)–N(7)	116(1)	N(8)–C(24)–C(2)	121(2)
Nitrates			
O(1)–N(1)–O(2)	115(2)	O(4)–N(2)–O(5)	119(2)
O(1)–N(1)–O(3)	123(1)	O(4)–N(2)–O(6)	121(3)
N(5)–C(12)–O(3)	122(1)	O(5)–N(2)–O(6)	120(3)
O(9)–N(9)–O(10)	120(2)		
O(9)–N(9)–O(11)	119(2)		
O(10)–N(9)–O(11)	120(2)		

dipropylamine in a 2:1 molar ratio). Analogous behaviour was observed for NiL_A, CuL_A, UO₂L_A ($\nu(\text{C}=\text{O}) = 1648\text{--}1630\text{ cm}^{-1}$). On the contrary, the $\nu(\text{C}=\text{O})$ for CuL_B and UO₂L_B ($\nu(\text{C}=\text{O}) = 1680\text{--}1671\text{ cm}^{-1}$) lies at frequencies close to that of the free ligand (1680 cm^{-1}), 1683 for H₂L_A.

The acyclic lanthanide complexes show IR bands in the range $1662\text{--}1634\text{ cm}^{-1}$ due to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{O})$; the cyclic complexes show $\nu(\text{C}=\text{N})$ practically in the same region as the acyclic complexes. It must be noted that while in the cyclic compounds there are two sharp strong bands, in the acyclic analogues the bands are very broad. These data make doubtful any correct assignment of the site occupancy of the lanthanide ion in the acyclic complexes.

The $\nu(\text{NH})$, $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ do not show significant trends on changing the lanthanide ion. IR spectra of the complexes containing only one nitrate group show absorption bands at 1386 cm^{-1} , while for the complexes with three nitrate groups, absorptions bands centered at 1430, 1280, 1030 and



*(when X = NH a ring contraction occurs in the free compartment)

Scheme 1.

820 cm^{-1} , attributable to bidentate nitrate groups, are also detectable in addition to the band at $\approx 1386\text{ cm}^{-1}$ due to free NO_3^- .

For the macrocyclic complexes with **VIII**, a further cyclization can occur, as already observed in the reaction between heptane-2,4,6-trione and diethylenetriamine, where the Schiff base gives rise to a fast cyclization with the elimination of a water molecule [32]. For the analogous macrocyclic complexes with **IX** the ligand does not suffer further reactions and it coordinates intact as pentadentate to the lanthanide ions.

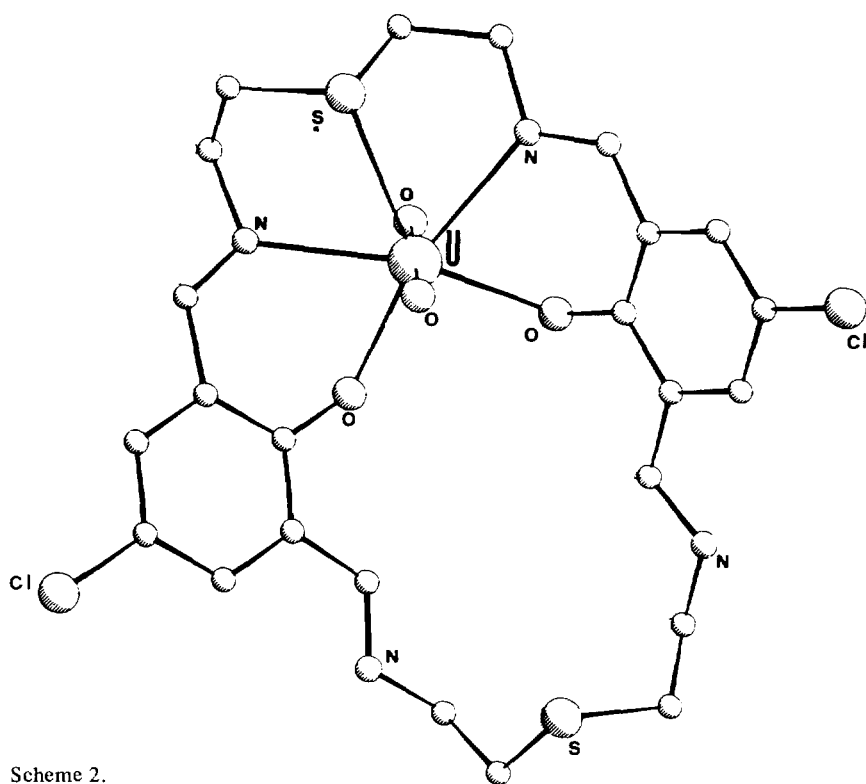
The X-ray structure of the uranyl(VI) complex with **IX** has been recently solved [33]. Five donor atoms of the ligand, including sulphur, are equatorially bonded to the O-U-O group to form discrete monomeric molecules with the seven coordinated metal ion in the usual distorted pentagonal bipyramidal coordination geometry (Scheme 2). The cyclic ligand includes a second compartment which could act as a second coordination set.

