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The template synthesis and characterization of new mono- and dinuclear Schiff base complexes of lanthanide(III) ions

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Abstract

As a result of [1 + 2] Schiff base condensation in reaction between 2,6-diacetylpyridine and 3,6-dioxaoctane-1,8-diamine in the presence of lanthanide(III) ions (Ln = La³⁺, Pr³⁺, Nd³⁺, Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Ho³⁺), the new mono- and dinuclear architectures containing ligand with N₅O₄ set of donor atoms with terminal amine groups were formed. The complexes were clear on the basis of the spectroscopic and thermogravimetric data and microanalyses.

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Keywords: Mono and dinuclear complexes; Schiff base podates; Template synthesis; Lanthanides

1. Introduction

Trivalent lanthanide complexes have been the subject of intense studies because of their peculiar properties and potential applications in many important areas of inorganic chemistry [1–3], biology [4–6] and medicine [7,8]. In previous papers, we have demonstrated the ability of trivalent lanthanide ions to form Schiff base macrocyclic and acyclic ligands by template method [9–12]. Monometallic macrocyclic complexes have been obtained for Dy(III), Er(III), Tm(III), Lu(III) [11] and acyclic monoand dinuclear complexes with terminal carbonyl groups for La(III), Sm(III), Eu(III) [11] and Eu(III), Tb(III), Ho(III), Lu(III) [12], respectively. In a present work, we wish to report formation of the podates with terminal amine groups achieved by direct template reaction (Fig. 1).

All of these complexes were characterized by spectral data (IR, NMR, FAB mass spectroscopy), thermogravimetric and elemental analyses. We have observed that mononuclear complexes have been formed when larger ion size lanthanides were used, and dinuclear complexes we have been obtained with heavier lanthanides.

2. Experimental details

2.1. Preparation of the lanthanide salts

The hydrated lanthanide(III) salts (chloride, perchlorate and nitrate) were prepared from their oxides and appropriate acid by treating 1g of lanthanide(III) oxide with 10 cm³ of aqueous acid (1:1). The resulting solution was evaporated and precipitate recrystallized from methanol. 2,6-diacetylpyridine (Aldrich Chemical Company) and 3,6-dioxaoctane-1,8-diamine (Merck) were used as received.

2.2. Preparation of the complexes—general procedures

All complexes were prepared under similar conditions. To a mixture of appropriate lanthanide salt (0.1 or 0.2 mmol) and 2,6-diacetylpyridine (0.1 or 0.2 mmol) in methanol (20 cm^3), 3,6-dioxaoctane-1,8-diamine (0.1 or 0.2 mmol) in methanol (10 cm^3) was added dropwise with stirring. The reaction mixture was stirred for 24 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. This precipitate was filtered off, washed with ether, and dried in vacuo. Yields: 72–80%.

The results of elemental analysis of the complexes are listed in Table 1.

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Fig. 1. The ligand L and computer simulation of its structure.

2.3. Measurements

IR spectra were recorded using CsI or KBr pellets in the range $4000-200 \text{ cm}^{-1}$ on a Perkin-Elmer 580 spectrophotometer and reported in cm⁻¹. ¹H NMR spectra were run in DMSO-d₆ on a Varian Gemini 300 spectrometer using TMS as an internal reference. Positive ion FAB-mass spectra were obtained on a AMD-604 mass spectrometer with the nitrobenzyl alcohol acid or glycerol as matrix. Thermogravimetric analyses were performed using Shimadzu TGA-50 derivatograph. Microanalyses were obtained using Elementar Vario El III microanalyzer.

