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Trinuclear to Dinuclear: A Radii Dependence Lanthanide(III) Self-Assembly Coordination Behavior of an Amide-Type Tripodal Ligand

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Lanthanide nitrate complexes with the heptadentate ligand L (6-[2-(2-(diethylamino)-2-oxoethoxy)ethyl]-*N*,*N*,12-triethyl-11-oxo-3,9-dioxa-6,12-diazatetradecanamide), $[Ln_2L(NO_3)_6]$ (Ln = La, Nd, Sm, Eu, Ho), have been prepared and characterized. The X-ray crystallographic studies show that, in $[La_2L(NO_3)_6(H_2O)]\cdot H_2O$ (**1**), two complex cations $[LaL(H_2O)]^{3+}$ are linked by a hexanitrato anion $[La(NO_3)_6]^{3-}$ and form a trinuclear cation. In $[Nd_2L(NO_3)_6(H_2O)]\cdot CHCl_3\cdot 1/2CH_3OH\cdot 1/2H_2O$ (**2**), one complex cation $[NdL(H_2O)]^{3+}$ and a hexanitrato complex anion $[Nd(NO_3)_6]^{3-}$ are linked by a bridging NO_3^- to form a dinuclear complex. In both complexes, the bridging nitrate is an unusual tetradentate ligand. The metal ions are 12-coordinated in hexanitrato anions and 10-coordinated in complex cations. The chainlike supramolecular structures of La^{3+} complex are parallel and have no hydrogen bonds in between, while, in the Nd^{3+} complex, a chiral cavity is formed by hydrogen bonds between two adjacent supramolecular chains. These influences are further investigated by assessing the separation efficiency of L and ^1H NMR spectra of its lanthanide nitrate mixtures in solution.

Introduction

Polynuclear lanthanide complexes usually exhibit fascinating properties that may have potential applications in biology, medicine, and material science.[1] But because of their variable coordination behavior,[2] trivalent lanthanide ions are difficult to introduce into organized molecular or supramolecular architectures selectively.[3] The assembly of oligonuclear coordination compounds is still a burgeoning field.[4]

Recently, c^{o}mplexes containing open-chain polyethers and tripodal ligands have been widely studied in view of their excellent ion selectivities[5] and controllable electronic, magnetic, and luminescent properties.[6] On the basis of these ligands, programmed secondary noncovalent interstrand interactions (π-stacking, hydrogen bonds, electrostatic repulsion) assist the complexation process leading to an ultrafine-tuning of the metallic coordination structures.[6,7] Up to now, a few mono-, di-, and polymetallic lanthanide complexes have been synthesized by use of the approaches mentioned above. However, the number of lanthanide supramolecular structures is still very poor in contrast with that of transition metal suprramolecular structures,[8] especially when using tripodal ligands as hosts.[9]

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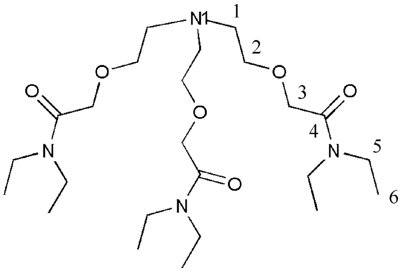
Chart 1



Our group is interested in the supramolecular coordination chemistry of amide tripodal ligands with Ln^{3+} ions and recently reported a one-dimensional chainlike coordination polymer generated from the reaction of $Eu(NO_3)_3$ with 1,1,1-tris{[(2-(benzylamino)formyl)phenoxyl]methyl}propane.[9] Work along these lines is also in progress. During this course, we find that L (Chart 1) can form one-dimensional chains in La^{3+} and Nd^{3+} complexes. Moreover, in Nd^{3+} complex, the helical arrangement of the hydrogen bonds forms a chiral cavity between two adjacent chains that are bridged by methanol molecules. To our knowledge, this type of chiral cavity is the first example in the complexes of amide tripodal ligands. Herein, we give a detailed description of the self-assembly behaviors of lanthanum and neodymium complexes controlled by both coordination and hydrogen bonds and show the effects of metal radii and the nitrate template on the formation of di- or trinuclear complexes. Solvent extraction studies of lanthanum(III) and neodymium(III) from nitric acid solutions show that the ligand L has a better selectivity for neodymium(III).

