

# Molecular Design of Crown Ethers. 16.<sup>1</sup> Calorimetric Titration of Complexation of Light Lanthanoid Nitrates with *N*-Benzylaza-16-crown-5 and 15,15-Dimethyl-16-crown-5 in Acetonitrile: Enhanced Selectivity for Pr<sup>3+</sup>

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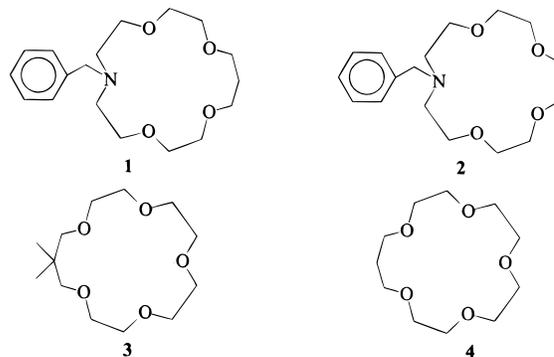
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Calorimetric titrations have been performed in anhydrous acetonitrile at 25 °C to give the complex stability constants ( $K_s$ ) and the thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) for the stoichiometric 1:1 complexation of light lanthanoid(III) nitrates (La–Gd) with *N*-benzylaza-16-crown-5 (**1**) and 15,15-dimethyl-16-crown-5 (**3**). Using the present and previous data, the effects of substitution and ring enlargement of crown-5 derivatives (**1**–**4**) upon complexation behavior are discussed comparatively from the thermodynamic point of view. Possessing a less-symmetrical skeleton and the same N-substitution as compared with *N*-benzylaza-15-crown-5 (**2**), *N*-benzylaza-16-crown-5 (**1**) gave lower complex stabilities by 1–2 orders of magnitude for all light lanthanoids examined, but exhibited significantly altered relative cation selectivity with much enhanced preference up to 8 for Pr<sup>3+</sup> over the other light lanthanoids. The lower complex stabilities for **3** than for the parent 16-crown-5 **4** are attributed to the reduced enthalpic gains caused by the steric hindrance between the axial methyl group introduced at C-15 and the accommodated cation, but the methyl substitution appears to help lock the ring conformation such that complexation can occur, as indicated by the positive entropic changes for most light lanthanoids. These results indicate that the introduction of a nondonating sidearm to C- and N-pivot 16-crown-5 alters significantly not only the binding constant but also the relative cation selectivity.

## Introduction

A wide variety of lariat ethers with donating or nondonating sidearm(s) attached to the parent crown ethers through a C- or N-pivot have been designed and synthesized in order to alter the original cation-binding ability and/or selectivity.<sup>2–7</sup> Indeed, lariat ethers with additional binding sites in their sidearms give much enhanced cation-binding ability and selectivity as compared with the parent crown ether.<sup>8–13</sup> However, the studies on the complexation thermodynamics with lariat ethers have been concentrated mostly on alkali, alkaline earth, and some heavy metal salts, while little attention has been paid so far to the complexation thermodynamics of trivalent lanthanoids.<sup>14</sup> We have recently shown that both C- and N-pivot lariat ethers display distinctly different cation-binding ability and selectivity for the light lanthanoid series.<sup>1c,15</sup> In particular, the N-pivot lariat 16-crown-5, which carries a donating sidearm, shows specific cation-binding ability and selectivity for Nd<sup>3+</sup> in the light lanthanoids. This indicates that the increased conformational freedom of the ligand is more suitable for the recognition of trivalent lanthanoid ions by lariat ethers. On the other hand, we also revealed that the introduction of nondonating alkyl groups to 16-crown-5 at C-15 alters not only the complexing ability with alkali, alkaline earth, and some heavy metal salts but also the relative cation selectivity significantly.<sup>16</sup> Unfortunately, thermodynamic study of less-symmetrical crown ethers with nondonating sidearms upon complexation with trivalent

## CHART 1



lanthanoid ions has been not performed, to our best knowledge. Therefore, these results prompted us to investigate the complexation behavior of less-symmetrical C- and N-pivot 16-crown-5 bearing a nondonating sidearm with lanthanoid nitrates from a thermodynamic viewpoint.