3. Results and discussion

As a continuation of our studies on the macrocyclic [9,11] and acyclic [10–12] complexes generated in the template process involving the condensation reaction between dicar-

Table 1 Analytical data for the L complexes

bonyls and many different primary diamines in the presence of rare earth ions, we now report synthesis and characterization of the new acyclic complexes containing the Schiff base ligand terminated by two amine groups. The products of the template reactions between 2,6-diacetypyridine, 3,6-dioxaoctano-1,8-diamine and rare earth elements with chlorides, nitrates, perchlorates and triflates as counterions, run at the molar ratios 1:2:1 and 2:2:1, appear to be mononuclear complexes with aminooxapodand ligand **L**. The change of the molar ratio of the reagents into 1:2:2 led to a formation of dinuclear complexes comprising this ligand.

These complexes are orange solids, moderately soluble in DMSO. The formulations of these complexes as $LnLX_3 \cdot nH_2O$, where $Ln = La^{3+}$, Pr^{3+} , Nd^{3+} , Eu^{3+} ; $X = Cl^-$, NO_3^- , ClO_4^- , $CF_3SO_3^-$; n = 1-6 for mononuclear complexes and $Ln_2LX_6 \cdot nH_2O$, where $Ln = Gd^{3+}$, Tb^{3+} , Dy^{3+} , Ho^{3+} ; $X = Cl^-$, NO_3^- , ClO_4^- ; n = 5-8 for dinuclear complexes follow from spectral data (IR, ¹H NMR, FAB mass spectroscopy), thermogravimetric and elemental analyses. The important IR spectral frequencies along with their assignments are given in Table 2.

The IR spectra of all the complexes show the broad band centered at $3500-3400 \text{ cm}^{-1}$ due to the stretching and bending modes of water. In addition, weak bands are detectable at $870-810 \text{ cm}^{-1}$ which may be assigned to rocking or wagging modes of water molecules coordinated to the metal ions. The important feature common to all complexes is the occurrence of strong absorption bands at $3081-2830 \,\mathrm{cm}^{-1}$ assigned to the NH₂ stretching vibration, indicating the formation of the open-chain products containing terminal amine groups and suggests coordination through the nitrogen atoms to the metal ion. All the spectra confirm the Schiff base condensation by the presence of a strong band at $1646-1567 \text{ cm}^{-1}$ characteristic of C=N stretching modes. The bonding of the pyridine nitrogen atom is shown by the presence of bands at 1597-1501, 1024-940, 670-639 and $472-420 \text{ cm}^{-1}$. The C-O-C stretching mode occurs at $1115-1030 \,\mathrm{cm}^{-1}$ indicating ether oxygen coordination. The spectra of chloride complexes show medium absorp-

Compound	Found			Calculated				
	C (%)	H (%)	N (%)	S (%)	C (%)	H (%)	N (%)	S (%)
LaLCl ₃ ·4H ₂ O	36.67	5.89	8.82	_	34.06	6.08	9.46	_
LaL(ClO ₄) ₃ .6H ₂ O	23.13	4.09	7.88	_	23.08	4.48	8.41	_
LaL(CF ₃ SO ₃) ₃ ·3H ₂ O	27.67	3.95	6.27	8.73	27.10	4.07	6.58	9.04
$PrL(ClO_4)_3 \cdot H_2O$	27.14	4.19	7.47	_	28.64	4.43	7.95	_
NdLCl ₃ ·3H ₂ O	34.68	6.29	10.29	_	34.64	5.91	9.62	_
$NdL(NO_3)_3 \cdot 5H_2O$	27.05	5.24	12.34	_	26.21	4.92	11.64	_
EuL(NO ₃) ₃ ·2H ₂ O	29.58	4.89	14.45	_	31.63	5.15	14.05	_
$EuL(CF_3SO_3)_3 \cdot 3H_2O$	26.59	3.76	6.80	8.74	26.77	4.02	6.50	8.93
$Gd_2LCl_6 \cdot 5H_2O$	24.30	5.09	6.41	-	23.04	4.88	6.40	_
$Tb_2L(NO_3)_6 \cdot 8H_2O$	20.56	4.23	11.73	_	20.06	4.25	12.25	_
$Dy_2L(ClO_4)_6 \cdot 7H_2O$	18.46	3.58	4.68	-	17.14	3.47	4.76	_
$Ho_2LCl_6.5H_2O$	22.72	4.19	6.23	_	23.88	4.49	6.63	_