Experimental Section

General Details. α-Chloride-*N*,*N*-diethylacetamide was prepared by following the literature method.[10] THF and triethanolamine were dried by 4 Å molecule sieve. The other chemicals were of A R grade and used without further purification.

X-ray diffraction data were collected at room temperature on a R3M/E four-circle diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The unit-cell parameters were determined by least-squares refinement of 24−25 reflections. The data sets were corrected for Lorents and polarization effects. IR spectra were recorded on a Nicolet 170SXFT-IR instrument using KBr disks in the 220−4000 cm^{-1} region. ^1H NMR spectra were measured on a FT-300A spectrometer in CD_3COCD_3 solution with TMS as an internal standard. Extraction procedures were carried out according to the literature.[11] The cation concentration remaining in aqueous phase was determinated spectrophotometrically using Arsenazo III as indicator.

Preparation of the Ligand. A solution of triethanolamine (1.5 g, 10 mmol) in THF was added dropwise into a THF solution that was suspended with NaH (1.2 g, 60%, 30 mmol), and the mixture was stirred under nitrogen at room temperature until no gas appeared. Then a solution of α-chloride-*N*,*N*-diethylacetamide (4.9 g, 33 mmol) in THF was added dropwise into the mixture. After the mixture was refluxed for 6 h, the THF was evaporated and the residue was washed by column chromatography (silica gel, 2:1 $CHCl_3/CH_3CO_2Et$) resulted a yellow oil (4.3 g, yield = 56%). ^1H NMR: $\delta = 1.08$ (m, 18H; H6), 2.82 (t, 6H; H1), 3.33 (m, 12H, H5), 3.59 (t, 6H; H2), 4.13 ppm (s, 6H; H3). IR: $\nu = 1646$ (C═O), 1121 (C−O−C), 1087 cm^{-1} (C−N).

Table 1. Analytical Data for the Complexes (%)

complex	found (calcd)			
	C	H	N	Ln
$[La_2L(NO_3)_6]$	25.69 (25.31)	4.21 (4.22)	12.38 (12.30)	24.05 (24.42)
$[Nd_2L(NO_3)_6]$	25.37 (25.08)	4.43 (4.18)	11.98 (12.20)	24.82 (25.11)
$[Sm_2L(NO_3)_6]$	24.75 (24.81)	4.38 (4.14)	11.95 (12.06)	25.44 (25.91)
$[Eu_2L(NO_3)_6]$	24.80 (24.74)	4.14 (4.12)	12.01 (12.03)	25.98 (26.12)
$[Ho_2L(NO_{36}]$	24.08 (24.20)	4.04 (4.03)	11.94 (11.77)	27.97 (27.73)

Synthesis of the Complexes. Lanthanide nitrates (0.2 mmol) were dissolved in absolute C_2H_5OH (5 cm^3), and the solution was added dropwise to a solution of L (0.2 mmol) in absolute C_2H_5OH. The mixture was stirred at room temperature for 4 h, and the obtained white powder was redissolved in the solvent of 1:1 $CH_3OH/CHCl_3$; after evaporation for several months, crystals suitable for single-crystal X-ray studies were obtained.

Solvent Extraction Procedure. Standard lanthanide solutions were made from high-purity lanthanide oxides (99.99%) dissolved in nitric acid. Lithium nitrate was introduced to obtain stock source phase solutions containing 0.2 mM lanthanide and 0.1 M $LiNO_3$. The aqueous solution was altered to the required pH with lithium hydroxide and dilute nitric acid. The pH was maintained at 6.7 ± 1 in the experiments. Dissolving the desired amount of L in chloroform produced the extractant solvent phase.

