AZAOXA MACROCYCLIC AND ACYCLIC COMPLEXES OF LANTHANIDES

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The template reactions of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine in the presence of dysprosium(III), thulium(III) and lutetium(III) chlorides and erbium(III) perchlorate produce the complexes of 15-membered macrocyclic ligand with an N_3O_2 set of donor atoms as a result of the [1+1] Schiff base cyclocondensation. In contrast, analogous reactions involving the lighter lanthanide ions (lanthanum(III), samarium(III) and europium(III)) yield the acyclic complexes with terminal acetylpyridyl groupings as products of the partial [2+1] condensation. The complexes were characterized by spectral data (IR, UV-VIS, ^{1}H NMR, MS), and thermogravimetric and elemental analyses.
Key words: Complexes of Schiff bases; Template synthesis; Lanthanide complexes; Infrared spectra; Macrocyclic Complexes; Chelates.

The design and synthesis of macrocyclic and acyclic lanthanide complexes is currently attracting considerable attention since they can be used as supramolecular devices[1], contrast agents in magnetic resonance imaging[2], potential radiopharmaceuticals[3], possible bioinorganic models for the active sites in metallobiomolecules[4,5], and as synthetic nucleases for *in vivo* application[6]. Macrocyclic Schiff bases have been widely studied because they can selectively chelate particular metal ions according to the number, type and position of their donor atoms, the ionic radius of the metal center, coordinating properties of counterions, *etc*.[7].

Many synthetic routes to macrocyclic ligands involve the use of the metal ion template to orient the reacting groups of the ligand into the desired conformation for optimum ring closure. The favorable enthalpy for the formation of the metal–ligand bonds may overcome the unfavorable entropy from the ordering the multidentate ligand around the metal ion and thereby promote the cyclization reaction[8–10].

In searching for new stable complexes of the rare earth elements in view of their potential applications and continuing our studies on the effectiveness of metal ions of

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varying radii and electron configurations in the synthesis of macrocyclic and acyclic compounds, we have previously reported the first example of the template action of yttrium(III) ion in the synthesis of pentadentate Schiff base macrocyclic ligand[11]. The close similarity of this ion to the heavier lanthanides in both size and chemical behaviour has prompted us to extend our investigation to the lanthanide-promoted synthesis of azaoxa macrocyclic systems. The preparation and characterization of new macrocyclic and acyclic Schiff base complexes formed in the template reaction of lanthanides with 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine is the subject of this paper.

EXPERIMENTAL

The hydrated lanthanide(III) chlorides and perchlorates were prepared by dissolving the appropriate oxide (99.99%, Fluka) in a slight excess of appropriate acid. The solutions were evaporated and the precipitates recrystallized from methanol. 2,6-Diacetylpyridine (Aldrich) and 3,6-dioxaoctane-1,8-diamine (Fluka) were used without further purification.

Preparation of the Complexes. General Procedure

All syntheses of the complexes were performed under similar conditions. To a mixture of appropriate metal salt (0.1 mmol) and 2,6-diacetylpyridine (0.1 mmol) in methanol (20 cm^3), 3,6-dioxaoctane-1,8-diamine (0.1 mmol) in methanol (10 cm^3) was added dropwise with stirring. The reaction was carried out for 3 h. The solution volume was then reduced to 10 cm^3 by roto-evaporation and an orange precipitate, formed on addition of a small amount of diethyl ether, was filtered off, washed with ether, and dried *in vacuo*. The yields were 77–82%. The results of elemental analysis of the complexes are listed in Table I.

Measurements

IR spectra were recorded in the range 4 000–200 cm^{-1} on a Perkin–Elmer 580 spectrophotometer using CsI pellets. Electronic spectra were measured in the range 200–500 nm on a Shimadzu UV-160 spectrophotometer. ^{1}H NMR spectra were run in deuterated DMSO on a Varian Gemini 300 spectrometer using TMS as an internal reference. Low resolution mass spectra were recorded on a Jeol-JMS D100 mass spectrometer operating on electron impact (EI, 70 eV, 300 A, ion source temperature 200 °C) conditions. Thermogravimetric measurements were performed using Shimadzu TGA-50 derivatograph (up to 250 °C, heating rate 10 °C min^{-1}, on air).