Table 2					
Selected infrared and	l FAB mass	s spectral da	ata for the	complexes	of L

Complex	$IR(cm^{-1})$						FAB		
	ОН	NH ₂	COC	C=N	Ру	X ⁻	m/z	Assignment	
LaLCl ₃ ·4H ₂ O	815 3420	2880 3040	1080	1620	660 1005 1590	235	617.2	[LaLCl·H ₂ O] ⁺	
LaL(ClO ₄) ₃ .6H ₂ O	810 3500	2830 3020	_	1630	420 940 1565	620 980 1100 1180	933.6 614.6 424.9	$\begin{split} & [LaL(ClO_4)_3\cdot 4H_2O]^+ \\ & [LaL\cdot 3H_2O]^+ \\ & [L]^+ \end{split}$	
LaL(CF ₃ SO ₃) ₃ ·3H ₂ O	815 3494	2925 3141	1030	1629	639 1568	518 577 761 1169 1252	1080.8	[LaL(CF ₃ SO ₃) ₃ ·4H ₂ O] ⁺	
$Pr \mathbf{L}(ClO_4)_3 \cdot H_2O$	820 3420	3035	_	1630	420 940 1575	624 970 1080 1140	665.3	[PrL(ClO ₄)] ⁺	
NdLCl ₃ ·3H ₂ O	810 3430	2915 3020	1100	1630	440 670 1580	285	691.4	[NdLCl ₃] ⁺	
$NdL(NO_3)_3 \cdot 5H_2O$	815 3400	2920 3040	1080	1590	472 667 1580	825 1383 1460–1306 1763	806.6 749.7	$[NdL(NO_3)_3 \cdot 3H_2O]^+$ $[NdL(NO_3)_2 \cdot 3H_2O]^+$	
$EuL(NO_3)_3 \cdot 2H_2O$	850 3400	2926 3020	1102	1567	423 660 1501	825 1384 1762	700.4	$[EuL(NO_3)_2]^+$	
$EuL(CF_3SO_3)_3 \cdot 3H_2O$	846 3484	2929 3169	1115	1620	638 1587	518 576 764 1169 1254	1097.9 1044.2	$[EuL(CF_3SO_3)_3 \cdot 4H_2O]^+$ $[EuL(CF_3SO_3)_3 \cdot H_2O]^+$	
$Gd_2LCl_6.5H_2O$	833 3480	3041 3081	1102	1596	423 1024 1502	259	987.1 955.1 706.9 599.3	$\begin{array}{l} [{\rm Gd}_2 {\bf L} {\rm Cl}_6 \cdot 2 {\rm H}_2 {\rm O}]^+ \\ [{\rm Gd}_2 {\bf L} {\rm Cl}_5 \cdot 2 {\rm H}_2 {\rm O}]^+ \\ [{\rm Gd} {\bf L} {\rm Cl}_3 \cdot {\rm H}_2 {\rm O}]^+ \\ [{\rm Gd} {\bf L}]^+ \end{array}$	
$Tb_2 L(NO_3)_3 \cdot 8H_2O$	863 3423	2922 3054	1094	1627	429 662 1597	825 1261–1465 1399 1762	939.3 857.2 663.4 424.9	$\begin{array}{l} [{\rm Tb}_2 {\bf L}({\rm NO}_3)_2 \cdot 4{\rm H}_2 {\rm O}]^+ \\ [{\rm Tb}_2 {\bf L}({\rm NO}_3) \cdot 3{\rm H}_2 {\rm O}]^+ \\ [{\rm Tb} {\bf L}({\rm NO}_3) \cdot {\rm H}_2 {\rm O}]^+ \\ [{\bf L}]^+ \end{array}$	
$Dy_2 L(ClO_4)_6 \cdot 7H_2O$	870 3420	3050	_	1620	660 1590	625 1025 1140 1180	1140.0 874.8 823.9 606.1 424.1	$\begin{array}{l} [Dy_2 L(ClO_4)_3 \cdot 5H_2O]^+ \\ [Dy L(ClO_4)_2 \cdot 5H_2O]^+ \\ [Dy L(ClO_4)_2 \cdot 2H_2O]^+ \\ [Dy L \cdot H_2O]^+ \\ [L]^+ \end{array}$	
$Ho_2LCl_6\cdot 5H_2O$	818 3409	2920 2958	1102 665 1596	1646	436	246	901.0 866.1 662.6	$\begin{array}{l} [\mathrm{Ho}_{2}\mathbf{L}\mathrm{Cl}_{2}{\cdot}4\mathrm{H}_{2}\mathrm{O}]^{+}\\ [\mathrm{Ho}_{2}\mathbf{L}\mathrm{Cl}_{2}{\cdot}2\mathrm{H}_{2}\mathrm{O}]^{+}\\ [\mathrm{Ho}\mathbf{L}\mathrm{Cl}_{2}]^{+} \end{array}$	