In the present study, we synthesized N- and C-pivot 16-crown-5 with nondonating sidearm(s) (**1** and **3**) (Chart 1) and investigated their complexation thermodynamics with light lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) in acetonitrile, using titration calorimetry. The thermodynamic quantities obtained, together with those reported for *N*-benzylaza-15-crown-5 (**2**)<sup>17</sup> and 16-crown-5 (**4**),<sup>15</sup> will provide further understanding of the complexation behavior of N- and C-pivot 16-crown-5 possessing nondonating sidearm(s) with light lanthanoid nitrates. It is another point of interest to examine the influence of the ligand's cavity size, substitution, and the pivot

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atom upon complexation of less-symmetrical 16-crown-5 with light lanthanoids from the thermodynamic point of view.

## Experimental Section

**General Procedure.** IR spectra were recorded on a JASCO A-100 spectrometer. Mass spectra were obtained on a Hitachi RMU-6E instrument.  $^1\text{H}$  NMR spectra were recorded on a JEOL GX-400 spectrometer.

**Materials.** Less-symmetrical **1** was synthesized in 11% (5.3 g) yield by the reaction of *N*-benzylidethanolamine (in 200 mL THF) (29.9 g, 0.15 mol) with the ditosylate of 3,7-dioxanonane-1,9-diol (in 200 mL THF) (70.0 g, 0.14 mol) for 24 h in the presence of NaH (60% in oil) as a base in tetrahydrofuran. Purification by column chromatography (alumina, 0.5% ethyl acetate in *n*-hexane) and the subsequent distillation under reduced pressure gave the pure product (**1**):<sup>18</sup> bp 175–181 °C/0.5 Torr; MS (70 eV) *m/z* 323 ( $\text{M}^+$ ); NMR (400 MHz;  $\text{CDCl}_3$ )  $\delta$  1.83–1.86 (q, 2H), 2.80–2.83 (t, 4H), 3.59–3.61 (t, 6H), 3.62 (s, 8H), 3.65–3.68 (t, 4H), and 7.22–7.34 (m, 5H); IR/ $\text{cm}^{-1}$  2860, 1600, 1460, 1110, and 740. Anal. Calc for  $\text{C}_{18}\text{H}_{29}\text{O}_4\text{N}$ : C, 66.84; H, 9.04; N, 4.33; Found: C, 66.30; H, 9.06; N, 4.46. Compound **3** was synthesized from tetraethylene glycol bis(*p*-toluenesulfonate) and 2,2-dimethyl-1,3-propanediol according to the method reported previously.<sup>16</sup> Analytical-grade acetonitrile was dried over calcium hydride and then distilled fractionally to give the anhydrous solvent ( $<5 \times 10^{-7}$  S  $\text{cm}^{-1}$ ) for calorimetry.

Light lanthanoid(III) nitrates (La–Gd) were prepared by dissolving the corresponding oxides of 99.9% purity (Baotou Rare Earth Chemical Co.) in 50% aqueous nitric acid while heating for about 10 min. After evaporation, the solid residue was dehydrated with  $\text{P}_2\text{O}_5$  in vacuo for several days to give a powdery product. The lanthanoid nitrates obtained were dissolved in anhydrous acetonitrile and refluxed for 24 h over molecular sieves for further removal of water. The concentrations of the lanthanoid nitrate solutions in acetonitrile were determined by the EDTA titration using xylenol orange as an indicator. The conductometric measurements showed that these light lanthanoid nitrates behave as nonelectrolytes in anhydrous acetonitrile solution.<sup>19</sup>

