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Synthesis and characterization of lanthanide complexes of 1,4,7,10,13-pentaazacyclopentadecane

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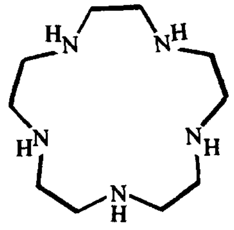
Abstract—Twelve new complexes of lanthanide nitrates with 1,4,7,10,13-pentaazacyclopentadecane (L) have been prepared under nitrogen using anhydrous acetonitrile as reaction medium. The complexes having the composition $M(L)(NO_3)_3$ (M = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, Tm, Yb and Y) were characterized by elemental analysis, IR spectra and conductivity measurements. An X-ray crystallographic structural determination of the lanthanum complex shows that the five nitrogen atoms from the ligand coordinate to the metal ion on one side and the three bidentate nitrate groups coordinate on the opposite side. The coordination number of the metal ion is eleven. © 1997 Elsevier Science Ltd

Keywords: lanthanide complexes, 1,4,7,10,13-pentaazacyclopentadecane, synthesis and structure.

In recent years there has been considerable interest in stable complexes of lanthanide cations with polyazamacrocyclic ligands as effective NMR shift reagents [1] and as contrast agents for magnetic resonance imaging [2]. The thermodynamic stability constants and kinetic properties of some of these polyazamacrocyclic complexes have been investigated [3–7]. Most of these studies have been restricted to solution, while the studies on the solid lanthanide polyazamacrocyclic complexes were reported much less [8]. As part of a systematic investigation on the rare earth complexes with macrocyclic ligands [9], this paper reports the preparation and characterization of the complexes of lanthanide nitrates with 1,4,7,10,13-pentaazacyclopentadecane.



1,4,7,10,13-pentaazacyclopentadecane

EXPERIMENTAL

Reagents

Lanthanide nitrates were prepared by dissolving the corresponding M_2O_3 (AR) in 1 : 1 nitric acid. The ligand 1,4,7,10,13-pentaazacyclopentadecane was synthesized according to the literature method [10]. All other chemicals were AR grade and all the solvents were dried before use.

Chemical and physical measurements

The metal ion contents were determined by EDTA titration using xylenol orange as an indicator. Carbon, nitrogen and hydrogen contents were determined using a Carlo Erba 1106 elemental analyser. The IR spectra were recorded in 4000–200 cm^{-1} region using KBr pellets and 170 SX FTIR spectrometer. Conductivity measurements were carried out with a DDS-11A type conductivity bridge for freshly prepared

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solution in DMF (10^{-3}M). The crystal data were collected on a CAD-4 diffractometer.

Preparation of the complexes

A solution of 0.5 mmol ligand in 10 cm^3 anhydrous acetonitrile was added to a solution of 0.5 mmol $M(NO_3)_3 \cdot nH_2O$ in 10 cm^3 anhydrous acetonitrile. The mixture solution was refluxed for 3–4 h under nitrogen. A little precipitate produced in the solution was rapidly filtered off and the filtrate was allowed to slowly evaporate at room temperature under nitrogen atmosphere. After about one month, the complex crystals formed from the solution. The crystals were isolated by filtration and dried *in vacuo* over P_4O_{10} for 3 days. Yield 40–50%. Before being dried *in vacuo* some good single crystals of lanthanum complex were selected for X-ray diffraction.

X-ray structure determination

Crystal data. monoclinic system, space group $P2_1/a$, $a = 16.247(2)$, $b = 16.190(2)$, $c = 16.514(4)$ Å, $\beta = 105.53(2)°$, $V = 4185(1)$ Å^3, $Z = 4$.

A single crystal of dimensions 0.20 × 0.20 × 0.40 mm was selected for the data collection on an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Cu-K_α radiation, ω–2θ scan. 5717 reflections were collected in the range of $2 < 2\theta < 110°$, 4941 reflections with $I > 3\sigma(I)$ were used in the structure determination and refinement. Lorentz polarization and absorption corrections were applied. The structure was solved by direct methods and Fourier techniques, refined by full-matrix least-squares with anisotropic temperature parameters for all non-hydrogen atoms and isotropic thermal parameters for hydrogen atoms. Final $R = 0.066$, $R_w = 0.085$. Atomic coordinates, thermal parameters and full set of bond lengths and angles have been deposited with the Editor as Supplementary material.

