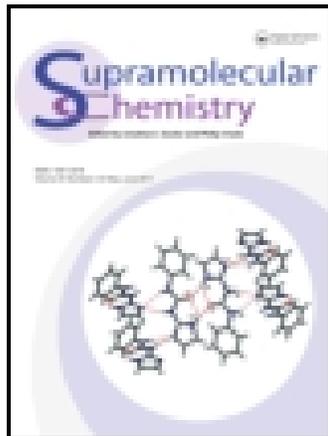


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### Molecular Design of Crown Ethers. 17[1]. Complexation Thermodynamics of Light Lanthanoid Nitrates with N-Benzylaza-21-crown-7 in Acetonitrile

Yu Liu , Shu-Ping Dong <sup>a</sup> , Hao Zheng <sup>a</sup> , Yoshihisa Inoue <sup>b</sup> & Mikio Ouchi <sup>c</sup>

<sup>a</sup> Department of Chemistry , Nankai University , Tianjin, 300071, China

<sup>b</sup> Faculty of Engineering , Osaka University , Yamadaoka, Suita, 565, Japan

<sup>c</sup> Department of Applied Chemistry , Himeji Institute of Technology , Shosha, Himeji, 671-22, Japan

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# Molecular Design of Crown Ethers. 17[1]. Complexation Thermodynamics of Light Lanthanoid Nitrates with *N*-Benzylaza-21-crown-7 in Acetonitrile

YU LIU<sup>a,\*</sup>, SHU-PING DONG<sup>a</sup>, HAO ZHENG<sup>a</sup>, YOSHIHISA INOUE<sup>b</sup> and MIKIO OUCHI<sup>c</sup>

<sup>a</sup> Department of Chemistry, Nankai University, Tianjin 300071, China;

<sup>b</sup> Faculty of Engineering, Osaka University, Yamadaoka, Suita 565, Japan;

<sup>c</sup> Department of Applied Chemistry, Himeji Institute of Technology, Shosha, Himeji 671-22, Japan

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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 ( $\Delta G^0$ ,  $\Delta H^0$  and  $\Delta S^0$ ) for the complexation of light lanthanoid(III) nitrates (La–Gd) with *N*-benzylaza-21-crown-7. Data analyses, assuming 1:1 stoichiometry, were successfully applied to all light lanthanoid-azacrown ether combinations employed. Using the present and previous data on 15- to 21-membered *N*-benzylazacrown ethers 1–3, the effect of ring size upon complexation behavior was discussed comparatively and globally from the thermodynamic point of view. The complexation behaviors are analyzed in terms of the size-fit concept, *N*-substituent coordination numbers, and lanthanoid's surface charge density. Thermodynamically the complexation of light lanthanoids with azacrown ethers is enthalpy-driven, while the cation selectivity is generally entropy-driven in acetonitrile.

**Keywords:** Crown ether, complexation thermodynamics, light lanthanoid nitrates, calorimetric titration, lariat ether

## INTRODUCTION

The molecular design and synthesis of host crown compounds possessing high cation selectivity have been one of the major subjects in the chemical science and technology [2–7]. Hence, a good deal of effort has been devoted to the investigations of the synthesis and complexation thermodynamics of a wide variety of crown ether [8]. In particular, lariat ethers are of special interest, since the additional binding site(s) introduced in the side chain have been shown to enhance the cation binding ability and selectivity of the original crown ether [9–15]. However, little attention has been paid to the complexation thermodynamics of lariat ethers with trivalent lanthanoid ions. We have recently shown that the nitrogen-pivot lariat ethers,

\*Corresponding author. Fax: Int.code +(22)2350-4853, e-mail: yuliu@public.tpt.tj.cn

which possess the structural flexibility as compared with the corresponding carbon-pivot lariat ethers, are more suitable for the discriminative recognition of trivalent lanthanoid ions [1a]. Interestingly, *N*-(2-methoxyethyl)aza-16-crown-5 with a donating side arm shows high cation binding ability and selectivity for  $\text{Nd}^{3+}$  and  $\text{Pr}^{3+}$  in the light lanthanoid series, while *N*-benzylaza-16-crown-5, lacking the donating side arm behaves quite differently, showing high selectivity for  $\text{Pr}^{3+}$  [1a]. More recently, we have also revealed that the *N*-benzylazacrown ethers of different ring sizes alter both the cation binding constant and the relative cation selectivity more drastically than the unsubstituted (non-aza-) crown ethers [1b].