Interesting behaviour is found with the cyclic complexes, where non-coordinated NH groups are present, which is represented by the ring contraction reaction shown in eqn. (1). This type of reaction

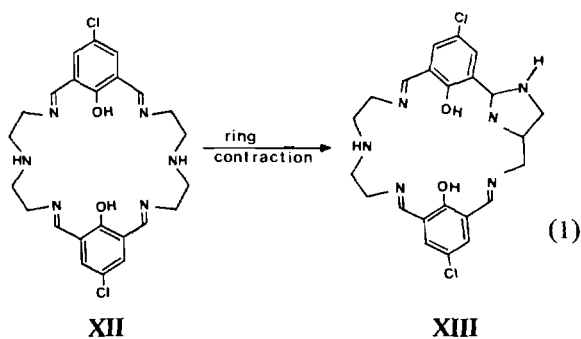
is not uncommon and has been generally found when a ring contraction of the macrocycle and/or a lowering in denticity makes the ligand more suitable for the metal ion employed [34–36].

For the macrocycle, obtained by template reaction of 2,6-diacetylpyridine and diethylenetriamine, a {24} → {18} ring contraction shown in eqn. (2) was observed for Ba^{2+} , Sr^{2+} and Ca^{2+} , but not for Mg^{2+} . It was argued that the 24-membered macrocycle is too large to form stable mononuclear complexes with these ions; Mg^{2+} is too small for the macrocycle even in its contracted form. A ring expansion of the coordinated macrocycle {18} → {24} occurs on treatment of $\text{Sr}(\text{XV})(\text{ClO}_4)_2$ with AgClO_4 ; the binuclear silver perchlorate complex $\text{Ag}_2(\text{XIV})(\text{ClO}_4)_4$ is formed. The ring contraction has been seen [34–36] as a consequence of the nucleophilic addition of two secondary amine functions of the ligand across adjacent azomethine bonds. This causes the expulsion of two five-membered imidazoline rings from the inner large ring and a reduction in the denticity of the macrocycle.

In the prepared complexes, the ring contraction is not obtained by a lowering of the coordination denticity, but through the formation of an imid-

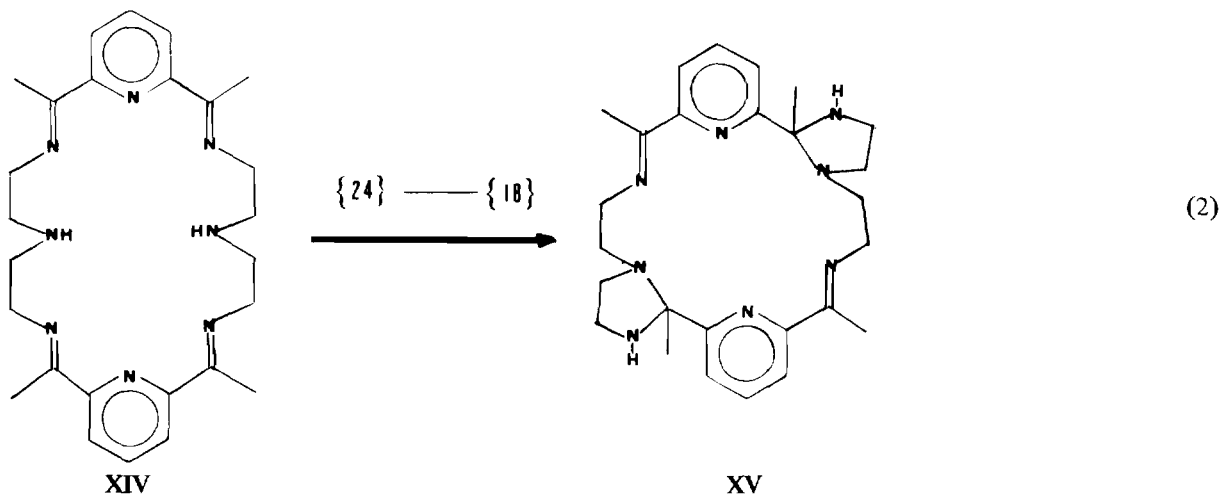


Scheme 2.



azoline ring in the aliphatic chain of the free compartment. This makes the ligand more compact hence allowing a more appropriate spatial arrangement of the donor atoms of the macrocyclic ligand around the lanthanide ion.