tion bands at $285-235 \text{ cm}^{-1}$ region attributable to the M–Cl frequency indicating the interaction of at least part of the chloride counterions with the metal. The IR spectra of perchlorate complexes feature split bands attributable to asymmetric Cl–O stretching mode at $1180-970 \text{ cm}^{-1}$ and the asymmetric Cl–O bending mode at 620–625 cm⁻¹, suggesting that both bound and free anions are present. However, as ν (C–O–C) for the ether chains of the ligand also falls in this region it is impossible to define precisely the coordination mode. The nitrate vibration of complexes is seen as bands at 1763 or 1762, 1465–1261, 1399–1384 and 825 cm^{-1} . The separation of modes has been used as a criterion to distinguish between mono- and bidentate chelating nitrates. The magnitude of this separation of ca. 160–200 cm⁻¹ may be indicative of a bidentate interaction of the nitrate anions with the lanthanide ions. The occurrence of a strong absorption at 1383, 1384 or 1399 cm⁻¹ in addition to the above bands indicates the presence of both ionic and bidentate nitrates in the complexes. The vibrational modes for the triflate anions are split suggesting the presence of coordinated species [13].

The FAB mass spectra (Table 2) provide strong evidence for the formation of the complexes containing one or two metal ions. In all of the FAB mass spectra the peak corresponding to $[Ln_2L]^+$ was observed. The presence of the nitrate counterions and water molecules in inner sphere of the complexes is confirmed by the stepwise loss of these species which appears to be a common route of fragmentation. The FAB mass spectra reveal an intense peak corresponding to $[Ln_xLX_y(H_2O)_z]^+$, where x = 1 or 2, y = 1-6, and z = 0-5. The occurrence of peak due to the free ligand as a result of demetallation of the species under FAB conditions supports the formation of the complexes of podate type with ligand L as product of [1 + 2] (dicarbonyl + diamine) template condensation process.

The thermogravimetric diagrams of the mononuclear complexes are similar. For example, the compound NdLCl₃·3H₂O begins to lose two of its crystal lattice water molecules below 100 °C. The complex loses a remaining water molecule at 130 °C. In the coordination sphere of this type of complexes is only one water molecule. Thermal behavior of all dinuclear complexes is the resembling. TGA of the complexes of general formula $Ln_2LX_6 \cdot nH_2O$, where n = 5-8 show a first dehydration step at 60-80 °C associated with the loss of n - 4 molecules of water followed by second step at 95–150°C corresponding to the loss of remaining water molecules supporting the presence of water bound in two different ways: lattice and coordinated to the metal ions. The number of these two kinds of water molecules per mole of metal ion was calculated from the weight loss observed for the complexes at these two temperature ranges.