RESULTS AND DISCUSSION

The template reactions of 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine in the presence of dysprosium(III), thulium(III) and lutetium(III) chlorides and erbium(III) perchlorate produce the 15-membered macrocyclic complexes with an N$_3$O$_2$ set of donor atoms as a result of [1+1] Schiff base cyclocondensation. The formulations of these complexes as LnL^1(H$_2$O)$_{2+n}$X$_3$, where L^1 is Me$_2$pyo[15]triene–N$_3$O$_2$, Ln(III) = Dy, Er, Tm, Lu, X = Cl$^-$ or ClO$_4^-$, n = 1, 3, 4 follow from spectral data (IR, UV-VIS, ^{1}H NMR, MS) and thermogravimetric and elemental analyses. The complexes are orange air stable solids, moderately soluble in CH$_3$CN and DMSO.

Attempts to obtain these macrocyclic compounds in the presence of lanthanide(III) nitrates were unsuccessful. The nitrate anions, contrary to chlorides and perchlorates, are very good complexing agents for lanthanides. The involvement of nitrate groups in the coordination with these elements may result in increasing the ionic radii to the values, for which the metal ions do not perfectly fit to the cavity of the macrocycles. Therefore, the chloride and perchlorate salts were employed to reduce the effect of donor anions on the primary coordination sphere around the metal ion.

L^1
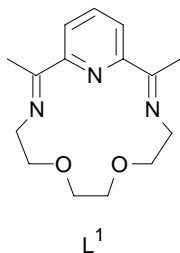
The infrared spectra of these complexes are very similar (Table II) and confirm the formation of the macrocyclic compounds by the absence of bands characteristic of carbonyl and amine groups of the starting materials. An important feature is the occurrence of a strong band at 1 640–1 620 cm^{-1} attributable to C=N stretching modes indicating the Schiff base condensation. The spectra exhibit medium to strong bands at 1 595–1 590 cm^{-1} as expected for the high-energy ring vibrations of the coordinated pyridine. The bonding of the pyridine nitrogen atom is also shown by the presence of the bands at 1 020–995 cm^{-1} and 670–665 cm^{-1} attributable, respectively, to the ring-breathing frequency and the low-energy pyridine ring vibrations[12]. The C–O–C stretching mode occurs at 1 120–1 080 cm^{-1} indicating ether oxygen coordination[13]. Information about the bonding mode of the counterions in these complexes may also be obtained from IR spectra. The spectra do not exhibit absorptions characteristic of coordinated anions[14]. The Ln–Cl frequency usually occurs around 240–220 cm^{-1}. The spectra of the dysprosium(III), thulium(III) and lutetium(III) chloride L^1 complexes do not show any absorption bands in this region indicating the absence of the coordinated chloride anions. The presence of uncoordinated perchlorates is inferred from the broad band centered at 1 085 cm^{-1} and the sharp medium band at 620 cm^{-1} observed in the spectrum of the erbium(III) perchlorate L^1 complex. The complexes show the broad diffuse band centered at *ca* 3 420 cm^{-1} due to the stretching and bending modes of water. In addition, weak bands are detectable around 820 cm^{-1} which may be assigned to rocking or wagging modes of water molecules coordinated to the metal ion[15]. The presence of water bound in two different ways is supported by the results of thermogravimetric analysis. All the complexes lose two water molecules at 140–170 °C. Moreover, below 100 °C, the L^1 complexes of erbium(III) and lutetium(III) ions show the loss of one water mole-

cule, whereas the L^1 complexes of dysprosium(III) and thulium(III) lose three and four water molecules, respectively.

The electronic spectra of the acetonitrile solutions of the complexes taken in the range 200–500 nm contain strong and medium bands with maxima at 214–215 nm and 273–274 nm attributable to the $\pi \rightarrow \pi^*$transition of the coordinated macrocycle[16].

The ^{1}H NMR spectrum of deuterated DMSO solution of the diamagnetic L^1 lutetium complex strongly suggests the presence of the macrocyclic ligand. Two well-resolved triplets of the methylene protons in the $=NCH_2CH_2O$ chain are observed in the 1 : 1 ratio; the protons adjacent to the nitrogen give rise to a triplet at δ 3.64 (4-H) and the other protons to a triplet at δ 2.96 (4-H) (J = 5.4 Hz). A sharp singlet at δ 3.58 (4-H) assigned to the methylene protons in the $-OCH_2CH_2O$ bridge is in accordance with the planarity of donor atom arrangement in the coordination sphere of the ion. The pyridine protons and methyl protons appear as a multiplet at δ 7.8–8.3 (3-H) and as singlet at δ 2.50 (6-H), respectively. The integrated relative intensities of the above signals are in good agreement with the required ratios consistent with the proposed formulation of the com-
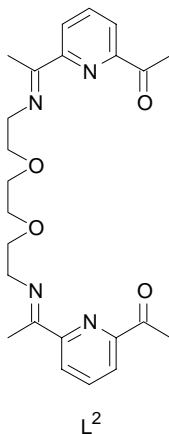
TABLE I
Analytical data for the L^1 and L^2 complexes

