The Synthesis of Macrocyclic Lanthanide Complexes Derived from 2,5-Furandialdehyde and α,ω-alkanediamines

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The synthesis of macrocyclic lanthanide complexes via the reaction of 2,5-furandialdehyde with 1,2-diaminoethane, 1,2-diaminopropane and 1,3-diaminopropane in the presence of lanthanide nitrates as templating agents is described. The potential application of the complexes in transmetallation reactions is discussed.

Introduction

Condensation reactions between dicarbonyl compounds and primary diamines have played an important role in the development of synthetic macrocyclic ligands. It has been found that many syntheses of macrocyclic Schiff base ligands require the presence of a suitable metal ion as a 'template' [1]. In recent years some macrocyclic complexes of lanthanides have been reported. The ligands involved have been polyazamacrocycles derived from 2,6-diacetylpyridine and 1,2-diaminoethane, 1,2-diaminobenzene and hydrazine [2–5].

For the 14-membered macrocycle the lighter lanthanides were found to be ineffective as templates and complexes of Tb^{+++} to Lu^{+++} were obtained [2]; for the 18-membered macrocyles the converse was found and complexes of La^{+++} and Ce^{+++} were obtained with the heavier lanthanides ineffective as templating agents [3–5].

Although 2,6-dicarbonylpyridines have been extensively exploited in macrocyclic Schiff base synthesis [6] less attention has been paid to 2,5-furandicarbaldehyde. Complexes have been reported in which alkaline earth metals (Ca^{++}, Sr^{++}, Ba^{++}) [7], lead(II) [8], and copper(II) [9] (formed by transmetallation reaction with a barium species) are present, but no report has been made of a lanthanide complex.

We report here the syntheses of macrocyclic lanthanide complexes derived from 2,5-furandicarbaldehyde and α,ω-primary diamines. The lighter lanthanides (La^{+++} to Sm^{+++}) were found to be effective as template ions depending on the diamine used. The complexes were kinetically labile and the complexed template ion could be exchanged with copper(II) to afford binuclear Cu(II) complexes in the same way that the corresponding alkaline earth metal complexes do [9].

Experimental

2,5-Furandicarbaldehyde was prepared by the oxidation of 2,5-furandimethanol with MnO_2 using the method of Oleinik and Novitskii [10]. The diamines were used as purchased.

(i) 2 mmol of 2,5-furandicarbaldehyde, 2 mmol of 1,2-diaminoethane and 1 mmol of $Ln(NO_3)_3$, nH_2O, (Ln = La–Sm, except Pm), were mixed in methanol (30 ml). Powdery compounds were formed within five minutes of heating and stirring; these were filtered, washed with cold methanol and dried *in vacuo*.

(ii) 2 mmol of 2,5-furandicarbaldehyde, 2 mmol of either 1,2-diaminopropane, or 1,3-diaminopropane, and 1 mmol of $Ln(NO_3)_3$, nH_2O, (Ln = La–Pr), were mixed in absolute alcohol (30 ml), stirred and heated for 10 minutes. A fine powdery precipitate was obtained which was filtered off, washed with cold absolute alcohol and dried *in vacuo*.

(iii) 1 mmol of $Cu(ClO_4)_2$, $6H_2O$ in 20 ml of absolute alcohol and 0.05 mmol of $La(L_2)(NO_3)_3$ in 30 ml of absolute alcohol were mixed and stirred at reflux for 20 minutes. A green precipitate was formed which was filtered off, washed with cold absolute alcohol and dried *in vacuo*.

Microanalyses were carried out by the University of Sheffield Microanalytical Service and are given in Table I. Infra-red spectra were recorded in the 4000–600 cm^{-1}, region using a Perkin Elmer 297 IR instrument using KBr discs. Mass spectra were recorded using a Kratos MS25 spectrometer, and ^1H NMR spectra were recorded at 220 MHz using a Perkin Elmer R34 spectrometer.

Results and Discussion

The formation of macrocyclic Schiff base complexes in the template reactions of 2,5-furandicarbal-

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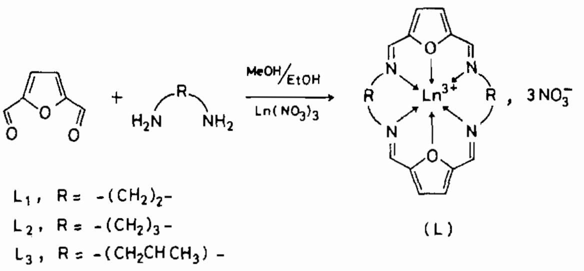
TABLE I. Microanalytical Data.