We were able to grow crystals of some complexes prepared from a dimethylformamide/diethyl ether solution. The complexes do not ever incorporate solvent molecules as solvate. For the terbium(III) nitrate complex, $[\text{Tb}(\text{H}_2\text{L}_c)(\text{NO}_3)_2]\text{NO}_3$, an X-ray investigation was carried out. Its crystal structure, together with the numbering scheme used is shown



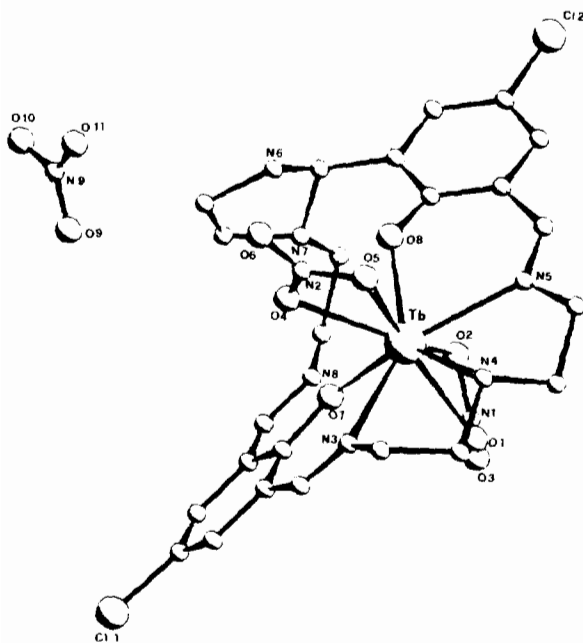


Fig. 1. The crystal structure of $[\text{Tb}(\text{H}_2\text{LC})(\text{NO}_3)_2]\text{NO}_3$.

in Fig. 1. The terbium ion is nona-coordinate, being bound to five donor atoms from the cyclic polydentate ligand and to four oxygen atoms of two bidentate nitrate groups, the third nitrate being ionic. Very roughly, the oxygen and nitrogen atoms of the macrocycle form a pentagon around the metal ion while the two bonded nitrate groups are chelate on the opposite sides in bisphenoidal positions (Fig. 2).

The coordination polyhedron around Tb can be best described as a distorted tricapped trigonal prism

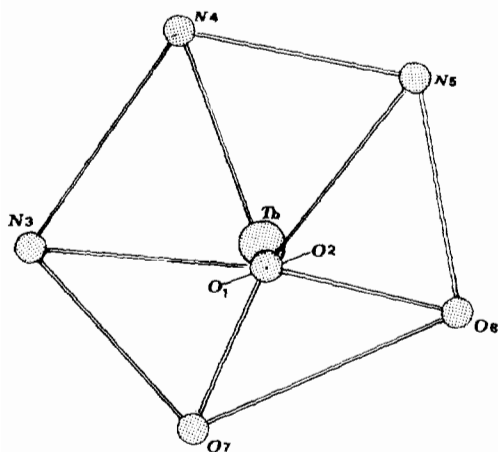


Fig. 2. The crystal structure of $[\text{Tb}(\text{H}_2\text{LC})(\text{NO}_3)_2]\text{NO}_3$. Projection of the coordination polyhedron along the $\text{N}(1)\cdots\text{N}(2)$ direction. The five donor atoms from the macrocycle form a distorted pentagon around Tb. (For distances of atoms from the mean plane through the pentagon see Table VII).

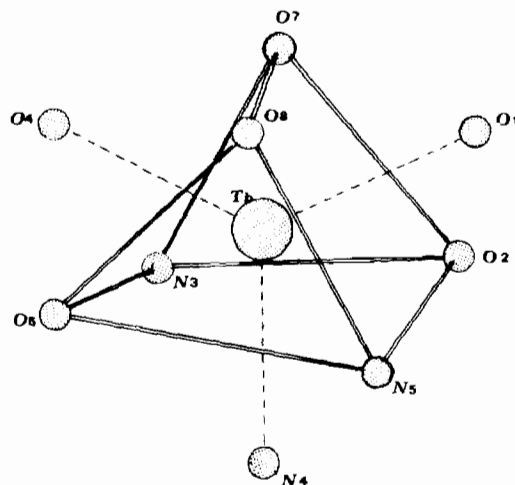


Fig. 3. Crystal structure of $[\text{Tb}(\text{H}_2\text{LC})(\text{NO}_3)_2]\text{NO}_3$. The coordination polyhedron around Tb can be described as a distorted tricapped trigonal prism.

in which (O2), (O4) and (N4) are the caps, as shown in Fig. 3. Distortions from the idealized geometry mainly arise from the asymmetry of the pentadentate ligand and from geometrical constraints due to the rigid structure of the nitrate groups. Metal–ligand interatomic distances fall within three categories: Tb–O(nitrate) (mean 2.46 Å), Tb–O(phenolic) (mean 2.25 Å), and Tb–N (mean 2.54 Å).