**Apparatus and Procedures.** Calorimetric titrations were performed at atmospheric pressure in a temperature-controlled water bath maintained at 25.0 °C, by using a TRONAC model 458 isoperibol titration calorimeter connected to a personal computer for automated titration and data processing.<sup>20</sup> The principle of the measurement and the detailed experimental procedures were reported elsewhere.<sup>21,22</sup> Typically, a crown ether solution (40–50 mM) in anhydrous acetonitrile was continuously introduced at a rate of 0.3321  $\text{cm}^3 \text{min}^{-1}$  into a lanthanoid nitrate solution (1.5–2.5 mM) placed in the calorimeter. To obtain the net heat of complexation ( $Q_{\text{net}}$ ), the total apparent heat observed ( $Q_{\text{obs}}$ ) was corrected for the dilution of titrant ( $Q_{\text{D}}$ ), the nonchemical contributions ( $Q_{\text{HL}}$ ), including agitation, heat flow between the vessel and its surroundings, and resistance heating by the thermistor used, and the temperature difference between titrant and titrate ( $Q_{\text{TC}}$ ) in each run:  $Q_{\text{net}} = Q_{\text{obs}} - Q_{\text{D}} - Q_{\text{HL}} - Q_{\text{TC}}$ . A titration curve was obtained by plotting the temperature change (measured by voltage) against the amount of the crown ether solution added, from which the complex stability constant ( $K_s$ ) and enthalpy change ( $\Delta H^\circ$ ) are calculated. Reliability of the whole system and the calculation procedures were doubly checked as previously<sup>23,24</sup> by comparison of the obtained thermodynamic parameters with the reported values,<sup>25</sup> and satisfactory results were obtained.

## Results

Assuming 1:1 stoichiometry<sup>26,27</sup> for the complexation of  $\text{Ln}(\text{NO}_3)_3$  ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{and Gd}$ ) with **1** and **3** (CE in eq 1), the complex stability constant ( $K_s$ ) and the enthalpy change ( $\Delta H^\circ$ ) were calculated by using the least-squares method to minimize the  $U$  value (eq 2):<sup>28,29</sup>



$$U(K_s, \Delta H^\circ) = \sum_{i=1}^m (Q_i - \Delta H^\circ N_i)^2 \quad (2)$$

where  $Q_i$  refers to the net heat of complexation measured at time  $t$  in minutes, and  $N_i$  denotes the amount in moles of the complex formed at time  $t$  and is directly related to the complex stability constant  $K_s$ .

The stability constant  $K_s$  and the enthalpy change  $\Delta H^\circ$  for the complexation of lanthanoid nitrates ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{and Gd}$ ) with **1** and **3** were calculated by computer simulation by continuously changing  $K_s$ , i.e.,  $N_i$ , to minimize the  $U$  value. For each lanthanoid–crown ether combination, the measurement was repeated more than three times, and the  $U$  value obtained was minimized satisfactorily in each case to give the optimized set of  $K_s$  and  $\Delta H^\circ$  with standard deviations. No serious deviation was found in the fitting process, verifying the 1:1 stoichiometry of complexation as assumed above. The complex stability constants and thermodynamic parameters obtained are listed in Table 1. For comparison purpose, the thermodynamic quantities reported for the complexation with **2** and **4** in acetonitrile are also included in Table 1.

## Discussion

**Molecular Symmetry and Substituent Effect.** As shown in Table 1, the introductions of an extra methylene group into **2**, giving the less-symmetrical compound **1**, and of the axial methyl substituents at C-15 for **4**, giving **3**, alter significantly not only the cation-binding constant but also the relative cation selectivity for the trivalent lanthanoid ions. To visualize the cation-binding properties and relative cation selectivity of crown ethers **1–4**, the changing profile of the complex stability constant ( $K_s$ ) is plotted as a function of reciprocal ionic diameter of the lanthanoid in Figure 1.