In the present paper, we report our results of the thermodynamic study on complexation of light lanthanoid(III) nitrates ( $\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}$  and  $\text{Gd}$ ) with *N*-benzylaza-21-crown-7 (Chart 1) in acetonitrile using titration calorimetry. The thermodynamic quantities obtained, together with those reported previously for *N*-benzylaza-15-crown-5 [17] and *N*-benzylaza-18-crown-6 [18], will serve our further understanding of this thermodynamically less-investigated area of azacrown ethers. It is another point of interest to examine the ring-size effect upon complexation behavior of azacrown ethers carrying a nondonating side chain with trivalent lanthanoid ions from the thermodynamic point of view.

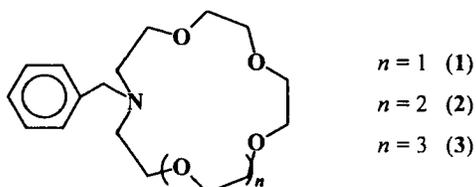


CHART 1

## EXPERIMENTAL SECTION

### Materials

*N*-benzylaza-21-crown-7 was prepared according to the procedures reported previously [1b].

Analytical-grade acetonitrile was dried over calcium hydride and then distilled fractionally to give the anhydrous solvent ( $< 5 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$ ) for calorimetry. Light lanthanoid(III) nitrates ( $\text{La} - \text{Gd}$ ) were prepared by dissolving the corresponding oxides of 99.9% purity (Baotou Rare Earth Chemical Co.) in 50% aqueous nitric acid while heating for *ca.* 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 were dissolved in anhydrous acetonitrile and refluxed for 24 h over molecular sieves for further removal of water. The concentrations of lanthanoid nitrates in acetonitrile solutions were determined by EDTA titration using xylenol orange as an indicator. The conductometric measurements showed that these light lanthanoid nitrates behave as nonelectrolytes in anhydrous acetonitrile solution [19].

### Apparatus and Procedures

Calorimetric titrations were performed at atmospheric pressure in a temperature-controlled water bath maintained at  $25.0^\circ\text{C}$  by using a TRONAC model 458 isoperibol titration calorimeter connected to a personal computer for automated titration and data processing [20]. The principle of the measurement and the detailed experimental procedures have been described previously [21, 22]. Typically, an azacrown ether solution (40.6 mM) in anhydrous acetonitrile was continuously introduced at a rate of  $0.3321 \text{ cm}^3 \text{ min}^{-1}$  into a lanthanoid nitrate solution (1.8–3.2 mM,  $50.0 \text{ cm}^3$ ) placed in the calorimeter. In order 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 surrounding, and the temperature difference between titrant and titrate ( $Q_{\text{TC}}$ ) in each run: *i.e.*,  $Q_{\text{net}} = Q_{\text{obs}} - Q_{\text{D}} - Q_{\text{HL}} - Q_{\text{TC}}$ . A titration curve was obtained by plotting the temperature change (measured by

voltage) against the amount of azacrown ether solution added, from which the complex stability constant ( $K_S$ ) and enthalpy change ( $\Delta H^0$ ) are calculated. Reliability of the whole system and the calculation procedures were doubly checked as previously [23,24] by comparison of the obtained thermodynamic parameters with the reported values [25], and satisfactory results were obtained.