It is noteworthy that the Tb–O distances with the neutral ligand are significantly shorter than the corresponding distances with the charged nitrate groups: the apparent contradiction is further evidence that the Tb–nitrate distances are largely determined by the geometry of these ligands. The Tb ion makes two hexa-atomic and two penta-atomic rings with the organic ligand. As shown in Table VI, the two O–Tb–N angles (both are 73°) are only few degrees larger than the N–Tb–N ones (mean 67°), while the O(7)–Tb–O(8) angle is very large. The smallest angles, of 51° , are those subtended by the nitrate groups, as expected if we consider the short $\text{O}\cdots\text{O}$ distances in these ligands.

The organic ligand is puckered with respect to the equatorial mean plane but two moieties, those corresponding to planes 2 and 3 of Table VII, are planar and form comparable dihedral angles (25° and 29°) with the mentioned mean plane. Nitrogen atoms in the ligand are of two types: N(3), N(5) and N(8) are sp^2 -hybridized and form one single and one double bond, with the adjacent carbon atoms, N(4), N(6) and N(7) are sp^3 -hybridized and form single C–N bonds.

Bond angles at the nitrogen atoms are in accordance with this scheme. In particular, bond angles in the narrow range 108° to 112° at N(4) indicate that coordination of this atom is realized along the ideal direction of its lone pair, while N(3) and N(5)

TABLE VII. Equations of Selected Mean Planes and Lines. x , y and z are Orthogonalized Coordinates. Distances (Å) of Atoms from the Planes or Lines are in Parenthesis

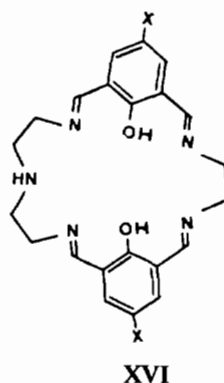
Plane 1: O(7), N(3), N(4), N(5), O(8)	
$0.009x + 0.296y - 0.955z = -1.991$	
[O(7) 0.53, N(3) -0.54, N(4) 0.04, N(5) -0.79, O(8) -0.49, Tb 0.04]	
Plane 2: C(1) to C(7), C(24), N(3), O(7), N(8)	
$0.290x + 0.014y + 0.957z = 6.280$	
[C(7) 0.08, C(24) 0.01, N(3) 0.06, O(7) -0.08]	
Plane 3: C(12) to C(19), N(5), O(8)	
$0.307x + 0.606y + 0.734z = 6.863$	
[C(12) 0.05, C(19) 0.13, N(5) 0.20, O(8) -0.14]	
Plane 4: N(1), O(1), O(2), O(3)	
$0.456x - 0.538y - 0.709z = 6.134$	
these atoms are coplanar	
Plane 5: N(2), O(4), O(5), O(6)	
$0.989x + 0.138y - 0.051z = 14.459$	
these atoms are coplanar	
Line 1: N(1), N(2)	
$\frac{y - 14.869}{0.025} = \frac{y - 0.511}{(-0.357)} = \frac{z - 2.316}{0.934}$	
[Tb 0.45]	

Planes	Angles (°)	Planes	Angles (°)
Angles between planes			
1-2	24.9	2-4	56.4
1-3	28.6	2-5	103.9
1-4	58.6	3-4	86.9
1-5	84.4	3-5	100.5
2-3	38.5	4-5	65.6

show the same type of asymmetry in the two Tb-N-C angles (of 119° and 130° respectively), probably due to the circumstance that these atoms belong to the planar and geometrically rigid moieties of the ligand. Other structural details appear to be normal.

A second coordination site is, for all the prepared complexes, available for subsequent coordination by an appropriate metal ion. On the basis of the above results we suggest that complexes containing the asymmetric ligand XVI would be the most suitable for the formation of heterobinuclear complexes (*i.e.*, Ln-Cu, Ln-Ni, etc.), while the symmetric ligand H_2L_D seems to be a good candidate for the synthesis of homobinuclear lanthanide complexes with the metal ions inside the ligand.

Preliminary results suggest that under mild conditions (alcoholic solution at room temperature without addition of base) the second metal ion is not stoichiometrically coordinated to the complex



$[La(H_2L_D)(NO_3)_2]NO_3$. A scanning electron microscope (SEM) investigation [37] has shown the prepared samples are almost homogeneous with a La/M/S/Cl ratio approximately 1/0.5/2/2 ($M = Zn^{2+}, Cu^{2+}$). The elemental analyses agree with a stoichiometry $\{[La(H_2L_D)(NO_3)_2]NO_3\}_2M(CH_3COO)_2$; the second metal ion would not be incorporated into the free chamber. Further investigations are in progress for an understanding of the best experimental procedure for the synthesis of homo- and hetero-polynuclear species.

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