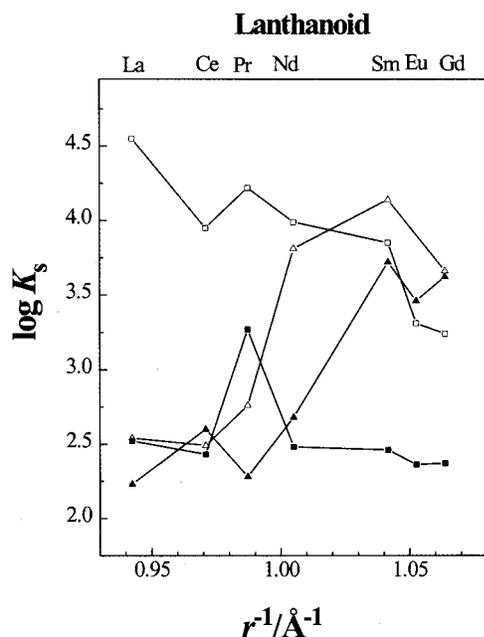
As can be seen from Figure 1, the profile of  $K_s$  for **2** displays a small local peak at  $\text{Pr}^{3+}$  and gradually declines with increasing atomic number or decreasing ionic radius from  $\text{Pr}^{3+}$  to  $\text{Gd}^{3+}$ . This result indicates that **2** possesses the highest cation selectivities primarily for  $\text{La}^{3+}$  and secondly for  $\text{Pr}^{3+}$ . The declining profile of  $K_s$  for light lanthanoids may be attributed to the increasing surface charge density due to the lanthanoid contraction and the subsequent tighter solvation for heavier lanthanoids,<sup>15</sup> since the size-fit concept does not appear to rationalize the preferred complexation of **2** (1.7–1.9 Å) with  $\text{La}^{3+}$  (2.12 Å) and  $\text{Pr}^{3+}$  (2.03 Å).

It is very interesting and significant that the introduction of an extra methylene group to **2**, affording less-symmetrical **1**, leads to the cation-binding constants and relative cation selectivities totally different from those for the reference compound **2**, as shown in Figure 1. The ring enlargement in **1** drastically lowers the complex stability ( $K_s$ ) for all lanthanoids by 1–2 orders of magnitude, but its effect upon  $K_s$  is not uniform in the light lanthanoid series. The decrease in  $K_s$  caused by the ring enlargement declines in general with increasing atomic number from  $\text{La}^{3+}$  to  $\text{Gd}^{3+}$ , flattening the  $K_s$  profile of

**TABLE 1: Complex Stability Constants ( $\log K_s$ ) and Thermodynamic Parameters (in kcal mol<sup>-1</sup>) for Complexation of Light Lanthanoid(III) Nitrates with 1, 2, 3, and 4 in Anhydrous Acetonitrile at 25 °C**