Complex	Required			Found		
	%C	%H	%N	%C	%H	%N
$La(L_1)(NO_3)_3$	30.93	2.60	15.78	31.65	2.94	16.16
$Ce(L_1)(NO_3)_3$	30.87	2.59	15.75	30.24	2.72	14.96
$Pr(L_1)(NO_3)_3$	30.83	2.59	15.73	30.94	2.82	15.77
$Nd(L_1)(NO_3)_3$	30.65	2.57	15.65	30.18	2.73	15.87
$Sm(L_1)(NO_3)_3$, H_2O	29.53	2.78	15.06	29.44	2.56	13.99
$Eu(L_1)(NO_3)_3$, $2H_2O$	28.66	3.00	14.62	28.47	2.67	13.88
$La(L_2)(NO_3)_3$	33.29	3.10	15.10	33.85	3.12	15.76
$Ce(L_2)(NO_3)_3$, H_2O	32.33	3.31	14.67	32.62	3.41	14.73
$Pr(L_2)(NO_3)_3$, H_2O	32.29	3.31	14.65	32.44	3.14	15.54
$La(L_3)(NO_3)_3$	33.29	3.10	15.10	34.04	3.24	15.42
$Ce(L_3)(NO_3)_3$, H_2O	32.33	3.31	14.67	32.74	3.50	14.94
$Pr(L_3(NO_3)_3$, H_2O	32.29	3.31	14.65	32.51	3.52	14.85

dehyde and α,ω-primary diamines in the presence of the lighter lanthanide cations (Scheme 1) can be seen from the IR spectra recorded (Table II). The absence of any carbonyl or primary amine bands and the appearance of an imine band indicates that cyclisation has occurred. That this is a [2 + 2] condensation is confirmed by the presence of a peak of highest abundance corresponding to the macrocycle, with no peaks at higher mass number, in the mass spectra (Table III). The ^1H NMR, where available, shows no peaks due to free carbaldehyde and are also consistent with a cyclic species [11]. In the absence of metal ions only viscous oils were recovered which, from their nature, are probably polymeric. The role of the lanthanides in promoting the macrocyclic synthesis is clearly indicated.



Scheme 1.

The template reactions of 2,5-furandicarbaldehyde with 1,2-diaminoethane in the presence of the heavier lanthanide nitrates (Gd–Lu), however, gave compounds the analyses of which suggest a three metal cation to two macrocyclic unit ratio (see Table III). The IR spectra are similar to those recorded for the complexes of the lighter lanthanides and showed no free carbonyl or amine bands. The presence of macrocyclic ligands was further evidenced by the presence of the molecular ion ($P^+ = 296$) in the mass spectra (Table III). It was not possible to grow crystals of these complexes.

TABLE II. Major Infrared Bands for $Ln(L)(NO_3)_3$ Complexes (cm^{-1}; KBr disc).

Complex	C=N	NO_3	Other bands
$La(L_1(NO_3)_3$	1614s	1382sh, 1018s, 818m	1445, 1320, 1248, 1040
$Ce(L_1)(NO_3)_3$	1616s	1385sh, 1020s, 819m	1450, 1330, 1245
$Pr(L_1)(NO_3)_3$	1610s	1380sh, 1019s, 815m	1441, 1332, 1240
$Nd(L_1)(NO_3)_3$	1615s	1382sh, 1020s, 818m	1448, 1308, 1246
$Sm(L_1)(NO_3)_3$, H_2O	1620s	1385m, 1030s, 819m	3300br, 1450, 1310, 1252
$Eu(L_1)(NO_3)_3$, $2H_2O$	1619s	1381sh, 1025s, 818m	1450, 1308, 1250
$La(L_2)(NO_3)_3$	1625s	1386m, 1035s, 838m	1450, 1310, 1065, 980
$Ce(L_2(NO_3)_3$, H_2O	1628s	1390m, 1038s, 840m	3450br, 1447, 1312, 1060, 980
$Pr(L_2)(NO_3)_3$, H_2O	1638s	1395m, 1040s, 841m	3400br, 1450, 1311, 1062, 978
$La(L_3)(NO_3)_3$	1618s	1386m, 1030s, 818m	1453, 1315, 1245
$Ce(L_2)(NO_3)_3$, H_2O	1619s	1388m, 1035s, 826m	3350br, 1486, 1305, 1244
$Pr(L_2)(NO_3)_3$, H_2O	1630s	1394m, 1025s, 820m	3400br, 1490, 1310

TABLE III. Mass Spectral Data.

