# Complexation Thermodynamics of Rare Earth(III) with Crown Ethers. 1.<sup>1</sup> Calorimetric Titration of Complexation of Light Lanthanoid Nitrates with 15-Crown-5, 16-Crown-5, and 16-Crown-5 Lariat in Acetonitrile

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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 quantities for the complexation of light lanthanoid(III) nitrates (La-Gd) with 15-crown-5 (1), less-symmetrical 16-crown-5 (2), and the related lariat ether 15-(2,5-dioxahexyl)-15methyl-16-crown-5 (3). These structurally related crown-5 derivatives gave stoichiometric 1:1 complexes with light lanthanoids, displaying strikingly different cation selectivity profiles. Thus, the complex stability as a function of reciprocal ionic diameter of lanthanoid showed a monotonically declining pattern for 1, a unique profile for 2 characterized by a sudden jump of  $K_s$  at Nd and a subsequent plateau, and a relatively flat pattern for 3. Thermodynamically, the complexation is absolutely enthalpy-driven, while the cation selectivity is evidently entropy-governed. The unique complexation behavior of 2 is attributed to the entropic loss that is minimized only when a strict size match is materialized between the cavity of 2 and the ionic diameter of the lanthanoids, i.e., Nd-Gd. On the other hand, the poor cation selectivity for 3 is ascribed to the adjustable three-dimensional cavity induced upon lariat ligation, making the operation of strict size fitting difficult.

Thermodynamic studies on cation-crown ether complexation started immediately after the first syntheses of the ligand in order to elucidate the nature of the cation-binding behavior in terms of the enthalpy and entropy changes.<sup>2</sup> However, the works on the complexation thermodynamics with various crown ethers have concentrated mainly on alkali, alkaline earth, and some heavy metal salts,<sup>3,4</sup> while little attention has been paid so far to the trivalent lanthanoids, except for early works using common 18crown-6 by Izatt et al.<sup>5</sup> and Ammann and Bünzli.<sup>6</sup>

We have recently shown that the introduction of an extra methylene group into symmetrical 3m-crown-m(m = 4-6) causes drastic changes in the cation-binding ability and selectivity of the resulting less-symmetrical (3m + n)-crown-m (n = 1-4) by the altered cavity size and donor-atom orientation.7-15 In particular, 14-crown-4 and 16-crown-5 show much enhanced relative cation selectivities for Li<sup>+</sup> and Na<sup>+</sup>, respectively, than the reference compounds 12-crown-4 and 15-crown-5 both in solvent extraction and in homogeneous solution, for which the fine-tuning of crown ether cavity to cation diameter is responsible.7-15 More recently, we have demonstrated that a 16-crown-5 lariat which carries a donating side arm shows specific enhancement in complex stability and cation selectivity for the size-fitted Na<sup>+,1,11,16-18</sup> Thus, the molecular symmetry and the lariat effect have been proved to be convenient but effective tools for controlling cation-binding ability and selectivity. These results prompted us to investigate the complexation behavior of these less-symmetrical crown/lariat ethers with lanthanoid nitrates.

In this paper, we report our results of the thermodynamic study on complexation of light lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) with 15-crown-5 (1, Chart I), less symmetrical 16-crown-5 (2), and its lariat derivative (3) using titration calorimetry. The thermodynamic parameters for the

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complexation of light lanthanoid nitrates with these uncommon crown ethers (2 and 3), together with those for 15-crown-5 (1)and 18-crown-6 (4),<sup>5,6</sup> will serve our further understanding of this thermodynamically less investigated area of crown ether chemistry.<sup>3,4</sup> It is another point of interest to examine the scope and limitations of the size-fit concept and the lariat effect from the thermodynamic point of view.

### **Experimental Section**

Materials. Commercially available 15-crown-51 (Merck) was used without further purification. 16-Crown-5 2 and its lariat derivative 3 were prepared, according to the procedures reported previously.8,11

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. Solutions of light lanthanoid-

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## Thermodynamics of Rare Earth(III)-Crown Ethers

(III) nitrates (La-Gd) were prepared by dissolving the corresponding oxides of 99.9% purity (Shanghai Yuelun Chemical Co.) in 50% aqueous nitric acid. The concentrations of 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 under atmospheric pressure in a water bath thermostated at 25.0 °C, by using an LKB 8721.2 precision calorimeter connected to a personal computer for automated titration and data processing.<sup>20</sup> The principle of 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 0.43 mL/min into a lanthanoid nitrate solution (1.5-2.5 mM) placed in the calorimeter. A titration curve was obtained by plotting the temperature change (measured by E/mV) against the amount of the crown ether solution added, from which the complex stability constant  $(K_s)$  and the enthalpy change  $(\Delta H)$  were calculated. Reliability of the whole system and the calculation procedures was doubly checked as previous<sup>23</sup> by comparison of the obtained thermodynamic data with the reported values,<sup>24,25</sup> and satisfactory results were obtained.