Equal volumes (3 cm3) of each solution were thoroughly mixed by stirring in a stoppered tube at 20 ± 1 °C for 30 min. After phase separation by centrifugation, the concentration of the cation remaining in the aqueous phase was monitored spectrophotometrically with arsenazo(III) as a colored indicator. A 5 cm^3 volume of arsenazo solution (6×10^{-4}) and 1 cm^3 sodium monochloroacetate/monochloroacetic acid buffer were added to 1 cm^3 aqueous phase, and the volume was finally adjusted to 10 cm^3 with distilled water. The absorbances were then determined at 660 nm. Since the concentration of arsenazo(III) is at least 15 times higher than the concentration of the cation, complete complexation of the cation can be assumed. The concentration of the nitrate in the aqueous phase was then determined.

Results and Discussion

Physical Measurements. Analytical data for the complexes conform to a 2:1 (metal:L) stoichiometry, $[Ln_2L(NO_3)_6]$ (Table 1). All the complexes are soluble in DMSO, acetone, CH_3CN, and $CHCl_3$ and slightly soluble in CH_3OH.

The IR spectrum of free L shows bands at 1646, 1121, and 1087 cm^{-1}, which may be assigned to ν(C═O), ν(C−O−C), and ν(C−N1), respectively. In the IR spectra of the lanthanide complex, three bands shift by 30, 13, and 59 cm^{-1} toward lower wavenumbers, thus indicating that the C═O, ether O, and N1 atoms take part in coordination to the metal ion.

^1H NMR spectra of L and its 1:2 mixtures with lanthanide nitrates in deuterated acetone are presented in Figure 1. For the $La(NO_3)_3$ mixture, the signals of H1, H2, and H3 move to lower field (0.28, 0.51, and 0.70 ppm for H1, H2, and H3, respectively) than those of the free ligand, suggesting the coordination of C═O, ether O, and N1 atoms (see Figure

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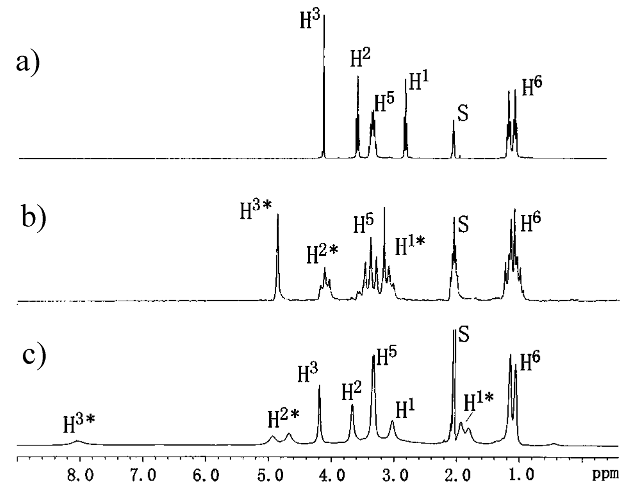

Figure 1. ^1H NMR spectra in deuterated acetone at 298 K of (a) L, (b) a 1:2 mixture of L and $La(NO_3)_3$, and (c) a 1:2 mixture of L and $Nd(NO_3)_3$. Asterisks denote the signals of complexed ligand, and S indicates the solvent signal.