RESULTS AND DISCUSSION

The composition of the complexes

The elemental analytic data for the newly synthesized complexes, listed in Table 1, indicate that all the complexes conform a 1 : 1 stoichiometry of metal ion to macrocyclic polyamine.

IR spectra

The most important IR peaks of the ligand and the complexes are reported in Table 2. In the IR spectra of the complexes the characteristic peaks of the ligand do not show distinct shifts comparing with those of

Table 1. Elemental analysis and molar conductance data

Compound	C% Found (Calc.)	N% Found (Calc.)	H% Found (Calc.)	RE% Found (Calc.)	Molar conductance (Ω^{-1} cm^2 mol^{-1})
$La(L)(NO_3)_3$	22.3	20.6	4.4	25.9	37.2
	(22.2)	(20.7)	(4.7)	(25.7)	
$Pr(L)(NO_3)_3$	22.0	20.7	4.5	25.6	38.7
	(22.2)	(20.7)	(4.7)	(26.0)	
$Nd(L)(NO_3)_3$	22.2	20.4	4.4	26.7	39.6
	(22.0)	(20.5)	(4.6)	(26.4)	
$Sm(L)(NO_3)_3$	21.5	20.5	4.9	27.4	38.4
	(21.8)	(20.3)	(4.6)	(27.3)	
$Eu(L)(NO_3)_3$	22.0	20.5	4.8	27.7	39.2
	(21.7)	(20.3)	(4.6)	(27.5)	
$Gd(L)(NO_3)_3$	21.7	19.9	4.7	28.1	40.4
	(21.5)	(20.1)	(4.5)	(28.2)	
$Tb(L)(NO_3)_3$	21.7	20.1	4.5	28.6	39.6
	(21.4)	(20.0)	(4.5)	(28.4)	
$Dy(L)(NO_3)_3$	21.5	20.0	4.4	29.0	39.0
	(21.3)	(19.9)	(4.5)	(28.8)	
$Er(L)(NO_3)_3$	21.1	19.6	4.3	29.5	40.1
	(21.1)	(19.7)	(4.4)	(29.4)	
$Tm(L)(NO_3)_3$	20.7	19.9	4.5	29.9	39.4
	(21.1)	(19.7)	(4.4)	(29.6)	
$Yb(L)(NO_3)_3$	21.3	19.6	4.5	30.2	38.7
	(20.9)	(19.5)	(4.4)	(30.1)	
$Y(L)(NO_3)_3$	24.8	23.0	5.3	18.5	40.8
	(24.5)	(22.9)	(5.1)	(18.1)	

Table 2. IR spectrum bands (cm^{-1})

Compound	$\nu_{N\text{-}H}$	$\delta_{N\text{-}H}$	δ_{CH_2}	$\nu(NO_3^-)$			
				ν_1	ν_2	ν_5	$\Delta\nu(\nu_1-\nu_5)$
L	3328m	726m	1452s				
$La(L)(NO_3)_3$	3326m	731m	1454s	1482s	1035m	1297s	185
$Pr(L)(NO_3)_3$	3331m	734m	1452s	1484s	1037m	1306s	178
$Nd(L)(NO_3)_3$	3334m	737m	1449s	1490s	1036m	1316s	174
$Sm(L)(NO_3)_3$	3335m	736m	1436s	1498s	1040m	1322s	176
$Eu(L)(NO_3)_3$	3334m	741m	1453s	1492s	1030m	1314s	178
$Gd(L)(NO_3)_3$	3307m	732m	1450s	1502s	1028m	1328s	174
$Tb(L)(NO_3)_3$	3304m	739m	1459s	1516s	1029m	1329s	187
$Dy(L)(NO_3)_3$	3306m	741m	1457s	1499s	1031m	1315s	184
$Er(L)(NO_3)_3$	3310m	742m	1454s	1489s	1036m	1306s	183
$Tm(L)(NO_3)_3$	3309m	744m	1453s	1499s	1030m	1304s	195
$Yb(L)(NO_3)_3$	3310m	744m	1451s	1501s	1031m	1305s	196
$Y(L)(NO_3)_3$	3335m	742m	1452s	1490s	1033m	1315s	175