#### Results

Assuming the 1:1 stoichiometry<sup>26,27</sup> for the complexation of  $Ln(NO_3)_3$  (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) with ligands 1-3 the complex stability constants ( $K_s$ ) and the enthalpy change ( $\Delta H$ ) were determined by using the least-squares method to minimize the U value:

$$U(K_{\rm s},\Delta H) = \sum_{t=1}^{m} (Q_t - \Delta H \cdot N_t)^2$$

where  $Q_t$  refers to the net heat of complexation measured at time t in minute 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 the enthalpy change  $\Delta H$  for the complexation of lanthanoid nitrate with 1-3 were calculated by computer simulation by continuously changing  $K_s$ , i.e.  $N_t$ , to minimize the U value. For all ligand-lanthanoid combinations examined, the U value was minimized satisfactorily to give the optimized sets of  $K_s$  and  $\Delta H$  listed in Table I, along with their standard deviations. No serious deviation was found in the fitting process, verifying the 1:1 stoichiometry of complexation as assumed above. For the comparison purpose, the thermodynamic quantities reported for the higher homologue 18-crown-6 (4) in acetonitrile<sup>6</sup> and methanol<sup>5</sup> are also included in Table I.

## Discussion

Complexation Thermodynamics. As reported by Izatt et al.,<sup>5</sup> the complex formation of light lanthanoid ions with 18-crown-6 4 in methanol is exclusively entropy-driven with some negative enthalpic contributions, typically showing large positive entropy changes ( $T\Delta S = 5.6-8.1$  kcal/mol) and somewhat smaller positive enthalpy changes ( $\Delta H = 2.5-4.8 \text{ kcal/mol}$ ); see Table I. As a consequence of compensation between these positive  $T\Delta S$  and  $\Delta H$  values, the complex stability (K<sub>s</sub>) in methanol decreases in general with increasing atomic number, as illustrated in Figure 1. Amman and Bünzli<sup>6</sup> demonstrated that the use of acetonitrile as solvent enhances the  $K_s$  values for all lanthanoids by 1 order of magnitude, while the profile of the complex stability sequence is kept unchanged throughout the light lanthanoid series, see Figure 1. This coincidence in the cation selectivity sequence seems surprising if one examines the individual thermodynamic quantities in both solvents. In spite of the quite similar profiles

TABLE I: Complex Stability Constant (K<sub>s</sub>) and

Thermodynamic Parameters in kcal/mol for Complexation of Light Lanthanoid Nitrates with 15-Crown-5 (1), 16-Crown-5 (2), 16-Crown-5 Lariat (3), and 18-Crown-6 (4) in Anhydrous Acetonitrile or Methanol at 25 °C

ligand	solvent	cation	log K.	$-\Delta G$	$-\Delta H$	TΔS	ref
1	CH <sub>2</sub> CN	La <sup>3+</sup>	$5.17 \pm 0.01$	7.05	$10.92 \pm 0.08$	-3.87	
-		Ce <sup>3+</sup>	$4.62 \pm 0.05$	6.30	$9.15 \pm 0.10$	-2.85	a
		Pr <sup>3+</sup>	$4.45 \pm 0.03$	6.07	$6.77 \pm 0.06$	-0.70	a
		Nd <sup>3+</sup>	$3.93 \pm 0.02$	5.36	$8.09 \pm 0.13$	-2.73	a
		Sm <sup>3+</sup>	$2.81 \pm 0.03$	3.83	$10.93 \pm 0.03$	-7.10	a
		Eu <sup>3+</sup>	$2.26 \pm 0.08$	3.08	$7.96 \pm 0.01$	-4.88	a
		Gd <sup>3+</sup>	$2.03 \pm 0.08$	2.77	$8.05 \pm 0.12$	-5.28	a
2	CH₃CN	La <sup>3+</sup>	$2.54 \pm 0.03$	3.46	$14.51 \pm 0.09$	-11.05	а
		Ce <sup>3+</sup>	$2.49 \pm 0.01$	3.40	$8.47 \pm 0.11$	-5.07	а
		Pr <sup>3+</sup>	$2.76 \pm 0.03$	3.76	8.55 ± 0.01	-4.79	a
		Nd <sup>3+</sup>	$3.81 \pm 0.04$	5.20	$3.72 \pm 0.05$	1.48	а
		Sm <sup>3+</sup>	$4.14 \pm 0.08$	5.65	$5.75 \pm 0.08$	-0.10	а
		Gd <sup>3+</sup>	$3.66 \pm 0.07$	4.99	$5.46 \pm 0.05$	-0.47	а
3	CH <sub>3</sub> CN	La <sup>3+</sup>	3.76 ± 0.07	5.13	6.99 ± 0.03	-1.86	а
		Ce <sup>3+</sup>	3.18 ± 0.03	4.34	$5.05 \pm 0.05$	-0.71	а
		Pr <sup>3+</sup>	3.07 ± 0.02	4.19	5.57 ± 0.04	-1.38	а
		Nd <sup>3+</sup>	$3.04 \pm 0.02$	4.15	$2.49 \pm 0.09$	1.66	а
		Sm <sup>3+</sup>	3.01 ± 0.05	4.11	$7.54 \pm 0.06$	-3.43	а
		Gd <sup>3+</sup>	$3.10 \pm 0.01$	4.23	7.63 ± 0.01	-3.40	a
4	CH <sub>3</sub> CN	La <sup>3+</sup>	4.40	6.00	8.65	-2.65	b
		Ce <sup>3+</sup>	4.50	6.14	10.28	-4.14	Ь
		Pr <sup>3+</sup>	3.70	5.05	10.52	-5.47	Ь
		Nd <sup>3+</sup>	3.50	4.78	8.65	-3.87	b
		Eu <sup>3+</sup>	2.70	3.68	3.06	0.62	b
	CH <sub>3</sub> OH	La <sup>3+</sup>	3.29	4.49	-2.81	7.30	С
		Ce <sup>3+</sup>	3.57	4.87	-2.54	7.41	С
		Pr <sup>3+</sup>	2.63	3.59	-4.46	8.05	С
		Nd <sup>3+</sup>	2.44	3.33	-4.77	8.10	С
		Sm <sup>3+</sup>	2.03	2.77	-3.67	6.44	с
		Eu <sup>3+</sup>	1.84	2.51	-3.06	5.57	С