1b), while the case in the $Nd(NO_3)_3$ mixture is more complicated because of the effects of paramagnetic Nd^{3+} and steric structure of ligand. Compared to the $La(NO_3)_3$ mixture, the NMR spectrum shows for the $Nd(NO_3)_3$ mixture a partial dissociation of the ligand with distinct proton signals, in which H2 and H3 have larger shifts to low field (1.22 and 3.88 ppm for H2 and H3) and H1 shifts to upfield (0.98 ppm). Unchanged signals of H1, H2, and H3 indicate that the coordinated ligand is in equilibrium with free ligand in solution (Figure 1c). Similar states have also been reported in other papers,[12] and more investigations about ^1H NMR spectra of lanthanide complexes with L are still under way. All the ^1H NMR shifts mentioned above are listed in Table S1. ^1H NMR spectra of L and its 1:1 and 1:2 mixtures with $Nd(NO_3)_3$ are given in Figure S1. A two-dimensional homonuclear COSY correlation spectrum of the 1:2 mixture of L and $Nd(NO_3)_3$ is given in Figure S2, which could help us to understand the spectra more clearly.

X-ray Structure Determinations. Table 2 shows the molecular structure and the atomic numbering schemes for the crystal complexes, **1** and **2**. The single-crystal X-ray analyses of the complexes reveal that when coordinated to the metal ion, L acts as a heptadentate ligand with one nitrogen, three carbonyl oxygen, and three ether oxygen donor atoms. Three chains of L stretch around the metal ion and form a cuplike cavity to encapsulate the ion. In the molecule of **1**, two complex cations $[LaL(H_2O)]^{3+}$ and a hexanitrato complex anion $[La(NO_3)_6]^{3-}$ are linked by two bridging NO_3^- forming a trinuclear cation. Another separated hexanitrato complex anion is restricted to this cation by electrostatic force (Figure 2a), while, in the molecule of **2**, one complex cation $[NdL(H_2O)]^{3+}$ and a hexanitrato complex anion $[Nd(NO_3)_6]^{3-}$ are linked by a bridging NO_3^- forming a dinuclear complex (Figure 2b). For both complexes, the metal ions are 12-coordinated in hexanitrato anions and 10-coordinated in complex cations.

Table 2. Selected Crystal Data for **1** and **2**

param	**1**	**2**
formula	$C_{24}H_{52}N_{10}O_{26}La_2$	$C_{25.5}H_{54}Cl_3N_{10}O_{26}Nd_2$
M_r	1174.58	1311.62
space group	$P2/c$	$P2_12_12_1$
a (Å)	17.768(2)	12.969(5)
b (Å)	11.568(2)	15.359(4)
c (Å)	21.966(4)	25.553(8)
α (deg)	90	90
β (deg)	98.60(10)	90
γ (deg)	90	90
V (Å^3)	4464.1(12)	5090(3)
Z	4	4
ρ (mg cm^{-3})	1.748	1.712
T (K)	290(2)	288(2)
μ (mm^{-1})	1.985	2.263
R^a	0.0333	0.0432
$R_w{}^b$	0.0796	0.0979

[a] $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $R_w = \Sigma(w^{1/2}||F_o| - |F_c||)/\Sigma w^{1/2}|F_o$.

The bridging tetradentate nitrate in the two complexes has a bilaterally symmetrical structure somewhat resembling a butterfly; two wings of the butterfly-like structure form a mean dihedral angle of 177.50°. In the La^{3+} complex, three lanthanum ions are linked by two butterfly-like structures, and the distances between three bridged cations are 5.453 Å, respectively. The fourth separated lanthanum lies at a relatively further distance of 7.614 Å, while, in the Nd^{3+} complex, only two neodymium ions are linked by a tetradentate nitrate, the distance between them being 5.386 Å.

Both of the complexes form one-dimensional supramolecular chainlike structures through the linear repeating of the complex molecules. The chainlike structures of La^{3+} complex are parallel and have no hydrogen bonds between, while, in the Nd^{3+} complex, a chiral cavity is formed between two adjacent chains (Figure 3a) in which a CH_3OH molecule forms two hydrogen bonds with a bidentate NO_3^- from one chain and a coordinated H_2O molecule from another chain; the angle between two hydrogen bonds is 125.2°. Out of the helical chains, there is also a $C-H\cdots O$ hydrogen bond between a bidentate NO_3^- and a $CHCl_3$. From Figure 3b we can see that the oxide atoms adopt a helical arrangement.