## RESULTS

In the treatment of the experimental data obtained with the titration calorimeter, assuming the 1:1 stoichiometry [26,27] for the complexation of  $\text{Ln}(\text{NO}_3)_3$  ( $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu}$  and  $\text{Gd}$ ) with **3** (ACE in Eq. (1)), the complex stability constant ( $K_S$ ) and the enthalpy change ( $\Delta H^0$ ) were calculated by using the least-squares method to minimize the  $U$  value (Eq. (2)) [28,29]:



$$U(K_S, \Delta H^0) = \sum_{i=1}^m (Q_t - \Delta H^0 N_t)^2 \quad (2)$$

where  $Q_t$  refers to the net heat of complexation measured at time  $t$  in minutes, and  $N_t$  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 enthalpy change  $\Delta H^0$  for the complexation of lanthanoid nitrates ( $\text{Ln} = \text{La, Ce, Pr, Nd, Sm, Eu}$  and  $\text{Gd}$ ) with **3** were calculated by computer simulation by continuously changing  $K_S$ , *i.e.*,  $N_t$ , to minimize the  $U$  value. For each lanthanoid-azacrown 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  $\Delta H^0$  with standard derivations. No serious deviation was found in the fitting process, verifying the 1:1 stoichiometry

of complexation as assumed above. The complex stability constants ( $\log K_S$ ) and thermodynamic parameters ( $\Delta G^0$ ,  $\Delta H^0$  and  $T\Delta S^0$ ) obtained are listed in Table I. For comparison purpose, the thermodynamic quantities reported for the complexation with **1** and **2** in acetonitrile are also included in Table I.

## DISCUSSION

### Binding Constant and Cation Selectivity

As shown in Table I, azacrown ethers **1–3** with varying ring sizes and the same  $N$ -substituent, give the completely different complex stability constants, relative cation selectivities, and thermodynamic parameters for the complexation reactions with light lanthanoid nitrates. In order to visualize the cation-binding properties of these serial azacrown ethers, the changing profile of the complex stability constant ( $\log K_S$ ) is plotted as a function of the reciprocal ionic radius of lanthanoid in Figure 1.

As can be seen from Figure 1, the profile of  $K_S$  for compound **1**, possessing a small local peak at  $\text{Pr}^{3+}$ , shows a global decreasing tendency with increasing atomic number, or decreasing ionic radius, from  $\text{La}^{3+}$  to  $\text{Gd}^{3+}$ . This gradually decreasing trend of  $K_S$  may be ascribed to the relatively rigid structure of **1** and the size-fitted relationship between the cation and the cavity. Since compound **1** has a cavity size of  $2.20 \text{ \AA}$  which matches the cation diameter of  $\text{La}^{3+}$  ( $2.06 \text{ \AA}$ ) [30], it is reasonable for **1** to show the highest stability constant for  $\text{La}^{3+}$  and the lowest for  $\text{Gd}^{3+}$  ( $1.88 \text{ \AA}$ ).

In contrast, compound **2** gives almost opposite binding profile for the light lanthanoid series. Thus, the  $K_S$  value first drops at  $\text{Ce}^{3+}$  and then steadily increases up to  $\text{Gd}^{3+}$ . This trend cannot be simply accounted for in terms of the size-fit concept, and therefore the wrapping complexation of the lanthanoids (diameter *ca.*  $2.0 \text{ \AA}$ ) with larger-sized **2** (cavity *ca.*  $2.6\text{--}3.2 \text{ \AA}$ ) is considered to be responsible for the contrasting trend. Similar cation binding behavior has been observed

TABLE I Complexation stability constants ( $\log K_S$ ) and thermodynamic parameters (in  $\text{kcal mol}^{-1}$ ) for complexation of light lanthanoid(III) with 1, 2 and 3 in anhydrous acetonitrile at 25°C