Complex	m/e (amu)	Assignement
(1) $Ln(L_1)(NO_3)_3, xH_2O$	296 148	m/c^+ m/c^{2+}
(2) $Ln(L_2)(NO_3)_3, yH_2O$	324 162	m/c^+ m/c^{2+}
(3) $Ln(L_3)(NO_3)_3, yH_2O$	324 162	m/c^+ m/c^{2+}
(4) $Gd_3(L_1)_2(NO_3)_9, 4H_2O$	296 148	m/c^+ m/c^{2+}
(5) $Er_3(L_1)_2(NO_3)_9, 4H_2O$	296 148	m/c^+ m/c^{2+}

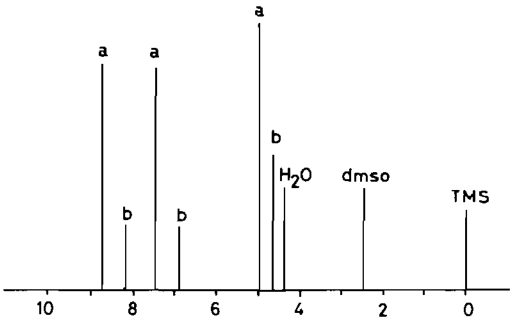
(1); where Ln = La–Eu, except Pm, x = 0 for La–Nd and x = 1 for Sm, Eu. (2) and (3); where Ln = La–Pr, x = 0 for La and x = 1 for Ce, Pr. (4) and (5). The microanalytical data for these compounds is as follows: $Gd_3(L_1)_2(NO_3)_9$, $4H_2O$: required, C = 22.68, H = 2.36, N = 14.05%; found, C = 22.80, H = 2.29, N = 13.10%; $Er_3(L_1)_2(NO_3)_9$, $4H_2O$: required, C = 22.28, H = 2.32, N = 13.81; found, C = 22.60, H = 2.35, N = 12.91%.

The observation of complexes of different stoicheiometry for the heavier lanthanides may be due to the decreased ion size (the lanthanide contraction) as the 'hole' of the 18-membered macrocycle may be too large for these cations and a sandwich structure in which groups of donors are shared could be preferred. In the template reactions using the diaminopropanes with the heavier lanthanides (Nd–Lu, except Pm) intractable materials were obtained.

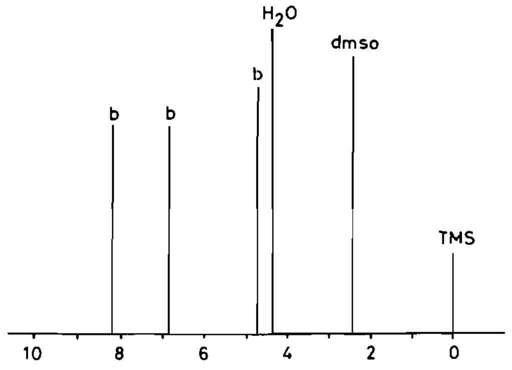
It is difficult to assign the nature of the nitrate bonding present. Three bands were identified in the regions 1350–1390, 1020–1100 and 805–830 cm^{-1}; generally, however, nitrato groups in lanthanide complexes have been found to prefer to act as bidentate ligands [12].

Dissolution of the lanthanide complexes in water leads to decomposition. This behaviour has been found for many lanthanide complexes of macrocyclic polyethers [13, 14]. It can be contrasted with the stability, in D_2O, of the lanthanum complex derived from 2,6-diacetylpyridine and 1,2-diaminoethane [3]. This could arise from a divergence from the 'best-fit' situation as the 'bite' in the terminal furan–diimine moiety would be larger than that in the corresponding pyridine–diimine moiety so giving a cavity of slightly larger diameter and a diminished ligand–metal interaction.

^1H NMR, in d_6-dmso, of $La(L_1)(NO_3)_3$ gave two sets of signals when run immediately. These correspond to the complex (δ ppm = 8.58, *s*, 1H, -C*H*N; 7.37, *s*, 1H, furan-*H*; 4.00, *s*, 2H, CH_2CH_2) and to the free macrocyle (δ ppm = 8.12, *s*, 1H, -C*H*N; 6.96, *s*, 1H, furan-*H*; 3.86, *s*, 2H, CH_2CH_2). If the spectrum is run again after *ca.* one hour only the signal corresponding to the free macrocycle remain (Fig. 1). This shows that the lanthanide ion can be displaced from the macrocycle, and has been observed in several of the complexes [11]. Attempts to isolate the free macrocycle have not yet been successful, suggesting that it breaks down during the isolation process probably *via* hydrolysis of the strained imine bonds.



(1) immediately in fresh dmso



(2) after more than one hour

Fig. 1. ^1H n.m.r. spectra for $La(L_1)(NO_3)_3$; a, signals corresponding to the macrocyclic lanthanide complexes; b, signals corresponding to the free macrocyclic ligand.

The lability of the lanthanide ion has been exploited in the transmetallation reaction of $La(L_2)(NO_3)_3$ with $Cu(ClO_4)_2$, $6H_2O$ which afforded the binuclear copper(II) complex, $[Cu_2(L_2)(ClO_4)_2(OH)_2]\cdot 3H_2O$. This differs only in the number of water molecules present from the complex prepared *via* transmetallation of $Ba(L_2)(ClO_4)_2$, EtOH [9]. Work is in progress to determine the generality of the transmetallation reaction commencing with lanthanide complexes.

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