J. of Basic Sciences, Cheju Nat'l Univ.
18(2), 165~172, 2005

기초과학연구 제주대학교
18(2), 165~172, 2005

Synthesis and Characterization of Pr(Ⅲ) and Sm(Ⅲ)-Nitrato Complexes with 22-Membered Phenol-Based N_4O_2 Compartmental Macrocyclic Ligand

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Abstract. A mononuclear lanthanide(III)-nitrato complexes, $[Ln(H_2[22]\text{-HMTADO})O_2NO](NO_3)_2 \cdot 2H_2O$ (Ln = $Pr^{3+}$and Sm^{3+}), with [2+2] symmetrical N_4O_2 compartmental macrocyclic ligand {H_2[22] -HMTADO; 5,5,11,17,17,23-hexamethyl-3,7,15,19-tetraazatricyclo[19,3,1,$1^{9,13}$]hexacosa-1(25),2,7,9,11, 13(26),14,19,21,23-decane-25,26-diol} containing bridging phenolic oxygen atoms was synthesized by condensation of 2,6-diformyl-*p*-cresol and 2-dimethyl-1,3-propandiamine, in lanthanide nitrate. The complexes have been elucidated by elemental analysis, molar conductance, FAB-mass, FT-IR, and electronic studies. The macrocyclic entity changed slowly up to 370℃, and then those complexes have been changed to Ln_2O_3.

Key words : lanthanide complex, compartmetal macrocyclic ligand

I. Introduction

Recognition of the importance of complexes containing macrocyclic ligands has led to a considerable effort being invested in developing reliable inexpensive synthetic routes for these compounds [1-4]. The ability of the lan -thanide(III) metal ions to promote the Schiff base condensation of the appropriate diamine and dicarbonyl precursors resulting in the formation of metal complexes of otherwise inaccessible macrocyclic ligands is well established [5-8]. Macrocyclic complexes of lanthanides are currently attracting much attention in the catalytic cleavage of RNA [9], in radioimmunotherapy [10-12], in radio -immunoscintigraphy [13,14], in positron emission tomography [15], as radiopharmaceuticals [10], as contrast enhancing agents in magnetic re -sonance imaging [16-20], as NMR shift reagents [21-24], as NMR shift and relaxation agents for proteins [25] and biological cations [24,26], as fluorescent probes in fluoroimmuno -assay [27,28] and as luminescent labels in luminescence immunoassay [29]. There is an emerging interest in the application of ma -crocyclic ligands as effective metal ion chelators [30-33] and in the separation of lanthanides [34-36].

Macrocyclic ligands form stable complexes with lanthanides and actinides and hence they serve as a springboard to explore the co -ordination chemistry of these metal ions. Synthesis of macrocyclic complexes of lan -thanides in identical ligand frameworks is essential to understand the influence of the structure and dynamics of the ligand frame -work on the stability and other physico -chemical properties of these metal ions. The design of ligands capable of forming stable lanthanide(III) complexes would not only allow further study of the coordination pro -perties of the rare earth metal ions but also would enable chemists to exploit more fully certain important emerging properties of these complexes. The challenge is to design potential macrocycles with appropriate ligand design features required to form stable complexes with all the lanthanide(III) cations. Symmetric [2+2] macrocycles which incorporate aromatic rings in the lateral and/or head units would exhibit moderate flexibility and form more stable complexes than the complexes of highly flexible macrocycles, derived from aliphatic precursors.

The size of the lanthanide(III) cations

decreases dramatically along the lanthanide series and consequently their acid character also changes. Therefore, macrocycles bearing both nitrogen and oxygen donors which exhibit hard and soft base character would form more stable complexes than the polyaza or polyoxa macrocycles with lanthanide(III) cations. Thus oxaaza macrocycles which incorporate aromatic head or lateral units are the versatile ligand systems to achieve coordination with all lanthanide(III) cations.

Therefore, we sought to synthesize the 22-membered dioxatetraaza macrocyclic ligand {H_2[22]-HMTADO ; 5,5,11,17,17,23-hexamethyl-3,7,15,19-tetraazatricyclo[19,3,1,$1^{9,13}$]hexacosa-1(25),2,7,9,11,13(26),14,19,21,23-decane-25,26-diol} in an attempt to obtain stable complexes of Pr^{3+} and Sm^{3+} cations in the same ligand framework.