Ligand	Cation	$\log K_S$	$-\Delta H^0$	$-\Delta G^0$	$T\Delta S^0$	Ref.
1	La <sup>3+</sup>	4.55 ± 0.04	12.36 ± 0.03	6.21	-6.15	a
	Ce <sup>3+</sup>	3.95 ± 0.04	9.47 ± 0.03	5.39	-4.08	a
	Pr <sup>3+</sup>	4.22 ± 0.02	11.09 ± 0.07	5.76	-5.33	a
	Nd <sup>3+</sup>	3.99 ± 0.02	11.16 ± 0.08	5.44	-5.72	a
	Sm <sup>3+</sup>	3.85 ± 0.02	11.87 ± 0.01	5.25	-6.62	a
	Eu <sup>3+</sup>	3.31 ± 0.03	13.99 ± 0.04	4.51	-9.47	a
	Gd <sup>3+</sup>	3.24 ± 0.03	15.54 ± 0.06	4.42	-11.12	a
2	La <sup>3+</sup>	3.77 ± 0.02	21.92 ± 0.40	5.14	-16.78	b
	Ce <sup>3+</sup>	3.46 ± 0.03	19.53 ± 0.12	4.72	-14.81	b
	Pr <sup>3+</sup>	3.62 ± 0.05	13.91 ± 0.26	4.94	-8.97	b
	Nd <sup>3+</sup>	4.05 ± 0.08	13.73 ± 0.32	5.53	-8.21	b
	Sm <sup>3+</sup>	4.33 ± 0.06	11.38 ± 0.21	5.91	-5.47	b
	Eu <sup>3+</sup>	4.35 ± 0.05	10.38 ± 0.28	5.93	-4.60	b
	Gd <sup>3+</sup>	4.59 ± 0.06	9.92 ± 0.13	6.26	-3.66	b
3	La <sup>3+</sup>	3.01 ± 0.03	5.89 ± 0.01	4.12	-1.78	c
	Ce <sup>3+</sup>	2.66 ± 0.07	4.02 ± 0.08	3.63	-0.39	c
	Pr <sup>3+</sup>	2.72 ± 0.04	5.47 ± 0.06	3.71	-1.76	c
	Nd <sup>3+</sup>	2.28 ± 0.01	11.76 ± 0.03	3.11	-8.65	c
	Sm <sup>3+</sup>	2.67 ± 0.04	9.10 ± 0.08	3.65	-5.50	c
	Eu <sup>3+</sup>	2.59 ± 0.02	11.04 ± 0.03	3.49	-7.54	c
	Gd <sup>3+</sup>	2.35 ± 0.06	16.12 ± 0.02	3.19	-13.04	c

<sup>a</sup> Reference [17].

<sup>b</sup> Reference [18].

<sup>c</sup> This work; Reported values are the averages of more than three independent measures.

for the complexation of the lanthanoids with dibenzo-18-crown-6 [31]. The increasing surface charge density of lanthanoid ions due to the lanthanoid contraction from La<sup>3+</sup> to Gd<sup>3+</sup> and the larger ligand flexibility jointly facilitate the operation of wrapping complexation of these formally size-mismatched cations with the aza-18-crown-6.

In this context, it is an intriguing logical extension to examine the cation binding behavior of *N*-benzylaza-21-crown-7 which possesses a still larger cavity (>3.5 Å). Somewhat unexpectedly, the aza-21-crown-7 gave substantially low  $K_S$  values throughout the light lanthanoid series, which are smaller than those obtained with 1 or 2 by more than one order of magnitude, and a relatively flat cation binding profile, which is analogous in shape to that observed for 1. Probably, the cation diameters of the lanthanoids (1.88–2.06 Å), obviously unfitted to the large cavity of 3, are still too small to be accommodated in the presumed three-dimensional cavity of 3 which would be formed upon wrapping

complexation. Even so, the size-fit concept still appears to play some roles in the (wrapping) complexation by 3, showing the weak but appreciable preference for the lighter lanthanoids, although its control becomes fairly loose. It is inferred that only a limited number of donor atoms on ligand 3 is directly involved in the complex formation, which eventually leads to the cation selectivity profile similar in shape to that for 1 and also to the much-lowered  $K_S$  values.

