Preparation and characterization of neodymium(III) and dysprosium(III) complexes with tetraaza macrocycles

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Abstract

The neodymium(III) and dysprosium(III) complexes with 14-, 18- and 22-membered tetraaza macrocycles have been prepared and characterized by elemental analyses, magnetic susceptibilities, IR and visible reflectance spectrophotometries and thermogravimetry. The analytical data indicate that these complexes have a formula of $Ln(L)(NO_3)_3 \cdot mH_2O$, where Ln is a lanthanide(III) ion, L is a tetraaza macrocycle, and m values vary from 3 to 6.

INTRODUCTION

Although metal complexes between first-row transition elements and tetraaza macrocyclic ligands have been extensively studied, their coordination chemistry toward lanthanide ions has been little studied except for porphyrins and phthalocyanines [1]. Because the lanthanide ions prefer an oxygen donor atom to a nitrogen one, lanthanide complexes with ligands containing only nitrogen donor atoms such as saturated tetraaza macrocycles can be prepared under conditions of complete removal of oxygen donors such as water molecules in the system. Therefore, many lanthanide complexes possess oxygen atoms as a donor, and lanthanide complexes with crown ethers and cryptands have been reported [2]. However, it can be expected that the coordination bond between a lanthanide ion and nitrogen donor atoms may become strong if unsaturated polyaza macrocyclic compounds are employed as ligand. In fact, some lanthanide complexes with unsaturated hexaaza macrocycles

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containing pyridine moieties have been prepared and characterized [3]. Recently, the lanthanide complexes with caged octaamines derived from tris(2-aminoethyl)amine and bis(dimethylamino)methane have been synthesized by a template method and their properties and molecular structures have been reported [4].

In our previous paper [5] we reported the preparation of the copper(II) complexes with 14-, 18- and 22-membered tetraaza macrocycles and their structurally characteristic properties: the copper(II) complex with the 14-membered macrocycle is planar, that with the 18-membered one is the pseudo-tetrahedral, and that with the 22-membered one is bi- and trinuclear. In this paper we report the preparation of the neodymium(III) and dysprosium(III) complexes with these macrocycles and their characterization by elemental analyses, magnetic susceptibilities, IR and visible reflectance spectrophotometries, and thermogravimetry.

EXPERIMENTAL

Preparation of lanthanide(III) complexes with tetraaza macrocycles

A preparative scheme for the lanthanide(III) complexes with tetraaza macrocycles is shown in Fig. 1. Neodymium(III) nitrate hexahydrate or dysprosium(III) nitrate hexahydrate (5 mM) was dissolved in absolute ethanol (200 cm^3). The solution was refluxed and then an equimolar amount of the macrocyclic ligand (5,7,12,14-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-5,7,12,14-tetraene, 1,9,16,18-tetramethyl-1,6,10,15-tetraazacyclooctadeca-7,9,16,18-tetraene or 9,11,20,22-tetramethyl-1,8,12,19-tetraazacyclodocosa-9,11,20,22-tetraene) was added to it. A white precipitate deposited immediately, and the mixture was further refluxed for 30 min. After the mixture had been cooled to room temperature, the resulting precipitate was collected on a glass filter, washed with ethanol and dried in vacuo. The yields were about 60%. The neodymium(III) and dysprosium(III) complexes are slightly soluble in N,N-dimethylformamide but insoluble in water and chloroform.
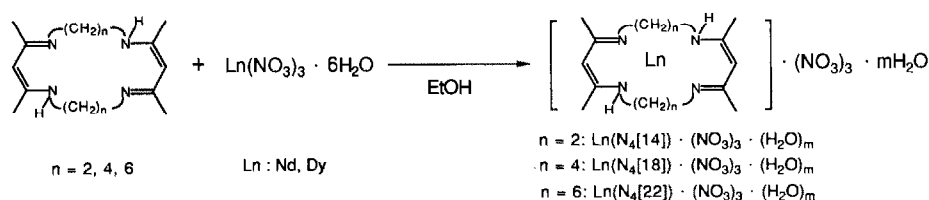

n = 2, 4, 6   Ln : Nd, Dy

n = 2: Ln(N$_4$[14]) · (NO$_3$)$_3$ · (H$_2$O)$_m$
n = 4: Ln(N$_4$[18]) · (NO$_3$)$_3$ · (H$_2$O)$_m$
n = 6: Ln(N$_4$[22]) · (NO$_3$)$_3$ · (H$_2$O)$_m$

Fig. 1. Preparative scheme for neodymium(III) and dysprosium(III) complexes with tetraaza macrocycles.