<sup>a</sup> This work; values are the averages of more than three independent measurements. <sup>b</sup> Reference 6. <sup>c</sup> Reference 5.

of  $K_s$  in methanol and acetonitrile, the thermodynamic parameters behave completely oppositely in these two solvents; the complexation of lanthanoids with 4, through *entropy-driven* in methanol, is absolutely *enthalpy-driven* in acetonitrile. This is exactly the case with the present systems using the crown-5 derivatives 1-3 of smaller ring sizes, which afford highly negative  $\Delta H$  and  $T\Delta S$  values for all ligand-lanthanoid combinations, as shown in Table I.

These opposing results may be attributed to the nature of the lanthanoid salt and solvent used. In methanol, both dissociated trivalent lanthanoid ion and free ligand are heavily solvated through ion-dipole and hydrogen-bonding interactions, respectively. Hence, the complexation demands fairly extensive desolvation of both cation and ligand, affording the highly positive entropy change upon complexation, as observed actually (Table I). On the other hand, lanthanoid nitrates are not dissociated in acetonitrile as indicated by the conductometric measurement, and therefore the solvation to the salts is not so heavy or tight as in methanol. Moreover, no strong solvation to free ligand is expected to occur in acetonitrile in the absence of the hydrogenbonding interaction with solvent. Under such circumstances, the complexation of lanthanoid nitrates with crown ethers, which is essentially a molecular association process, is driven mainly through the ion-dipole interaction without accompanying extensive desolvation, giving highly negative  $\Delta H$  and more or less negative  $T\Delta S$  values.

Size-Fit Concept. In the crown ether chemistry, the size-fit concept is the most widely accepted and frequently referenced basic idea in explaining relative cation selectivity of crown ethers of varying ring sizes.<sup>27</sup> Typically, the complexation behavior of univalent cations like alkali and some heavy metal ions is well accounted for in terms of the size relationship between crown ether cavity and cation diameter.<sup>27</sup> It has been demonstrated that, in general, size-matched combinations of crown ethers and

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Figure 1. Complex stability constant  $(K_s)$  at 25 °C as a function of reciprocal ionic radius  $(r^{-1})$  for the complexation of light lanthanoids with 15-crown-51 (O), 16-crown-52 ( $\blacktriangle$ ), 16-crown-5 lariat 3 ( $\square$ ), and 18-crown-64 ( $\spadesuit$ ) in acetonitrile and with 18-crown-64 ( $\blacksquare$ ) in methanol.