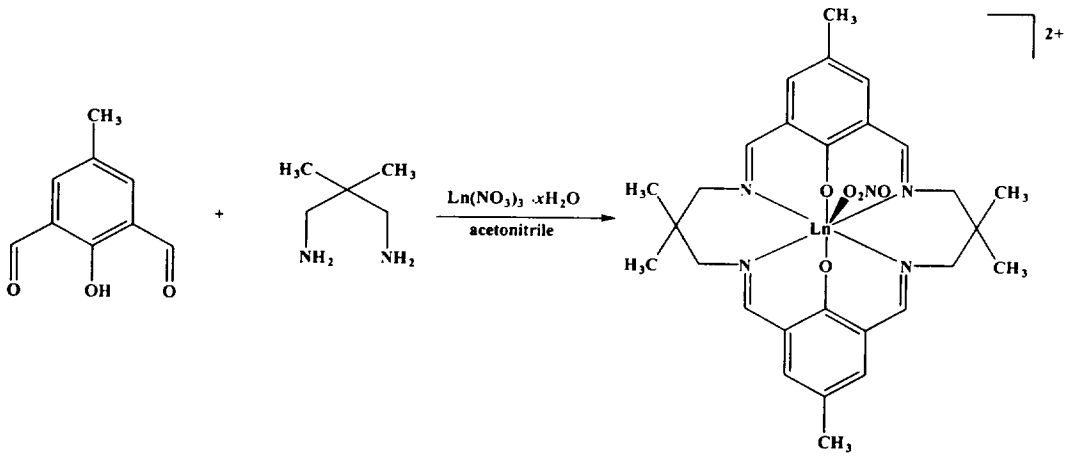
II. Experimental

1. Chemicals and Physical Measurements

All chemicals were commercial analytical reagents and were used without further purification. For the spectroscopic and physical measurements, organic solvents were dried and purified according to the literature methods. Nanopure quality water was used throughout this work. Microanalyses of C, H, and N was carried out using LECO CHN-900 analyzer. Conductance measurement of the complex was performed at 25±1℃ using an ORION 162 conductivity temperature meter. IR spectrum was recorded with a Bruker FSS66 FT-IR spectrometer in the range 4000-370 cm^{-1} using KBr pellets. Electronic absorption spectrum was measured at 25℃ on a UV-3150 UV-VIS-NIR Spectrophotometer (SHIMADZU). FAB-mass spectrum was obtained on a JEOL JMS-700 Mass Spectrometer using argon (6kV, 10mA) as the FAB gas. The accelerating voltage was 10 kV and glycerol was used as the matrix. The mass spectrometer was operated in positive ion mode and mass spectrum was calibrated by Alkali-CsI positive.

2. Preparations of lanthanide(III) complexes

The synthesis of 2,6-diformyl-*p*-cresol was prepared according to the literature methods previously reported [37, 38].



Scheme 1. Synthesis of the mononuclear lanthanide {Pr(III) and Sm(III)} complexes of phenol-based macrocyclic ligand ([22]-HMTADO).

1) *[Pr(H₂[22]-HMTADO)O₂NO](NO₃)₂ · 2H₂O.*

A solution of 2,6-diformyl-*p*-cresol (0.328 g) in the boiling acetonitrile (30 mL) was dropwise added to the yellow solution formed by mixing 2,2-dimethyl-1,3-propandiamine (0.206 g) with a solution of $Pr(NO_3)_3 \cdot 6H_2O$ (0.435 g) in acetonitrile (50 mL). The resulting yellow mixture was stirred at the reflux temperature for 3 h to give an yellow microcrystalline powder. It was collected by suction filtration, thoroughly washed with acetonitrile and dried *in vacuo*. Yield 0.642 g (78%). Anal. Calc. (Found) % for Pr -$(C_{28}H_{36}N_4O_2)(NO_3)_3(H_2O)_2$: C, 40.84 (40.82) ; H, 4.90 (5.04); N, 11.91 (11.58). Solubility : hot methanol, DMSO, DMF. UV-Vis (CH_3OH) [λ_{max} (ε, $M^{-1}cm^{-1}$) : 398 (18,520). Λ_M (CH_3OH) : 260 $ohm^{-1}cm^2mol^{-1}$.

2) *[Sm(H₂[22]-HMTADO)O₂NO](NO₃)₂ · 2H₂O.*

A solution of 2,6-diformyl-*p*-cresol (0.328 g) in the boiling acetonitrile (30 mL) was dropwise added to the yellow solution formed by mixing 2,2-dimethyl-1,3-propandiamine (0.206 g) with a solution of $Sm(NO_3)_3 \cdot 6H_2O$ (0.445 g) in acetonitrile (50 mL). The resulting yellow mixture was stirred at the reflux temperature for 3 h to give an yellow microcrystalline powder. It was collected by suction filtration, thoroughly washed with acetonitrile and dried *in vacuo*. Yield 0.626 g (75%). Anal. Calc. (Found) % for Sm -$(C_{28}H_{36}N_4O_2)(NO_3)_3(H_2O)_2$: C, 40.37(40.62) ; H, 4.84 (4.38); N, 11.77(11.45). Solubility : hot methanol, DMSO, DMF. UV-Vis (CH_3OH) [λ_{max} (ε, $M^{-1}cm^{-1}$) : 398 (17,120). Λ_M (CH_3OH) : 258 ohm^{-1} cm^2mol^{-1}.