RESULTS AND DISCUSSION

Elemental analysis and magnetic susceptibility

The analytical data for the neodymium(III) and dysprosium(III) complexes are listed in Table 1, together with their magnetic and IR spectral data. The analytical data indicate that these complexes have the formula $Ln(L)(NO_3)_3 \cdot mH_2O$, where Ln is a neodymium(III) or dysprosium(III) ion, L is a tetraaza macrocycle, and m values vary from 3 to 6 depending on the combination of metal ions and ligands. The presence of three nitrate ions per metal ion suggests that deprotonation of the macrocyclic ligands does not take place by complex formation, which is shown in Fig. 1. In addition, the 1:1 ratio of the metal ion to the macrocyclic ligand indicates that each of the complexes obtained may adopt a mononuclear or a stacking polymeric structure.

The effective magnetic moments of the neodymium(III) and dysprosium(III) complexes measured at room temperature show little deviation from the Van Vleck theoretical values, although the value for the dysprosium(III) complex with the 18-membered macrocycle is slightly smaller than its theoretical value.

IR spectra

Figure 2 shows the infrared spectra of the 14-membered tetraaza macrocycle and its neodymium(III) complex $Nd(N_4[14])(NO_3)_3 \cdot 6H_2O$ in a KBr disc. The spectrum of the neodymium(III) complex exhibits characteristic absorption bands [6] due to O–H stretching vibrations of lattice and coordinated water at 3190 and 3060 cm^{-1}, C=N stretching vibrations at 1580 cm^{-1} and NO_3 stretching vibrations at 1390 cm^{-1}, as well as other absorption bands at 2970, 1450, 1355, 1320, 1245 and 735 cm^{-1}. The band due to C=N stretching vibrations is shifted to frequencies lower by about 20 cm^{-1} compared with that of the free ligand, which suggests that the nitrogen donor atoms of the ligand coordinate to the neodymium(III) ion. In addition, the frequency position assigned to $v(NO_3)$ is almost the same as that of NO_3^-. Therefore the NO_3 groups may exist as an uncoordinated counter ion [6]. The IR spectrum of the dysprosium(III) complex $Dy(N_4[14])(NO_3)_3 \cdot 5.5H_2O$ is very similar to that for the corresponding neodymium(III) complex.

However, in the IR spectra of the 18- and 22-membered macrocyclic complexes, shifts to lower frequency by about 50 cm^{-1} for the C=N stretching vibrations are observed compared with those of the free ligands, which is a much larger figure than the shifts for the 14-membered macrocyclic complexes. The results indicate that the coordination bonds

TABLE 1

Elemental analyses, IR spectral data, effective magnetic moments (μ) and DTA peaks for neodymium(III) and dysprosium(III) complexes with 14-, 18- and 22-membered tetraaza macrocycles

Complex	Elemental analyses [a] (%)			IR (cm^{-1})			DTA peak (°C)	μ_{eff} [b] (BM)
	C	H	N	v(OH)	v(C=N)	v(NO$_3$)		
Nd(N$_4$[14])(NO$_3$)$_3$ · 6H$_2$O	24.34 (24.48)	5.38 (5.29)	14.25 (14.28)	3190 3060	1580	1390	58, 102, 130	3.53
Dy(N$_4$[14])(NO$_3$)$_3$ · 5.5H$_2$O	24.04 (24.16)	5.13 (5.08)	14.11 (14.09)	3200 3060	1580	1390	65, 90, 101, 155	11.11
Nd(N$_4$[18])(NO$_3$)$_3$ · 3H$_2$O	31.17 (31.38)	5.71 (5.57)	14.20 (14.24)	3250 3190 3050	1570	1390	58, 171	3.41
Dy(N$_4$[18])(NO$_3$)$_3$ · 4H$_2$O	29.69 (29.81)	5.64 (5.57)	13.43 (13.52)	3250 3200 3060	1570	1390	52, 182, 185	9.61
Nd(N$_4$[22])(NO$_3$)$_3$ · 3H$_2$O	35.25 (35.47)	6.35 (6.24)	13.24 (13.16)	3250 3070	1575	1395	45, 168	3.33
Dy(N$_4$[22])(NO$_3$)$_3$ · 4H$_2$O	33.77 (33.82)	6.32 (6.21)	12.59 (12.55)	3250 3070	1565	1395	66, 171, 185	10.43