Compound	Calculated/Found		
	%C	%H	%N
$DyL^1(H_2O)_5Cl_3$	28.40	4.89	6.63
	30.82	5.23	6.73
$ErL^1(H_2O)_3(ClO_4)_3$	22.66	3.40	5.29
	25.10	3.46	5.03
$TmL^1(H_2O)_6Cl_3$	27.35	5.02	6.38
	30.17	4.99	6.17
$LuL^1(H_2O)_3Cl_3$	29.50	4.46	6.88
	29.54	4.46	6.90
$LaL^2(H_2O)_6(ClO_4)_3$	29.30	4.27	5.69
	28.98	4.30	5.33
$SmL^2(H_2O)_6(ClO_4)_3$	28.96	4.22	5.63
	29.63	4.28	5.39
$EuL^2(H_2O)_6Cl_3$	35.81	5.22	6.96
	36.81	5.04	6.62

plex. The DMSO with strong donor properties is known to compete for the coordination sphere of the metal ions. The competition between the solvent and the ligand for the lanthanide ion could result in removal of the metal ion from the macrocycle, followed by ligand breakdown. The stability of the complexes in DMSO solution is demonstrated by the absence of any additional signals. Hence, it is evident that no metal–solvent interaction occurs.

Further evidence for the formation of the macrocycle comes from the mass spectra of the chlorides of lanthanide L^1 complexes. The fragment observed at m/z 275 corresponds to the molecular weight of the free macrocycle. The occurrence of a strong peak corresponding to the free macrocycle instead of the parent ion peak of the macrocyclic complex is quite common for the other related macrocycles[8]. The spectrum of the perchlorate complex was not masured.

Under the same reaction conditions the lighter lanthanides were found to be ineffective as templates in the synthesis of this 15-membered macrocycle. In the reactions, in which 2,6-diacetylpyridine is reacted with 3,6-dioxaoctane-1,8-diamine in the presence of lanthanum(III) or samarium(III) perchlorates and europium(III) chloride, the ring closure does not occur. Instead, the complexes with ligand L^2 as acyclic product of partial Schiff base condensation of two molecules of diketone with one molecule of diamine are formed.

L^2

The complexes are orange air stable solids, moderately soluble in CH_3CN and DMSO. They are formulated as $LaL^2(H_2O)_6(ClO_4)_3$, $SmL^2(H_2O)_6(ClO_4)_3$ and $EuL^2(H_2O)_6Cl_3$ on the basis of spectral and thermogravimetric analyses, as discussed below, and elemental analysis (Table I).

The IR spectra of these three complexes are all very similar except for the vibrational modes of anions (Table II). The most diagnostic is the C=N stretching band at 1 625–1 620 cm^{-1} which indicates the Schiff base condensation. The appearance of the band at 1 690–1 685 cm^{-1},

assigned to the C=O stretching vibration, confirms the formation of the acyclic product containing terminal acetylpyridyl groups. The shift of this band from $1\,705$ cm^{-1} in uncomplexed 2,6-diacetylpyridine is an evidence of the decrease in C=O double bond character owing to the coordination of the metal ion. The pyridine ring vibrations observed at $1\,590$, $1\,105$–990 and 660 cm^{-1} suggest the coordination of the pyridine nitrogen. The spectra exhibit the bands at $1\,115$–$1\,110$ cm^{-1} attributable to the C–O–C stretching mode. In the infrared spectra of perchlorate complexes there are single bands at 625 cm^{-1} which, along with strong bands at about $1\,145$ cm^{-1} and weak absorption at 940–930 cm^{-1}, indicate the presence of non-coordinated perchlorate anions. The infrared spectrum of the chloride complex does not exhibit the absorption characteristic of coordinated chloride ion. The broad diffuse band at $3\,520$–$3\,400$ cm^{-1} and a weak absorption at 825–810 cm^{-1} suggest the presence of lattice and coordinated water. This is supported by the results of thermogravimetric analysis, which indicate a loss of two molecules of water at 40–60 °C and four water molecules at 140–180 °C for the lanthanum(III) and samarium(III) complexes and four water molecules at 40–60 °C and two water molecules at 140–180 °C for the europium(III) complex.