III. Results

1. IR spectra of the lanthanide(III) complexes

IR spectra of the lanthanide(III) complexes were presented Figure 1. The strong and sharp absorption bands occurring at 1645 cm^{-1} in the IR spectra of the complexes are attributed to ν(C=N) of the coordinated [22]-HMTADO ligand [39,40], and the absence of any carbonyl bands associated with the diformyl-phenol starting materials or nonmarcrocyclic intermediates. The IR spectra displayed C-H stretching vibrations from 3000 to 2800 cm^{-1}. The present complexes exhibited three C-H deformation bands at 1478, 1390, and 1317 cm^{-1} regions and two out-of-plan vibration bands at 825 and 781 cm^{-1} regions. The absorption bands occurring in the IR spectra of the complexes in the 3430 cm^{-1} region may probably be due to the ν(OH) vibration of the lattice water.

The absorption bands occurring in the IR spectra of the complexes in the 1460, 1284 and 1035 cm^{-1} regions are assignable to the ν(N=O) (ν_1), $\nu_a(NO_2)$ (ν_5) and $\nu_s(NO_2)$ (ν_2) vibrations, respectively, of the chelating bidentate nitrate ion [40-42]. The absorption band observed at 815 cm^{-1} in the complexes is also characteristic of chelating bidentate nitrate [41]. The larger separation of 175-176 cm^{-1} between the two higher frequency bands (ν_1 and ν_5) indicates strong interaction of the oxygen atoms of the nitrate with the lanthanide ions and is typical of bidentate coordination [42,43]. The absorption band at 1385 cm^{-1} is characteristic of ionic nitrate present in the outer-coordination sphere [41].

2. FAB mass spectra

The FAB mass spectra of the lanthanide(III) complexes were shown in Figure 2 and 3. The FAB mass spectra of two complexes contain peaks corresponding to the molecular ion $[Ln(H_2[22]\text{-HMTADO})(NO_3)]^+$ for Ln = Pr^{3+} (m/z 661.8) and Sm^{3+} (m/z 672.3). The molecular ion loses the exocyclic nitrate ligand resulting in the formation of the fragment $[Ln(H_2[22]\text{-HMTADO})]^+$ for Ln = Pr^{3+} (m/z 598.7) and Sm^{3+} (m/z 609.3). These species are well observed in the FAB mass spectra. Removal of nitrate ion from the molecular ion is observed with a mass loss of 63 as HNO_3. For each metal containing species there is a set of peaks due to the different isotopes of the metal. In the FAB mass spectra of all the complexes there is a peak at m/z 460.8 corresponding to the species

$[H_2[22]\text{-HMTADO}]^+$. This indicates that the species $[Ln(H_2[22]\text{-HMTADO})]^+$ undergoes demetallation to give the tetraazadioxa macrocycle $H_2[22]$-HMTADO under FAB conditions. Peaks corresponding to sandwich complexes of the type $[Ln(H_2[22]\text{-HMTADO})_2]^+$ for Ln = Sm^{3+} (m/z 1069.2) ; and $[\{Ln(H_2[22]\text{-HMTADO})\}_2(NO_3)]^+$ for Ln = Pr^{3+} (m/z 1259.4) are observed in FAB mass spectra. These sandwich complexes might gave been formed during the FAB fragmentation process [40].

3. Thermal stability of lanthanide complexes

Thermogravimetry analysis (TGA) have been carried out simultaneously for the lanthanide complexes (Figure 4). Thermo -gravimetric details were given in Table 1. It was found out from the results that the prepared macrocycle compounds have relatively high thermal stability. The lattice water molecules were lost at ~ 300℃ ranges. The two nitrate ions were lost at 300 ~ 350℃ range. The coordinated nitrate ion was lost at 350 ~ 370℃ range. The macrocyclic entity changed slowly up to 37 0℃, and then those complexes have been changed to Ln_2O_3.