In the ¹H NMR spectrum of deuterated methanol solution of the diamagnetic lanthanum complex the resonance of protons α to nitrogen in the ethylene chain is observed as triplet at $\delta = 3.31$ (4H) (J = 1.8), the protons neighboring to oxygen give rise to a triplet at $\delta = 3.71$ (16H) (J = 5.1) and the protons adjacent to NH₂ to a quintet at $\delta = 3.10$ (4H) (J = 1.8). The signal of methyl protons of two CH₃C=N occurs at $\delta = 3.35$ (6H). The singlet signal at $\delta = 1.30$ (4H) may be assigned to the primary amino group protons. The pyridine protons appear at $\delta = 8.2-7.7$ (3H). The integrated relative intensities of the above signals are in

good agreement with the required ratios consistent with the proposed formulation of this complex.

Computer simulation of the structure of the ligand L has led to determination of the atomic dispositions with the minimum energy. The molecular model indicates that the ligand is in the atom arrangement suitable to incorporate two metal ions in its structure. It can be supposed that one metal in dinuclear complexes occupies a position in upper (pyridine) part of the ligand, while the other includes the amine groups in the coordination sphere. This process decreases the probability of the nucleophilic attack of the nitrogen atom on the carbon atom of the carbonyl group and inhibits the transamination pathway controlling the ring closure and stabilizes the open-chain product [14]. Lanthanide(III) cation complexes of the ligand with both nitrogen and oxygen donor atoms seem to be more stable than complexes with polyaza ligands of this kind.

This results confirm effectiveness of lanthanide(III) ions as templates in formation of the supramolecular aminopodates.

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References

- Ch.-D. Wu, C.-Z. Lu, W.-B. Yang, S.-F. Lu, H.-H. Zhuang, J.-S. Huang, Eur. J. Inorg. Chem. (2002) 797.
- [2] Y. Bretonnière, M. Mazzanti, J. Pécaut, M.M. Olmstead, J. Am. Chem. Soc. 124 (2002) 9012.
- [3] S. Nishihara, T. Akutagawa, T. Hasegawa, T. Nakamura, Inorg. Chem. 42 (2003) 2480.
- [4] K. Matsumara, M. Endo, M. Komiyama, J. Chem. Soc., Chem. Commun. (1994) 2019.
- [5] D. Magda, R.A. Miller, J.L. Sessler, B.L. Iverson, J. Am. Chem. Soc. 116 (1994) 7439.
- [6] D. Parker, Coord. Chem. Rev. 205 (2000) 109.
- [7] P. Caravan, J.J. Ellison, T.J. McMurry, R.B. Lauffer, Chem. Rev. 99 (1999) 2293.
- [8] B. O'Sullivan, D.M.J. Doble, M.K. Thompson, C. Siering, J. Xu, M. Botta, S. Aime, K.N. Raymond, Inorg. Chem. 42 (2003) 2577.
- [9] W. Radecka-Paryzek, V. Patroniak, M. Kubicki, Polyhedron 22 (2003) 2773.
- [10] W. Radecka-Paryzek, M.T. Kaczmarek, V. Patroniak, I. Pospieszna-Markiewicz, Inorg. Chem. Commun. 6 (2003) 26.
- [11] V. Patroniak-Krzyminiewska, W. Radecka-Paryzek, Collect. Czech. Commun. 63 (1998) 363.
- [12] W. Radecka-Paryzek, M. Kaczmarek, V. Patroniak, I. Pospieszna-Markiewicz, J. Alloys Compd. 323–324 (2001) 173.
- [13] G. Muller, J.-C. Bünzli, K.J. Schenk, C. Piguet, G. Hopgartner, Inorg. Chem. 40 (2001) 2642.
- [14] S.M. Nelson, C.V. Knox, M. McCann, M.G.B. Drew, J. Chem. Soc. Dalton Trans. (1981) 1669.