ligand	cation	$\log K_s$	$-\Delta G^\circ$	$-\Delta H^\circ$	$T\Delta S^\circ$	ref
<b>1</b>	La <sup>3+</sup>	2.52 ± 0.01	3.44 ± 0.01	10.48 ± 0.04	-7.04 ± 0.05	<i>a</i>
	Ce <sup>3+</sup>	2.43 ± 0.02	3.31 ± 0.03	9.82 ± 0.07	-6.51 ± 0.08	<i>a</i>
	Pr <sup>3+</sup>	3.27 ± 0.01	4.46 ± 0.01	4.70 ± 0.02	-0.24 ± 0.03	<i>a</i>
	Nd <sup>3+</sup>	2.48 ± 0.01	3.38 ± 0.01	14.40 ± 0.09	-11.02 ± 0.15	<i>a</i>
	Sm <sup>3+</sup>	2.46 ± 0.03	3.36 ± 0.04	14.48 ± 0.06	-11.12 ± 0.01	<i>a</i>
	Eu <sup>3+</sup>	2.36 ± 0.03	3.22 ± 0.05	14.51 ± 0.10	-11.29 ± 0.12	<i>a</i>
	Gd <sup>3+</sup>	2.37 ± 0.01	3.23 ± 0.01	14.59 ± 0.10	-11.36 ± 0.10	<i>a</i>
<b>2</b>	La <sup>3+</sup>	4.55 ± 0.04	6.21	12.36 ± 0.03	-6.15	<i>b</i>
	Ce <sup>3+</sup>	3.95 ± 0.04	5.39	9.47 ± 0.03	-4.08	<i>b</i>
	Pr <sup>3+</sup>	4.22 ± 0.02	5.76	11.09 ± 0.07	-5.33	<i>b</i>
	Nd <sup>3+</sup>	3.99 ± 0.02	5.44	11.16 ± 0.08	-5.72	<i>b</i>
	Sm <sup>3+</sup>	3.85 ± 0.02	5.25	11.87 ± 0.01	-6.62	<i>b</i>
	Eu <sup>3+</sup>	3.31 ± 0.03	4.51	13.99 ± 0.04	-9.47	<i>b</i>
	Gd <sup>3+</sup>	3.24 ± 0.03	4.42	15.54 ± 0.06	-11.12	<i>b</i>
<b>3</b>	La <sup>3+</sup>	2.23 ± 0.02	3.04 ± 0.03	6.21 ± 0.01	-3.17 ± 0.08	<i>a</i>
	Ce <sup>3+</sup>	2.60 ± 0.03	3.55 ± 0.05	2.85 ± 0.05	0.70 ± 0.09	<i>a</i>
	Pr <sup>3+</sup>	2.28 ± 0.05	3.11 ± 0.06	3.90 ± 0.15	-0.79 ± 0.13	<i>a</i>
	Nd <sup>3+</sup>	2.68 ± 0.08	3.66 ± 0.11	3.07 ± 0.01	0.59 ± 0.11	<i>a</i>
	Sm <sup>3+</sup>	3.72 ± 0.02	5.07 ± 0.02	1.76 ± 0.06	3.31 ± 0.05	<i>a</i>
	Eu <sup>3+</sup>	3.46 ± 0.04	4.72 ± 0.05	1.25 ± 0.05	3.47 ± 0.05	<i>a</i>
	Gd <sup>3+</sup>	3.62 ± 0.01	4.94 ± 0.02	0.82 ± 0.06	4.12 ± 0.06	<i>a</i>
<b>4</b>	La <sup>3+</sup>	2.54 ± 0.03	3.46	14.51 ± 0.09	-11.05	<i>c</i>
	Ce <sup>3+</sup>	2.49 ± 0.01	3.40	8.47 ± 0.11	-5.07	<i>c</i>
	Pr <sup>3+</sup>	2.76 ± 0.03	3.76	8.55 ± 0.01	-4.79	<i>c</i>
	Nd <sup>3+</sup>	3.81 ± 0.04	5.20	3.72 ± 0.05	1.48	<i>c</i>
	Sm <sup>3+</sup>	4.14 ± 0.08	5.65	5.75 ± 0.08	-0.10	<i>c</i>
	Gd <sup>3+</sup>	3.66 ± 0.07	4.99	5.46 ± 0.05	-0.47	<i>c</i>

<sup>a</sup> This work; average of more than three independent measurements. <sup>b</sup> Reference 17. <sup>c</sup> Reference 15.



**Figure 1.** Complex stability constant ( $K_s$ ) as a function of reciprocal ionic radius ( $r^{-1}$ , Å<sup>-1</sup>) for the complexation of light lanthanoids with **1** (■), **2** (□), **3** (▲) and **4** (△) in acetonitrile at 25 °C.

**1** except for Pr<sup>3+</sup>. Interestingly, the  $K_s$  for Pr<sup>3+</sup> does not adhere to this general tendency and decreases only by less than 1 order of magnitude from 4.22 for **2** to 3.27 for **1**, showing the highest selectivity of up to 8 for Pr<sup>3+</sup> over any other lanthanoids. This specific cation selectivity for Pr<sup>3+</sup> may be attributed to the appropriate ring size and donor orientation of **1** for Pr<sup>3+</sup>.