The electronic spectra of the acetonitrile solutions of these complexes recorded in the range 200–500 nm show similar features, containing strong and medium bands with maxima at 216–230 and 274–280 nm which may be assigned to the transition of the $\pi \rightarrow \pi^*$ type of the coordinated ligand.

TABLE II
Infrared spectral data (cm^{-1}) for the L^1 and L^2 complexes

Compound	OH	C=O	C=N	Pyridine	C–O–C	Anions
$DyL^1(H_2O)_5Cl_3$	3 420 br, 820 w		1 625 s	1 590 s, 995 m, 665 w	1 100 m	
$ErL^1(H_2O)_3(ClO_4)_3$	3 420 br, 820 w		1 620 s	1 595 s, 1 020 m, 665 w	1 110 m	1 085 sbr, 620 m
$TmL^1(H_2O)_6Cl_3$	3 420 br, 815 w		1 620 s	1 595 s, 1 015 m, 995 m, 665 w	1 080 m	
$LuL^1(H_2O)_3Cl_3$	3 420 br, 820 w		1 640 s	1 590 m, 995 m, 670 w	1 120 m	
$LaL^2(H_2O)_6(ClO_4)_3$	3 420 br, 820 w	1 685 s	1 625 m	1 590 m, 1 005 m, 660 w	1 115 m	1 145 sbr, 940 w, 625 m
$SmL^2(H_2O)_6(ClO_4)_3$	3 400 br, 825 w	1 690 s	1 620 m	1 590 m, 990 m, 660 w	1 110 m	1 140 sbr, 930 w, 625 m
$EuL^2(H_2O)_6Cl_3$	3 520 br, 810 w	1 690 s	1 625 m	1 590 m, 995 m, 660 w	1 115 m	

The ^{1}H NMR spectrum of deuterated DMSO solution of the diamagnetic L^2 lanthanum(III) complex shows the presence of pyridine protons at δ 7.8–8.1 (6-H). The methylene protons adjacent to the nitrogen in the =NCH$_2$CH$_2$O chain are observed at δ 3.69 (4-H) and the other protons at δ 2.92 (4-H). The methylene protons in the –OCH$_2$CH$_2$O bridge appear at δ 3.97 (4-H). The resonances of methyl protons of the two CH$_3$CO and two CH$_3$C=N groups occur at δ 3.56 (6-H) and δ 2.50 (6-H), respectively. The integrated relative intensities of the above signals are in good agreement with the required ratios, consistent with the proposed formulation of the complex.

On the basis of available data it can be concluded that the heavier lanthanide ions, contrary to lighter lanthanides, are effective templating agents for the synthesis of a 15-membered N$_3$O$_2$ macrocyclic compound. All five potential donor atoms of this ligand may be regarded as coordinated to the metal ion. Thus, the seven-coordination is tentatively assigned for L^1 complexes of dysprosium(III), erbium(III), thulium(III) and lutetium(III) cations with non-coordinating chloride and perchlorate counterions assuming the filling of the coordination sphere by an equatorial N$_3$O$_2$ set of macrocyclic donor atoms and two water molecules in axial positions. The triaza unit of the L^1 macrocycle is rigid and it seems unlikely that the remaining donor atoms could be other than coplanar with these three nitrogens[17]. References to the known structures of similar macrocyclic complexes[16,18–20] allow us to predict the pentagonal bipyramidal geometry for these macrocyclic complexes. Since there is no ligand field stabilization energy effect in the lanthanide(III) ions (d^0 configuration), their coordination environment is determined mainly by the chelating power of the ligand (preferred conformation of ligand, nature and disposition of donor atoms). Thus these ions can be accommodated by the particular stereochemical constraints enforced by the template process. Efforts to prepare free macrocycle in the reaction of the 2,6-diacetylpyridine with 3,6-dioxaoctane-1,8-diamine in the absence of metal ion were unsuccessful and resulted in the formation of insoluble yellow compounds of polymeric character terminated with carbonyl functions. The failure of this system to undergo complete condensation and cyclization confirms the importance of metal ion in directing the steric course of the condensation process, which ultimately ends with ring closure. This finding appears to be in accordance with the general observation that for the majority of macrocyclic compounds the metal-templated synthesis remains the best method of preparation. However, the results discussed in this paper along with our earlier investigations[21,22] lead to the conclusion that the chelation of lanthanide ions by the macrocyclic compounds strongly depends on the ratio of the diameter of the metal ion used as a template to the ligand cavity size. They confirm the importance of the idea of size-match selectivity in the design and synthesis of Schiff-base macrocyclic systems. The differences in the templating behaviour observed among the lanthanides may provide the basis for a novel means of separating these closely related materials.

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