Table 3. Selected bond lengths (Å) and angles (°)

La(1)—O(1)	2.734(4)	La(2)—O(10)	2.714(4)
La(1)—O(2)	2.699(4)	La(2)—O(11)	2.668(4)
La(1)—O(4)	2.661(4)	La(2)—O(13)	2.673(3)
La(1)—O(5)	2.704(4)	La(2)—O(14)	2.665(4)
La(1)—O(7)	2.672(4)	La(2)—O(16)	2.667(4)
La(1)—O(8)	2.687(4)	La(2)—O(17)	2.772(4)
La(1)—N(1)	2.793(4)	La(2)—N(9)	2.743(4)
La(1)—N(2)	2.744(4)	La(2)—N(10)	2.725(5)
La(1)—N(3)	2.727(4)	La(2)—N(11)	2.773(4)
La(1)—N(4)	2.773(5)	La(2)—N(12)	2.739(6)
La(1)—N(5)	2.739(4)	La(2)—N(13)	2.761(4)
O(1)—La(1)—O(2)	46.7(1)	O(10)—La(2)—O(11)	47.1(1)
O(1)—La(1)—O(4)	100.9(1)	O(10)—La(2)—O(13)	113.0(1)
O(1)—La(1)—O(5)	62.9(1)	O(10)—La(2)—O(14)	72.8(1)
O(1)—La(1)—O(7)	69.4(1)	O(10)—La(2)—O(16)	101.8(1)
O(1)—La(1)—O(8)	109.3(1)	O(10)—La(2)—O(17)	65.2(1)
O(1)—La(1)—N(1)	64.5(1)	O(10)—La(2)—N(9)	109.6(1)
O(1)—La(1)—N(2)	122.7(1)	O(10)—La(2)—N(10)	77.4(2)
O(1)—La(1)—N(3)	171.5(1)	O(10)—La(2)—N(11)	69.5(1)
O(1)—La(1)—N(4)	115.5(1)	O(10)—La(2)—N(12)	131.4(2)
O(1)—La(1)—N(5)	84.8(1)	O(10)—La(2)—N(13)	166.0(1)
N(1)—La(1)—O(2)	98.3(1)	N(9)—La(2)—O(11)	66.2(1)
N(1)—La(1)—O(4)	165.0(1)	N(9)—La(2)—O(13)	126.4(1)
N(1)—La(1)—O(5)	118.8(1)	N(9)—La(2)—O(14)	171.9(1)
N(1)—La(1)—O(7)	67.3(1)	N(9)—La(2)—O(16)	67.9(1)
N(1)—La(1)—O(8)	107.7(1)	N(9)—La(2)—O(17)	107.5(1)
N(1)—La(1)—N(2)	62.0(1)	N(9)—La(2)—N(10)	62.8(2)
N(1)—La(1)—N(3)	123.6(1)	N(9)—La(2)—N(11)	123.7(1)
N(1)—La(1)—N(4)	123.8(1)	N(9)—La(2)—N(12)	101.4(3)
N(1)—La(1)—N(5)	62.0(1)	N(9)—La(2)—N(13)	63.7(1)

the free ligand, and the coordination way of the ligand in the complexes cannot be inferred from the IR spectra. The characteristic frequencies of coordinating nitrate groups appear in the IR spectra of the complexes. The difference between the two strongest absorptions (ν_1 and ν_5) of nitrate groups lies in the range of 174–196 cm^{-1}, indicating that the nitrate groups in the complexes coordinate to the metal ions as bidentate ligands [11]. The absence of the absorptions around 1360 cm^{-1} indicates that all of the nitrate groups in the complexes coordinate to the metal ions [11]. This result is consistent with those of the molar conductance values (Table 1) and crystal structure determination.

Solubility and molar conductance

All the complexes are soluble in methanol, pyridine, DMF and DMSO, slightly soluble in ethanol, acetone and tetrahydrofuran, sparingly soluble in chloroform, ethyl acetate, ether and benzene. The molar conductance values measured in DMF at 20°C lie in the range of 37.2–40.8 Ω^{-1} cm^2 mol^{-1} (Table 1), indicating that all the complexes are non-electrolytes [12]. This shows that all the nitrate groups in the complexes are coordinated to the metal ions.