Metal Extraction. The overall extraction equilibrium between an aqueous solution of trivalent metal cation (M^{3+}) and nitrate anion (NO_3^-) and an organic solution of ligand (L) can be expressed as in eq 1. The extraction equilibrium constant (K_{ex}) can be written by eq 2. In view of the tracer amount of mental ions extracted, the distribution ratio, D, is given by eq 3. Modification of eq 2 leads to eq 4. The complexation stoichiometry (n) and the extraction equilibrium constant (K_{ex}) can be determined by use of the slope method according to eq 4. The total ligand concentration in organic phase is much higher than that of the metal ion in aqueous phase and the distribution of free ligand can be neglected, so the total ligand concentration was used here.

$$M^{3+}_{aq} + 3NO_3{}^-{}_{aq} + nL_{org} \leftrightarrow [M(L)_n(NO_3{}^-)_3]_{org} \quad (1)$$

$$K_{ex} = ([M(L)_n(NO_3{}^-)_3]_{org})/([M^{3+}]_{aq}[NO_3{}^-]^3{}_{aq}[L]^n{}_{org}) \quad (2)$$

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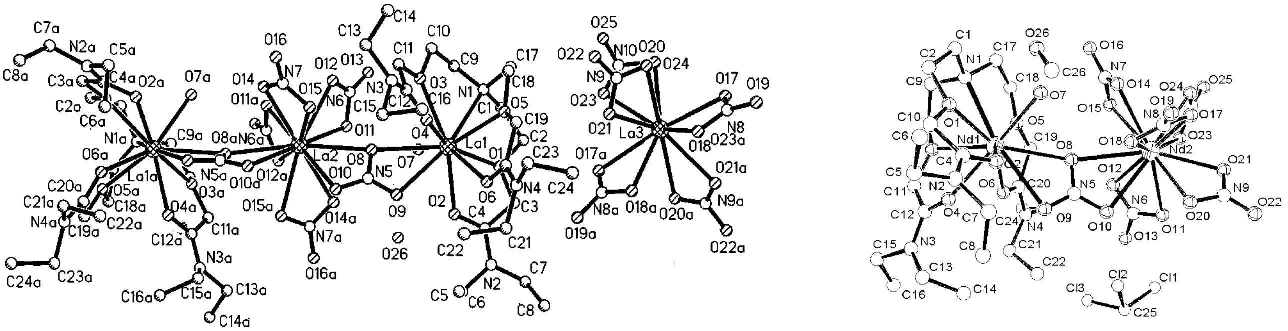

a b

Figure 2. Molecular structures of (a) **1** and (b) **2**. Thermal ellipsoids are represented in 50% probability.

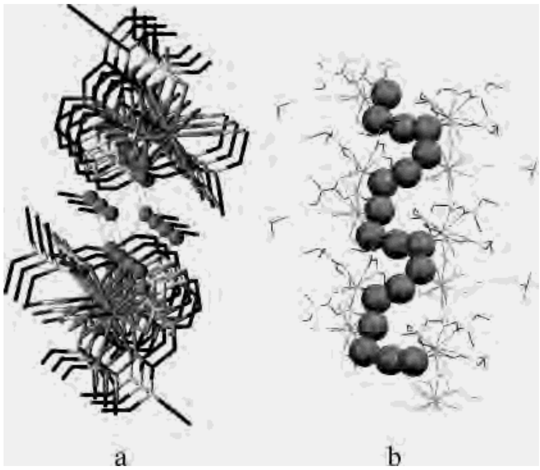

Figure 3. (a) Chiral cavity formed by H-bonds and (b) the helical arrangement of the oxide atoms.

