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Rare earth macrocyclic complexes derived from spermine

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Abstract

The yttrium and lanthanide perchlorates were found to act as templates for the cyclic [1+1] condensation of 2,6-diacetylpyridine with spermine (4,9-diazadodecane-1,12-diamine) to yield 19-membered pentadentate Schiff base macrocyclic complexes with an N_5 set of donor atoms. The complexes were characterized by spectral data (IR, ^{1}H NMR, FAB-MS), thermogravimetric and elemental analysis.

Keywords: Yttrium; Lanthanides; Macrocyclic Schiff base complexes; Template synthesis

1. Introduction

The macrocyclic yttrium and lanthanide complexes are currently attracting considerable attention because of their possible use as supramolecular devices [1,2], suitable bioinorganic probes for the active sites in metallobiomolecules [3,4], as synthetic nucleases for in vivo application [5,6], as contrast agents in magnetic resonance imaging [7], potential radioimmunopharmaceuticals for monoclonal antibody technology and sensitizers for photodynamic therapy [8,9]. Unlike the lanthanide chelates of linear ligands, the macrocyclic complexes of rare earth elements are extremely rigid and display kinetic inertness towards metal release, whereas the exocyclic ligands (anion or water molecules) are labile and easy to change. Many of the synthetic routes to Schiff base macrocycles involve the use of the metal ion template to orient the reacting groups of the substrats in the desired conformation for optimum ring closure [10–12]. The 4f cations have found to be very effective as template agents because they have little or no stereochemical requirements and can be accommodated by the particular stereochemical constraints enforced by the template process [13–16]. In view of potential applications it is of interest to search for new stable complexes of rare earth elements. The present paper deals with the template synthesis and characterization of the new yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium, dysprosium, holmium, erbium and ytterbium ion macrocyclic complexes derived from 2,6-diacetylpyridine and the biogenic amine spermine (4,9-diazadodecane-1,12-diamine).

2. Experimental

2.1. Preparation of the yttrium and lanthanide salts

The hydrated yttrium(III) and lanthanide(III) salts were prepared by dissolving the 99.99% oxides (Fluka) in a slight excess of perchloric acid. The solutions were evaporated and precipitates recrystallized from methanol. 2,6-Diacetylpyridine and spermine (4,9-diazadodecane-1,12-diamine (Aldrich) were used without further purification.

2.2. Preparation of the complexes — general procedures

All syntheses of the complexes were performed under similar conditions. To a mixture of the appropriate metal salt (0.1 mmol) in methanol (10 ml) and 2,6-diacetylpyridine (0.1 mmol) in methanol (10 ml), spermine (0.1 mmol) in methanol (10 ml) was added dropwise with stirring. The reaction was carried out for 2 h at ambient temperature. The solution volume was then reduced to 10 ml by roto-evaporation and a yellow precipitate formed on addition of a small amount of diethyl ether. This was filtered off, washed with ether, and dried in vacuo. The yields were 69–75%. The results of elemental analyses of the complexes are listed in Table 1.

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Table 1
Analytical data for the complexes of **L**

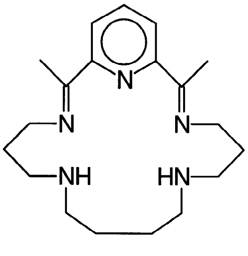
Complex	Found (%)			Calculated (%)		
	C	H	N	C	H	N
$\mathrm{Y}\mathbf{L}(\mathrm{H_2O})(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	29.18	5.00	9.03	29.61	4.84	9.09
$\mathrm{Pr}\mathbf{L}(\mathrm{H_2O})(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	28.57	4.75	8.70	27.74	4.53	8.51
$\mathrm{Nd}\mathbf{L}(\mathrm{H_2O})_2(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	26.41	4.42	7.67	27.03	4.65	8.29
$\mathrm{Sm}\mathbf{L}(\mathrm{H_2O})_2(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	27.14	4.45	7.82	26.84	4.62	8.24
$\mathrm{Gd}\mathbf{L}(\mathrm{H_2O})(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	28.10	4.78	8.37	27.20	4.44	8.34
$\mathrm{Dy}\mathbf{L}(\mathrm{H_2O})(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	26.51	4.37	7.93	27.03	4.42	8.29
$\mathrm{Ho}\mathbf{L}(\mathrm{H_2O})(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	27.82	4.43	8.21	26.95	4.40	8.27
$\mathrm{Er}\mathbf{L}(\mathrm{H_2O})(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	25.90	4.32	8.54	26.87	4.39	8.25
$\mathrm{Yb}\mathbf{L}(\mathrm{H_2O})(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$	26.05	4.47	8.24	26.69	4.36	8.19

2.3. Measurements

IR spectra were recorded using CsI pellets in the range 4000–200 $\mathrm{cm^{-1}}$ on a Perkin-Elmer 580 spectrophotometer. ^{1}H NMR spectra were run on a Varian Gemini 300 spectrometer using TMS as an internal reference. Fast atom bombardment (FAB) mass spectra were obtained on an AMD-604 mass spectrometer with glycerol as matrix. Thermogravimetric measurements were performed using Shimadzu TGA-50 derivatograph (up to 250°C, heating rate 10°C/min, air atmosphere). All data reported refer to isolated materials judged to be homogeneous by thin-layer chromatography performed on precoated silica-gel plates (0.2 mm 60 F-254, Merck) and visualized by UV light.