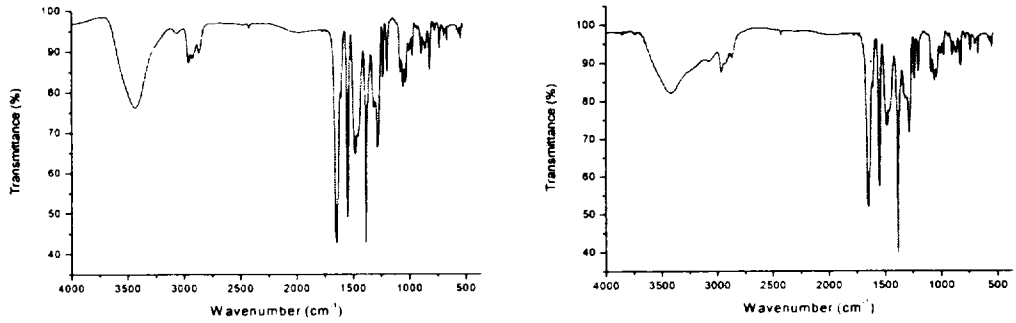
Table 1. TGA data of Pr^{3+} and Sm^{3+}complexes

Complexes	Temperature range (℃)	Moieties lost
$[Pr(H_2[22]\text{-HMTADO})O_2NO]$ $\text{-}(NO_3)_2 \cdot 2H_2O$	~ 306	$2H_2O$
	306 ~ 347	$2NO_3^-$
	347 ~ 365	NO_3^-
	365 ~	macrocycle
$[Sm(H_2[22]\text{-HMTADO})O_2NO]$ $\text{-}(NO_3)_2 \cdot 2H_2O$	~ 295	$2H_2O$
	295 ~ 343	$2NO_3^-$
	343 ~ 368	NO_3^-
	368 ~	macrocycle

IV. Discussion

The formation of lanthanide(III) complexes of $H_2[22]$-HMTADO demonstrates the template potential of these metal ions in the assembly of oxaaza macrocycles. As the size of the lanthanide(III) cations decreases along the lanthanide series the metal ions adopt different geometries in the complexes. Thus the template potential of the lanthanide(III) cations in the assembly of $H_2[22]$-HMTADO is due to the adaptability of the macrocycle to the geometrical requirements of the metal ions. The electronic and steric requirements of the central metal ions appear to be fully satisfied by coordination of the four nitrogen and two oxygen donors of the macrocycle and to the oxygen donors of a bidentate chelating nitrate ion. The coordination of the nitrate ion in each complex illustrates the influence of oxygen donor ligands to stabilize the lanthanide(III) cations in the macrocyclic framework. The remarkable ability of this ma -crocycle to coordinate with all the lanthanide(III) cations despite the large differences in their ionic radii is attributed to the flexibility of the macrocycle to fold according to the steric demands of the metal ions and the exocyclic ligands. The yield of the complexes of $H_2[22]$ -HMTADO increases with decreasing ionic radii of the metal ions. In the present case the increase in the yield of the complexes along the lanthanide series is attributed to the better match between the size of the heavier lanthanide(III) cations and the macrocyclic cavity.

The two OH protons of $H_2[22]$-HMTADO remain intact in the complexes. Thus the ligand acts as a neutral species even though it has two ionizable protons. Such a behavior is also observed in the case of the lanthanide (III) complexes of the [2+2] symmetric macrocycles obtained by the Schiff base condensation of 2,6-diformyl-4-chlorophenol with diethylenetriamine, 1,5-diamino-3-thiapentane [44,45] or N-dodecyldiethylenetriamine [46] by the metal template method or by the reaction of the respective preformed macrocycle with the hydrated lanthanide(III) nitrate.



(a) (b)

Figure 1. FT-IR spectra of $[Ln(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot 2H_2O$ {Ln = (a) Pr and (b) Sm}.