### Thermodynamic Parameters

In order to discuss the changing profile of the  $K_S$  and relative cation selectivity from the thermodynamic point of view, the complex stability ( $-\Delta G^0$ ), enthalpic gain ( $-\Delta H^0$ ), and entropic gain ( $T\Delta S^0$ ) for the complexation with 1–3 are plotted against the lanthanoids in Figure 2.

It should be noted that all of the complex formation of light lanthanoids with 1–3 are favored predominantly by the large enthalpic gains, which are however cancelled by the

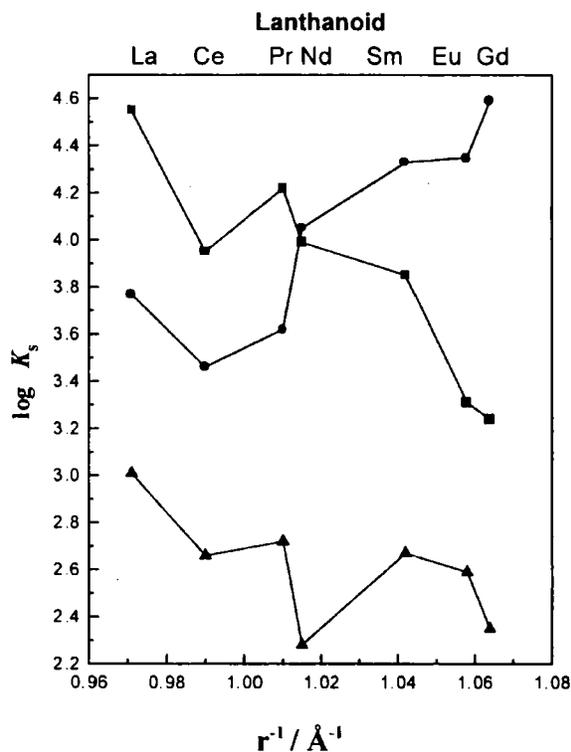


FIGURE 1 Complex stability constant ( $K_S$ ) at 25°C as a function of reciprocal ionic radius ( $r^{-1}$ ,  $\text{\AA}^{-1}$ ) for the complexation of light lanthanoids with *N*-benzylaza-15-crown-5 (1) (■), *N*-benzylaza-18-crown-6 (2) (●) and *N*-benzylaza-21-crown-7 (3) (▲) in acetonitrile.

similarly large entropic losses to varying extents depending on the combination of the ligand and lanthanoid. Thus, the complexation of azacrown ethers with trivalent lanthanoid ions is exclusively driven by the enthalpy term. However, the profile of the  $-\Delta G^0$  value as a function of the lanthanoid series is completely different, or even inverted, from that of the  $-\Delta H^0$  value, and the high enthalpic gains are cancelled out by the yet larger entropic losses for all cation-ligand combinations examined. It may be concluded therefore that, in the complexation of light lanthanoids with azacrown ethers, the ultimate cation binding ability and selectivity sequence is determined by the entropy term, although the complexation itself is driven by the enthalpy term.

Although one can see a general similarity in the changing profile of the thermodynamic

parameters for 1 and 3 as is the case with  $K_S$ , close examinations reveal that, in the first half of the lanthanoid series up to  $\text{Pr}^{3+}$ , the much smaller enthalpic gains for 3 than those for 1 are responsible for the low complex stabilities, while for the latter half (from  $\text{Nd}^{3+}$  to  $\text{Gd}^{3+}$ ) the fairly large enthalpic gains are extensively cancelled out by the similarly large entropic losses to give the fairly smaller complex stabilities for 3 than those for 1. The gradually increasing trends of the enthalpic gains from 9.47 to 15.54  $\text{kcal mol}^{-1}$  for 1 and from 4.02 to 16.12  $\text{kcal mol}^{-1}$  for 3 may be attributed to the increasing surface charge of the lanthanoids, which enhances the ion-dipole interactions between the ligand donors and the lanthanoid ions on one side but simultaneously induces more extensive structural freezing of the complex formed, accompanying much more negative entropic changes which cancel out the enthalpic gains obtained. The smaller  $\Delta H^0$  and  $\Delta G^0$  values for 3 may be ascribed to the partial weaker ligation of the donor atoms upon wrapping complexation by 3. On the other hand, the large ring size of 3 may compel it to change its conformation greatly and a more extensive desolvation may occur as it binds a lanthanide ion. These two energy-consumable processes may also result in small  $\Delta H$  and  $\Delta G$  values.