[a] Calculated values in parentheses.
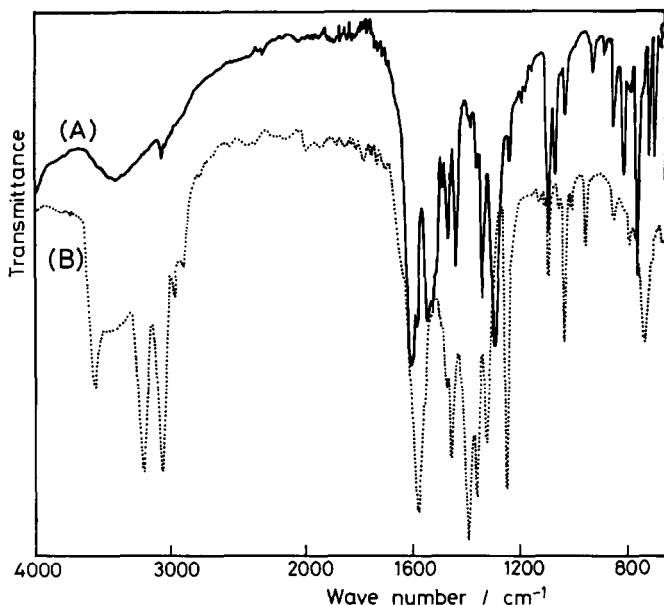[b] Measured at room temperature.

Fig. 2. IR spectra of 14-membered tetraaza macrocycle (curve A) and its neodymium(III) complex (curve B).

between the nitrogen donor atoms of the 18- and 22-membered macro-cyclic ligands and neodymium(III) and dysprosium(III) ions are stronger than those for the 14-membered ligand. A relatively large ionic radius of ·lanthanide ions may fit with the former two macrocycles because their cavity sizes are larger than that of the latter macrocycle.

Visible spectra

The diffuse reflectance spectra of all the neodymium(III) and dys-prosium(III) complexes have typical and sharp absorption bands at 802, 753, 746, 736, 682, 580, 525, 513 and 465 nm and at 808, 758 and 452 nm, respectively, independent of the macrocyclic ligand. These bands can be assigned to f–f transitions [7].

TG-DTA curves

Figure 3 shows the results of the thermal analysis of the neodymium(III) and dysprosium(III) complexes with the 14-membered macrocycle. For $Nd(N_4[14])(NO_3)_3 \cdot 6H_2O$ the DTA curve has three endothermic peaks. The first peak at 58°C is accompanied by a weight loss of 2.6% in the TG curve. This value agrees well with a value calculated from the assumption that one mole of H_2O is eliminated from one mole of the complex. The second peak at 102°C and the third peak at 130°C are
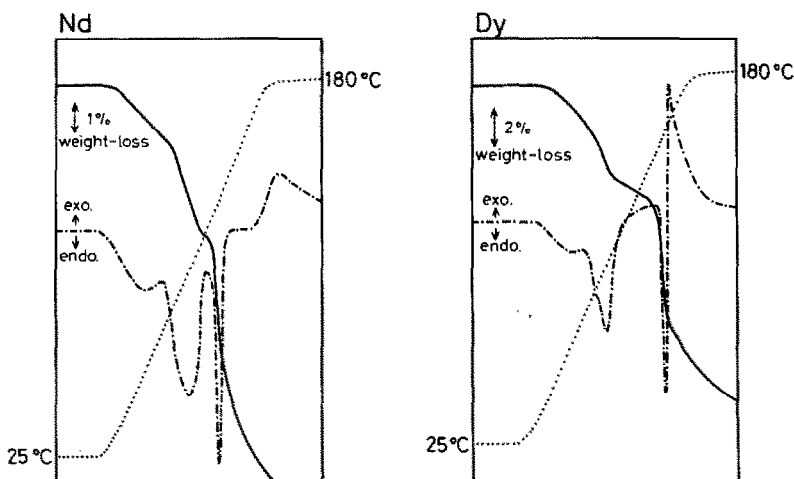
Fig. 3. TG–DTA curves of neodymium(III) and dysprosium(III) complexes with 14-membered macrocycle. (————): TG (- - - - -): DTA; (· · · · · · · ·): temperature.