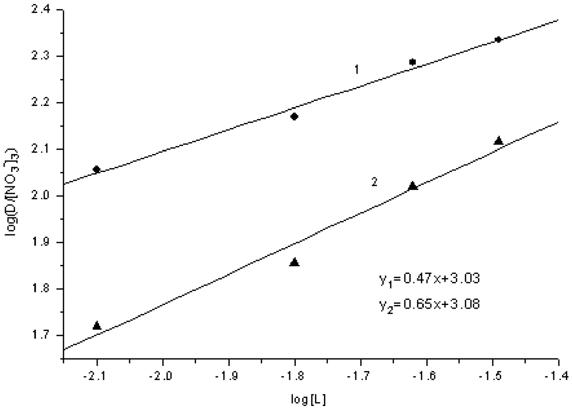

Figure 4. Plots of $\log(D/[\mathrm{NO_3}^-]^3_{\mathrm{aq}})$ versus $\log[\mathrm{L}]_{\mathrm{org}}$ obtained in extration experiments on L with lanthanum (1) and neodymium (2).

$$D = ([\mathrm{M(L)}_n(\mathrm{NO_3}^-)_3]_{\mathrm{org}})/[\mathrm{M}^{3+}]_{\mathrm{aq}} \qquad (3)$$

$$\log(D/[\mathrm{NO_3}^-]^3_{\mathrm{aq}}) = n \log[\mathrm{L}]_{\mathrm{org}} + \log K_{\mathrm{ex}} \qquad (4)$$

To characterize the extraction ability, the dependence of the distribution ratio D (Table 3) of a cation between the two phases upon the L concentration has been examined.

As exemplified in Figure 4, the slopes of linear plots for the extraction of La^{3+} and Nd^{3+} are nearly 0.5, indicating that L forms 1:2 extractives with La^{3+} and Nd^{3+} under the conditions employed. The $\log K_{\mathrm{ex}}$ value of Nd^{3+} (3.08) is a little higher than that of La^{3+} (3.03).

In general, the heptadentate ligand L can form 2:1 (metal/L) stoichiometry complexes with $\mathrm{Ln(NO_3)_3}$ (Ln = La, Nd, Sm, Eu, Ho) in solid state as well as in solution. IR and ^{1}H NMR spectra show that the C=O, ether O, and N1 atoms of the ligand take part in coordination to metal ions. More detailed solution NMR studies reveal that the ligand binds La^{3+} more strongly than binds Nd^{3+} in acetone with nitrate anion as counterion. The solid structures of the La^{3+} and Nd^{3+} complexes differ in crystal system, space group, or composition. The bridging tetradentate nitrates are key factors in the formation of polynuclear complexes. It is possible that these differences in the structures reflect a coordination selectivity of L for different lanthanide ions. In the Nd^{3+} complex, hydrogen bonds play an important role in the construction of supramolecular chiral cavity, which could be a significant extension in chiral recognition and chiral catalyst.

Table 3. Distribution Ratios and Separation Factors of La^{3+} and Nd^{3+}

	concn of the ligand (mol/L)			
	0.008	0.016	0.024	0.032
$D_{\mathrm{La(III)}}$	0.114	0.147	0.193	0.217
$D_{\mathrm{Nd(III)}}$	0.05	0.07	0.10	0.13
$\mathrm{SF}_{\mathrm{La/Nd}}$	2.28	2.10	1.93	1.67

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Supporting Information Available: ^{1}H NMR shifts of L and its 1:2 mixtures with $\mathrm{La(NO_3)_3}$ and $\mathrm{Nd(NO_3)_3}$ in Table S1, ^{1}H NMR spectra of L and its 1:1 and 1:2 mixture with $\mathrm{Nd(NO_3)_3}$ in Figure S1, a two-dimensional homonuclear COSY correlation spectrum of the 1:2 mixture of L and $\mathrm{Nd(NO_3)_3}$ in Figure S2, and X-ray crystallographic files in CIF format, for the two structures. This material is available free of charge via the Internet at http://pubs.acs.org.

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