Compound 2 shows totally different thermodynamic profiles. The enthalpic gain ( $-\Delta H^0$ ) is gradually diminished with increasing atomic number from  $\text{La}^{3+}$  to  $\text{Gd}^{3+}$ . The entropic loss ( $T\Delta S^0$ ) also shows a similar trend, but the decline is more mild, giving the higher complex stability for heavier lanthanoids, as shown in Figure 2. Although we do not have reasonable explanation for the decreasing enthalpic gain with heavier lanthanoids of higher surface charges, one possible explanation for the thermodynamic parameters obtained for 2 through the light lanthanoid series is the steric hindrance caused by the *N*-benzyl substituent, which particularly interferes the tight wrapping complexation of small lanthanoid ions with 2.

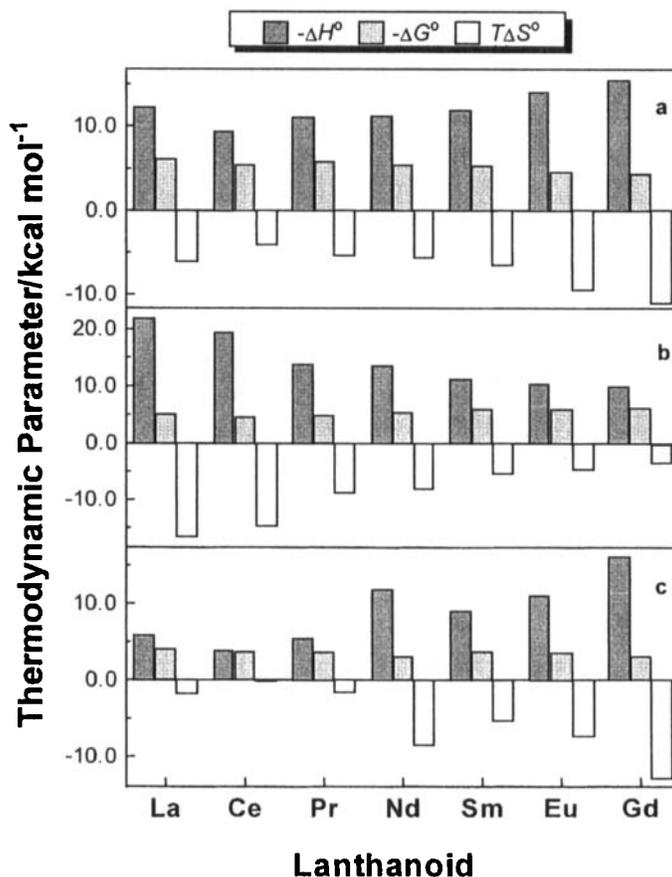


FIGURE 2 Thermodynamic parameters for the complexation of light lanthanoids (La–Gd) with (a) *N*-benzylaza-15-crown-5 (1), (b) *N*-benzylaza-18-crown-6 (2) and (c) *N*-benzylaza-21-crown-7 (3) in acetonitrile at 25°C.

We may conclude therefore that the enthalpic gain arises mostly from the ligation of donors to trivalent lanthanoid ions through the size-fit relationship, irrespective of the mode of complexation, but the steric hindrance caused by the *N*-substituent appears to play some crucial roles in addition to the size-fit concept in the complexation of azacrown ethers with a non-donating bulky side chain.

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