3. Results and discussion

The template reactions of 2,6-diacetylpyridine with spermine in the presence of trivalent yttrium, lanthanum, praseodymium, neodymium, samarium, gadolinium, dysprosium, holmium, erbium and ytterbium perchlorates in a 1:1:1 molar ratio of starting materials produce the 19-membered macrocyclic complexes with an N_5 set of donor atoms as a result of [1+1] Schiff base condensation. The formulation of these complexes as $\mathrm{Ln}\mathbf{L}(\mathrm{H_2O})_n(\mathrm{ClO_4})_3\cdot 2\mathrm{H_2O}$, where **L** is $\mathrm{Me_2pyo[19]triene\text{-}N_5}$, Ln=Y, La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, $n=1$ or 2, follow from spectral data (IR, ^{1}H NMR, FAB-MS) and thermogravimetric and elemental analyses. The complexes are yellow air stable solids, moderately soluble in $\mathrm{CH_3CN}$ and DMSO.



L

All the complexes give very similar infra-red spectra (Table 2) indicating the presence of the same ligand throughout the series. The occurrence of the band at 1653–1652 $\mathrm{cm^{-1}}$ attributable to C=N stretching modes which is diagnostic for the Schiff base condensation and the absence of bands characteristic of carbonyl groups confirm the formation of the macrocyclic compounds. The spectra contain medium to strong bands at 1590–1375 $\mathrm{cm^{-1}}$ 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 bands at 941–754 $\mathrm{cm^{-1}}$ and 668–630 $\mathrm{cm^{-1}}$ attributable to the ring breathing frequency and the low energy pyridine ring vibrations, respectively. The bands at 3104–2943 $\mathrm{cm^{-1}}$, in addition to the bands at 1498–1457 $\mathrm{cm^{-1}}$ suggest the coordination of the nitrogen atoms of the secondary amino groups. The complexes show the broad diffuse band centered at 3421–3378 $\mathrm{cm^{-1}}$ due to the stretching and bending modes of lattice and coordinated water. In addition, weak bands are detectable at the 890–825 $\mathrm{cm^{-1}}$ region which may be assigned to rocking or wagging modes of water molecules interacting with the metal ion. The presence of water in both the outer and inner spheres of the complexes is confirmed by the results of thermogravimetric analysis. All the complexes lose the water molecules in two steps: two water molecules below 70°C and the remaining one or two water molecules above 130°C corresponding to the lattice and coordinated water molecules, respectively. Information about the bonding mode of the perchlorate counterions in these complexes may also be obtained from the IR spectra. The appearance of the considerable broadening (1267–1000 $\mathrm{cm^{-1}}$) of the band typical of the asymmetric Cl–O stretching mode along with two weak bands at 637–626 $\mathrm{cm^{-1}}$ associated with the asymmetric Cl–O bending suggests, that the perchlorate counterions are partially involved in the coordination sphere of the metal ions [17,18].

FAB spectroscopy offers additional structural information on these complexes. FAB MS (Table 2) confirm the presence of perchlorate anions and water molecules in the inner sphere of the complexes. The stepwise loss of $\mathrm{ClO_4}$ and $\mathrm{H_2O}$ species appears to be a common route of fragmentation. All the spectra exhibit a peak due to the free ligand at m/z 329 providing strong evidence for the