accompanied by weight losses of 5.2 and 7.9% in the TG curve, which agree well with values calculated from the assumption that two and three moles of H_2O respectively are eliminated from one mole of the complex. This thermal analysis suggests that the water molecules in the complex are included in different fashions: one water molecule as lattice water, two water molecules weakly coordinated with the metal ion, and three water molecules coordinated rather strongly with it. A likely formula for this complex therefore is represented as $[Nd(N_4[14])(H_2O)_5]^{3+} \cdot (NO_3^-)_3 \cdot H_2O$, in which the central neodymium(III) ion adopts the frequently observed nine-coordination. For $Dy(N_4[14])(NO_3)_3 \cdot 5.5H_2O$, the DTA curve exhibits four endothermic peaks at 65, 90, 101, and 155°C, being accompanied with weight losses corresponding to those in the TG curve. Their percentages (2.6, 1.3, 2.6 and 7.8%) agree well with values calculated from the assumption that one, one-half, one and three water molecules, are respectively, successively eliminated from one molecule of the complex. A likely formula for this complex therefore is represented as $[Dy(N_4[14])(H_2O)_4]^{3+} \cdot (NO_3^-)_3 \cdot 1.5H_2O$, in which the central dysprosium(III) ion adopts the often observed eight-coordination. The coordination bonds between the dysprosium(III) ion and the aqua ligands are considered to be stronger than in the corresponding neodymium(III) complex. Similarly, the likely formulae for the other lanthanide(III) complexes with 18-membered and 22-membered tetraaza macrocycles are $[Nd(N_4[18])(H_2O)_2]^{3+} \cdot (NO_3^-)_3 \cdot H_2O$, $[Dy(N_4[18])(H_2O)_3]^{3+} \cdot (NO_3^-)_3 \cdot H_2O$, $[Nd(N_4[22])(H_2O)_2]^{3+} \cdot (NO_3^-)_3 \cdot H_2O$, and $[Dy(N_4[22])(H_2O)_3]^{3+} \cdot (NO_3^-)_3 \cdot H_2O$, in which the central neodymium(III) and dysprosium(III) ions adopt six- and seven-coordinations, respectively. A comparison of the temperatures observed for dissociation of coordinated water molecules

suggests that the coordination bond between the central metal(III) ion and the aqua ligands in the complexes becomes stronger in the order of $Nd-N_4[14] < Dy-N_4[14] < Nd-N_4[22] < Nd-N_4[18] < Dy-N_4[22] < Dy-N_4[18]$.

CONCLUSIONS

As we have already reported for the copper(II) complexes with the present macrocyclic Schiff base ligands, all the ligands are deprotonated by complex formation with the copper(II) ion [5], whereas in the lanthanide(III) complexes they coordinate with the metal ion as a neutral ligand. In addition, the 22-membered macrocycle formed bi- and tri-nuclear copper(II) complexes per one ligand molecule, in which copper(II) ions are bridged by acetato groups. On the other hand, these ligands formed lanthanide(III) complexes with a 1:1 ratio of the ligand to the metal ion. Such a significant difference between copper(II) and lanthanide(III) ions may result from the properties of the metal ions [8] themselves: (1) the lanthanide(III) ions have larger ionic radii than that of copper(II) ion, (2) the lanthanide(III) ions can adopt various coordination numbers (6–12), whereas those of the copper(II) ion are relatively restricted to 4–6, and (3) the lanthanide(III) ions behave as harder cations than the copper(II) ion, and their cation–ligand interactions are thus almost electrostatic in character.

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