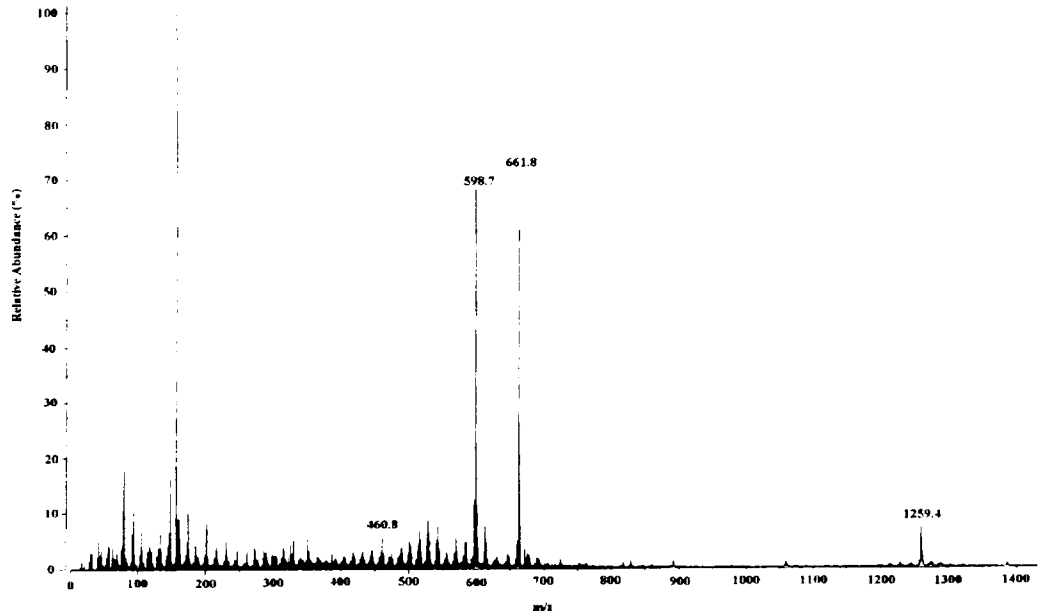


Figure 2. FAB-mass spectrum of $[Pr(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot 2H_2O$.

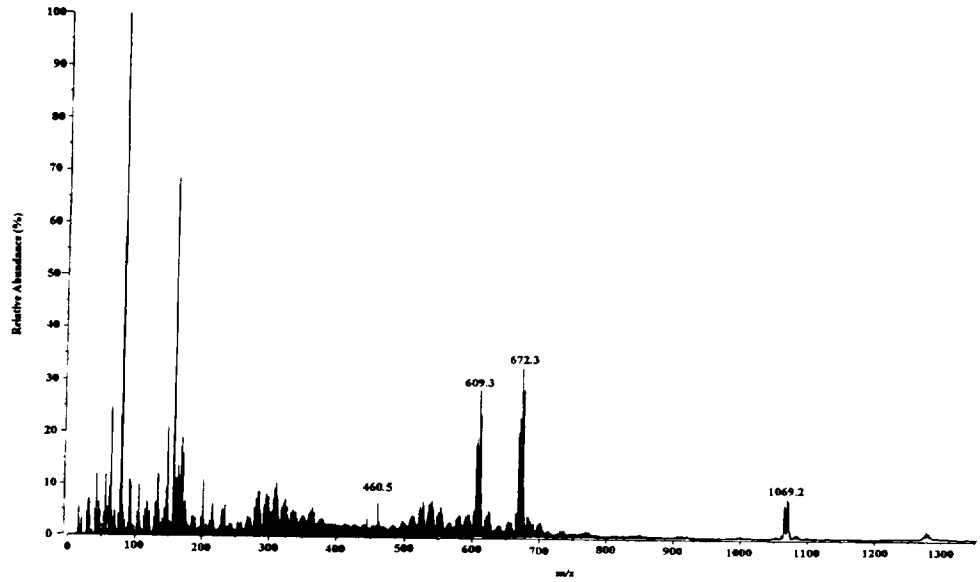
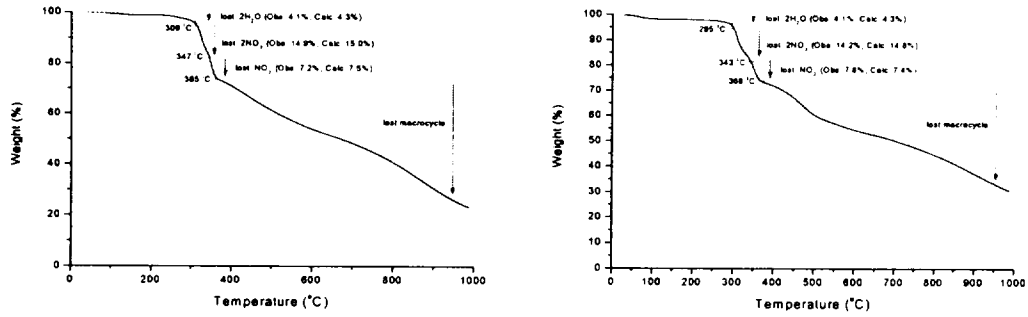


Figure 3. FAB-mass spectrum of $[Sm(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot 2H_2O$.



(a) (b)

Figure 4. TGA curves of $[Ln(H_2[22]\text{-}HMTADO)O_2NO](NO_3)_2 \cdot 2H_2O$ {Ln = (a) Pr and (b) Sm}.

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