On the other hand, the introduction of nondonating methyl group(s) to **4** at the 15-position is known to lower the binding constant significantly without any serious accompanying changes in the relative cation selectivity.<sup>15,16</sup> As shown in Figure 1,

analogous tendencies are seen with **4** and **3** in the complex stability constant ( $K_s$ ) for all light lanthanoids examined. Except for the generally lower  $K_s$  for **3**, there are small differences between **3** and **4**: the profile of  $K_s$  for **4** shows a sudden jump at Nd<sup>3+</sup> and keeps high  $K_s$  values over Nd–Gd, but that for **3** gives a sudden jump at Sm<sup>3+</sup> and keeps high  $K_s$  values over Sm–Gd. This is probably due to the steric hindrance between the axial methyl group introduced at C-15 and the accommodated cation.<sup>16</sup> These results may indicate that the size-fit concept is more rigorous in the complexation of trivalent lanthanoid ions,<sup>15</sup> since the ionic diameters (1.88–1.91 Å<sup>30</sup>) of Sm<sup>3+</sup> through Gd<sup>3+</sup> apparently match the cavity of 16-crown-5 (1.8–1.9 Å<sup>15</sup>). It is concluded therefore that the decreased molecular symmetry and the nondonating sidearm(s) introduced to crown-5 alter not only the binding ability for trivalent lanthanoid ions but also the relative cation selectivity significantly. In particular, **1** shows much enhanced selectivity for Pr<sup>3+</sup>.

**Thermodynamic Parameters.** As can be recognized more easily from Table 1, all the  $\Delta H^\circ$  values for the complex formation of crown ethers **1–4** with trivalent lanthanoid ions are negative with either negative or slightly positive entropy changes. This means that these reactions are chiefly enthalpy-driven in acetonitrile. The larger enthalpic gains ( $-\Delta H^\circ$ ) for **1** and **2** than for **3** and **4** may indicate stronger ion–dipole interactions between the lanthanoid cation and the donor nitrogen in aza-crown-5 **1–2**, but the large enthalpic gain does not immediately mean high complex stability and is often canceled by the larger entropic loss arising from structural freezing upon complexation, as is the case with the binding of most lanthanoids with **1**. Compared with **2**, an extra methylene group in **1** inevitably enhances the entropic loss ( $T\Delta S^\circ$ ) for La, Ce, and Nd–Gd by 0.24–5.3 kcal mol<sup>-1</sup>, leading to low complex stabilities, but specifically diminishes the entropic loss ( $T\Delta S^\circ$ ) for Pr<sup>3+</sup> by 5.09 kcal mol<sup>-1</sup>, thus affording the higher relative cation selectivity. It is concluded that the complexation

itself is enthalpy-driven in acetonitrile, but the cation selectivity is mainly governed by entropy change for all crown ethers examined.

It is also interesting and significant to compare thermodynamic parameters for the complexation of N- and C-pivot 16-crown-5 derivatives (**1** and **3**) with trivalent lanthanoid ions. As can be seen from Figure 1, the cation selectivity sequences and the thermodynamic profiles observed for both less-symmetric crown ethers with nondonating sidearms are totally different. CPK molecular model examination indicated that the ring skeleton of **3** is locked in part by the two methyl substituent groups at C-15 to enhance its molecular rigidity. Therefore, N-pivot lariat ether **1** possesses the relatively large structural flexibility as compared with the C-pivot lariat ether **3** and must suffer substantial conformational change upon complexation with lanthanoid ions associated with drastic entropic losses, which reflects directly on the complex stabilities. On the other hand, the positive  $T\Delta S^\circ$  or smaller entropic losses for the complexation of C-pivot 16-crown-5 **3** with lanthanoid ions indicate that the two methyl groups at C-15 lock the 16-crown-5 framework in a conformation favorable for complexation, but the axial methyl groups at C-15 of **3**, as examined by the CPK model,<sup>16</sup> do not lead the serious steric hindrance for the cation accommodated in the cavity of the crown ether to afford an analogous tendency to the parent **4** in the binding and thermodynamic profiles. In the meanwhile, the decreased enthalpic gain for **3** (0.65–8.3 kcal mol<sup>-1</sup>) caused by methylation is compensated by the increased entropic gain (3.21–7.88 kcal mol<sup>-1</sup>) to some extent. From these results we may conclude that the crown ether's molecular symmetry, structural flexibility/rigidity, and size-fit to the cation's diameter jointly play crucial roles in the recognition of the trivalent lanthanoid ions.<sup>31</sup>

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