Table 2
Selected infrared and FAB mass spectral data for the complexes of **L**

Complex	IR (cm^{-1})					FAB	
	OH	NH	C=N	py	ClO_4^-	*m/z*	Assigment
Y**L**$(H_2O)(ClO_4)_3\cdot2H_2O$	3420, 886, 857	3104, 1490	1653	1584, 1379, 941, 818, 768, 630	1267–1016, 636, 626	635.3	Y**L**$(ClO_4)_2\cdot(H_2O)$
						536.3	Y**L**$(ClO_4)\cdot(H_2O)$
						421.2	Y**L**
						329.3	**L**
Pr**L**$(H_2O)(ClO_4)_3\cdot2H_2O$	3420, 874, 856	2943, 1457	1653	1589, 1375, 941, 818, 754, 668	1254–1000, 626	689.7	Pr**L**$(ClO_4)_2\cdot(H_2O)$
						592.2	Pr**L**$(ClO_4)\cdot(H_2O)$
						490.3	Pr**L**$\cdot H_2O$
Nd**L**$(H_2O)_2(ClO_4)_3\cdot2H_2O$	3403, 890, 850	3102, 1490	1652	1584, 1380, 945, 818, 767, 668	1250–1016, 637,626	731.4	Nd**L**$(ClO_4)_2\cdot(H_2O)_3$
						709.2	
						592.3	Nd**L**$(ClO_4)_2\cdot(H_2O)_2$
						328.2	Nd**L**$(ClO_4)\cdot(H_2O)$
							L
Sm**L**$(H_2O)_2(ClO_4)_3\cdot2H_2O$	3392, 875, 825	3103, 1489	1653	1584, 1379, 925, 818, 767, 668	1200–1015, 637, 626	701.7	Sm**L**$(ClO_4)_2\cdot(H_2O)$
						679.4	Sm**L**$(ClO_4)_2$
						613.3	Sm**L**$(ClO_4)\cdot(H_2O)_2$
						329.1	**L**
Gd**L**$(H_2O)(ClO_4)_3\cdot2H_2O$	3378, 875, 850	2944, 1498	1652	1590, 1379, 940, 818, 770, 668	1200–1000, 637, 626	699.7	Gd**L**$(ClO_4)_2\cdot H_2O$
						645.6	Gd**L**$(ClO_4)\cdot(H_2O)_3$
						505.5	Gd**L**$\cdot H_2O$
						329.2	**L**
Dy**L**$(H_2O)(ClO_4)_3\cdot2H_2O$	3421, 885, 857	3103, 1490	1653	1585, 1379, 941, 818, 767, 668	1200–1000, 633, 626	613.2	Dy**L**(ClO_4)
Ho**L**$(H_2O)(ClO_4)_3\cdot2H_2O$	3420, 885	3103, 1490	1653	1584, 1379, 941, 818, 768, 665	1200–1015, 637, 626	696.1	Ho**L**$(ClO_4)_2$
						613.3	Ho**L**$(ClO_4)\cdot(H_2O)$
						538.2	Ho**L**$\cdot(H_2O)_2$
Er**L**$(H_2O)(ClO_4)_3\cdot2H_2O$	3421, 885	3103, 1490	1653	1584, 1379, 941, 818, 768, 668	1200–1015, 637, 626	718.1	Er**L**$(ClO_4)_2\cdot(H_2O)$
						599.3	Er**L**(ClO_4)
						532.1	Er**L**$\cdot(H_2O)_2$
						328.0	**L**
Yb**L**$(H_2O)(ClO_4)_3\cdot2H_2O$	3420, 886	3103, 1489	1653	1584, 1379, 941, 819, 768, 668	1200–1016, 637, 627	716.1	Yb**L**$(ClO_4)_2\cdot(H_2O)$
						643.9	Yb**L**$(ClO_4)\cdot(H_2O)_2$
						599.2	Yb**L**(ClO_4)
						327.1	**L**

formation of the macrocyclic complexes with **L** as a [1+1] macrocyclic product of the template condensation of one molecule of diketone with one molecule of spermine.

The ^1H NMR spectrum of the DMSO-d_6 solution of the diamagnetic yttrium complex strongly suggests the presence of the macrocyclic ligand. Three well-resolved multiplets of the methylene protons are observed in the 2:1:1 ratio — the protons adjacent to NH give rise to a triplet at δ 2.83 (8H) ($J=7.3$), the protons α to nitrogen to a triplet at δ 2.67 (4H) ($J=6.9$) and the protons β to nitrogen to a quintet at δ 1.67 (4H) ($J=7.1$). The remaining protons of the $-NHCH_2C\mathit{H}_2C\mathit{H}_2CH_2NH-$ chain occur at δ 1.47 (4H). The signal at δ 2.75 (2H) may be assigned to protons of the secondary amino groups. The pyridine protons and methyl protons appear as a multiplet at δ 7.9–8.2 (3H) and as singlet at δ 2.58 (6H), 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. 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 the 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.

The results discussed in this paper along with our earlier investigations lead to the conclusion that the yttrium(III) and lanthanide(III) ions may act as templates in the synthesis of the nitrogen donor macrocycles. The cavity of the new pentadentate 19-membered macrocyclic product of the template process with N_5 set of donor atoms appears to be sufficiently large to enclose the yttrium and lanthanides irrespective on the ionic radius size of central atoms. The high coordination number characteristic of these ions is achieved by the incorporation of water molecules and counterions in the coordination sphere of the complexes. Reactions conducted in the absence of the metal salt yielded amorphous yellow materials of low solubility and indefinite composition which gave broad, poorly resolved infrared spectra. The importance of the metal ion in promoting the macrocyclo-condensation process is thus apparent. This finding appears to be in accordance with the general observation that for the majority of macrocyclic Schiff bases the metal-templated synthesis remains the best method of preparation.

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