cations afford the largest enthalpy changes arising from the strongest ion-dipole interaction, as exemplified by the representative combinations of Na<sup>+</sup> or Ag<sup>+</sup> with crown-5 and of K<sup>+</sup> or Tl<sup>+</sup> with crown-6.15 Possessing ionic diameters (1.88-2.06 Å)<sup>28</sup> comparable to those of Na<sup>+</sup>  $(2.04 \text{ Å})^{28}$  and Ca<sup>2+</sup>  $(2.00 \text{ Å})^{28}$ trivalent lanthanoid ions are expected in principle to be best accommodated in the size-fitted cavity of crown-5 (1.7-1.9 Å)<sup>29</sup> rather than the larger cavity of crown-6 (2.6-3.0 Å).<sup>29</sup> This is true only in part, since apparently size-matched 15-crown-5 1 gives higher  $K_s$  for early light lanthanoids than 18-crown-6 4 does, but for the latter half of the light lanthanoids, the  $K_s$  for 1 is lower than that for 4. Another obvious deviation from the size-fit concept is the similar declining profiles of  $K_s$  for both 1 and 4 that bear distinctly different cavity sizes. This global tendency of  $K_s$  declining with increasing atomic number prevails in the complexation studies of lanthanoids with common crown ethers in some solvents such as methanol,5,30,31 propylene carbonate, 32-34 and acetonitrile, 6,35,36 and is mostly attributed to the increasing surface charge density due to the lanthanoid contraction and the subsequent tighter solvation for heavier lanthanoids. Consequently, the strict discrimination of specific lanthanoids is not easy to pursue even by using rigid benzocrown ethers or three-dimensional cryptands with more defined structures.<sup>30,34,37</sup> In this context, the profile of  $K_s$  observed for 16crown-5 2 is unique and outstanding, since this less-symmetrical crown ether gives higher  $K_s$  values not for the first half but for the latter half of the light lanthanoids.

In order to discuss the changing profile of  $K_s$  and the relative cation selectivity from the thermodynamic point of view, the individual thermodynamic quantities for each lanthanoid are plotted in Figure 2. As stated above and can be recognized more easily from Figure 2, the complex formation itself is undoubtedly enthalpy-driven in acetonitrile, irrespective of the ligand used. However, the large enthalpic gain  $(-\Delta H)$  does not immediately mean high complex stability, but is often cancelled by the larger



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Figure 2. Thermodynamic parameters for the complexation of light lanthanoids (La-Gd) with (a) 15-crown-5 1, (b) 16-crown-5 2, and (c) 16-crown-5 lariat 3 in acetonitrile at 25 °C.

entropic loss; rather, the cation-ligand combination accompanying smaller entropic loss leads to higher complex stability. It may be concluded that the complexation itself is enthalpy-driven in acetonitrile but *the cation selectivity is entropy-governed*. As can be seen from Figure 2b, the unique cation selectivity sequence observed for 16-crown-52 is attained by maximizing the entropic cancelling effect for the first half of the light lanthanoids and minimizing it for the latter half. Probably, the size-fit concept is more rigorous in the complexation of lanthanoids, and operates best only when very strict size-matching is realized between ligand cavity and cation diameter, as was the case with 16-crown-52 (1.8-1.9 Å) and Nd<sup>3+</sup> (1.97 Å) through Gd<sup>3+</sup> (1.88 Å).

Lariat Effect. In contrast to the reference compounds 1 and 2, the lariat ether 3 shows a very flat  $K_s$  profile. Thermodynamically, the complexation of lanthanoids with 3 is again enthalpy-driven, and is characterized by relatively small and mutually resembling enthalpy and entropy changes throughout the light lanthanoid series, as shown in Figure 2c. The small  $T\Delta S$  values would be somewhat unexpected in view of the possible substantial structural changes upon lariat ligation to lanthanoid ion accommodated in the cavity. However, the small  $T\Delta S$  values observed may be well accounted for in terms of the critical balance between the structural freezing and the accompanying extensive desolvation, both caused by the lariat ligation. Differing from the inherent two-dimensional cavity of crown ether, lariat ether forms an induced three-dimensional cavity upon complexation. However, this induced 3-D cavity differs in size and adjustability from the inherent one of 16-crown-5, so that the complexation in the induced 3-D cavity of lariat ether is not advantageous from the view point of the strict size-matching required for highly selective complexation of lanthanoids.

## Conclusions

The complexation of light lanthanoid nitrates with crown ethers is absolutely enthalpy-driven in acetonitrile, while the cation selectivity sequence is evidently entropy-governed. In sharp contrast to the monotonically declining profiles of  $K_s$  with increasing atomic number observed for symmetrical 15-crown-5 and 18-crown-6, the introduction of an extra methylene group into 15-crown-5 inverts the cation selectivity sequence of resulting less-symmetrical 16-crown-5, which shows much higher  $K_s$  values for the latter half of the light lanthanoids (Nd-Gd). Thermodynamically, this drastic change in the cation selectivity sequence is attributed to the entropy changes that are minimized only when a very strict size-fit relationship is attained between the cavity of 16-crown-5 and the ionic diameter of Nd-Gd. On the other hand, further modification of 16-crown-5 with a donating side arm leads to a much flatten  $K_s$  profile, which is caused by leveling of both the enthalpy and entropy changes throughout the light lanthanoid series. The lariat ether's three-dimensional cavity of similar size may be responsible for the poor cation selectivity and the leveling of the thermodynamic quantities.

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