Crystal and molecular structure of lanthanum complex

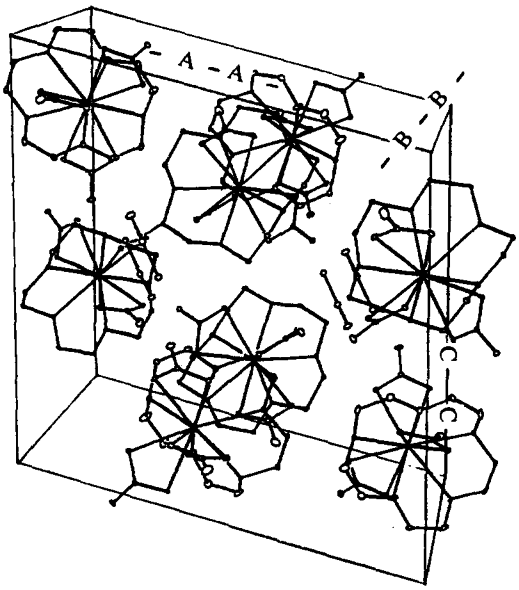

Fig. 2. Molecular packing in the unit cell.

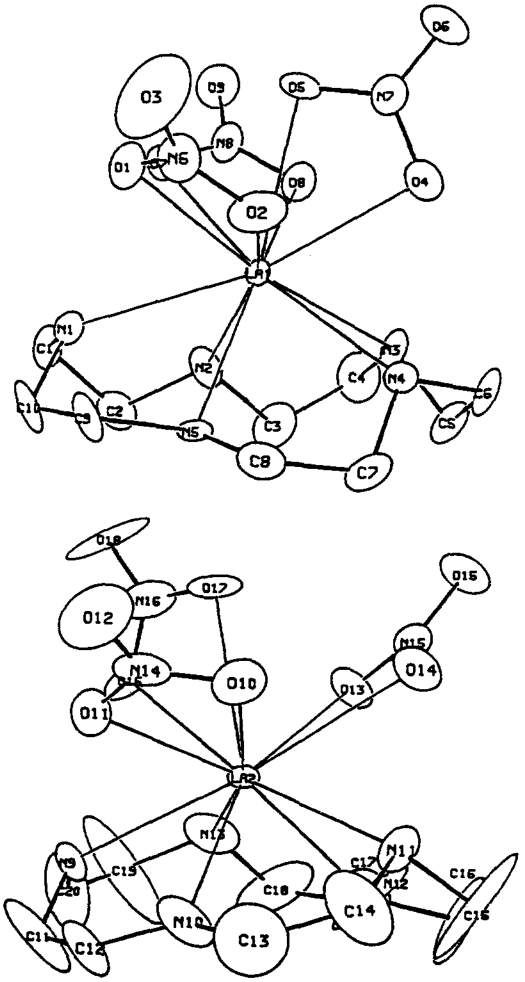

Fig. 1. Molecular structure of the lanthanum complex.

Selected bond lengths and bond angles are given in Table 3. Figure 1 shows the molecular structure of the lanthanum complex. Fig. 2 illustrates the molecular packing arrangement in the unit cell.

The unit cell consists of the complex molecules and separate uncoordinated acetonitrile molecules. There are two independent complex molecules in the asymmetric unit. Both molecules adopt the same conformation. In each of them a polyazamacrocyclic ligand with five nitrogen atoms coordinates to the metal ion on one side and three bidentate nitrate groups coordinate on the opposite side. The La—N(L) distances have values between 2.725 and 2.793 Å (mean 2.752 Å) and the La—O (nitrate) distances have values between 2.661 and 2.772 Å (mean 2.693 Å). A noteworthy feature of the molecular structure is the eleven-coordinate polyhedron around the metal ion. Undecacoordination is not common in inorganic chemistry [13,14].

In conclusion, the polyazamacrocylic ligand 1,4,7,10,13-pentaazacyclopentadecane, can react with lanthanide nitrates in non-aqueous medium to form 1 : 1 (metal-to-ligand) solid complexes. In these complexes the organic ligand and nitrate groups act as pentadentate and bidentates, respectively.

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