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Molecular Design of Crown Ethers. 21.[1,2] Synthesis of Novel Double-Armed Benzo-15-crown-5 Lariats and Their Complexation Thermodynamics with Light Lanthanoid Nitrates in Acetonitrile[†]

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Three new disubstituted benzo-15-crown-5 derivatives (**3**−**5**) have been synthesized from 4′,5′-bis(bromomethyl)benzo-15-crown-5 (**2**) and the corresponding alkanols in the presence of Na_2S_2, and their complexation thermodynamics with light lanthanoid(III) nitrates (La−Gd) have been studied in anhydrous acetonitrile at 25 °C. Plots of K_S against the reciprocal ionic diameter of lanthanoid exhibited monotonically declining pattern for the parent benzo-15-crown-5 (**1**) and **3** but showed a characteristic peak at Ce^{3+} for **4** and **5**. It is interesting to note that the simple extension of the alkyl side chains in **4** and **5** can alter the cation selectivity profiles of **1** and **3**. Possessing two 2-oxapropyl groups, **3** gave a comparable K_S for La^{3+} but a significantly decreased K_S for Ce^{3+} compared with the corresponding values for **1**, thus exhibiting an exceptionally high La^{3+}/Ce^{3+} selectivity of 11. Thermodynamically, the complexation of lanthanoid perchlorates with **1** is absolutely entropy-driven in acetonitrile, while the complexation of lanthanoid nitrates with **3**−**5** is primarily driven by exothermic enthalpy changes with accompanying moderate entropic gain or small entropic loss.

Introduction

Lariat ethers, i.e., crown ethers with additional donor atom(s) in the side arm(s), have been designed and synthesized in order to alter the cation binding ability and selectivity of the parent crown ethers through further ligation of the side arm donor(s) to a cation accommodated in the crown cavity.[3−8] Indeed, lariat ethers give much enhanced cation-binding abilities and selectivities as compared with the parent crown ethers.[9−14] However, the foregoing studies on the complexation thermodynamics of lariat ethers have been concentrated mostly on alkali, alkaline earth, and some heavy metal salts,[15] while little attention has been paid to the complexation thermodynamics of trivalent lanthanoid ions.[16] We have recently shown that both carbon- and nitrogen-pivot 16-crown-5 lariats display distinctly different cation-binding abilities and selectivities for the light lanthanoid series.[1a,17] The obtained thermodynamic quantities clearly indicate that the binding abilities and selectivities of lariat ethers are governed by the type and number of additional donor atom(s) in the side arm. Unfortunately, no thermodynamic study has hitherto been reported on the complexation of trivalent lanthanoid ions with lariat benzocrown ethers in which donating side arm(s) are introduced at the benzene ring. Such a situation prompted us to synthesize a series of novel benzocrown ethers with donating side arms and investigate their complexation behavior with lanthanoid nitrates from a thermodynamic point of view.

In the present study, we synthesized a series of 4′,5′-bis(2-oxaalkyl)benzo-15-crown-5 (**3**, **4**, and **5**) (Chart 1) from 4′,5′-bis(bromomethyl)benzo-15-crown-5 (**2**) and in-

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[†] Dedicated to Professor Tadao Hakushi at the Himeji Institute of Technology on the occasion of his 70th birthday.

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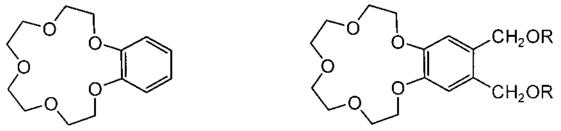
Chart 1



1

3 R = CH_3

4 R = CH_2CH_3

5 R = $CH_2CH_2CH_3$

vestigated their complexation thermodynamics with light lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) in acetonitrile at 25 °C, using titration calorimetry. The obtained thermodynamic quantities, when compared with the relevant data reported for benzo-15-crown-5 (**1**),[18] will promote further understanding of the complexation behavior of benzo-15-crown-5 lariats with light lanthanoid nitrates. It is also interesting to examine the effects of the introduced side arms and their chain length upon complextion thermodynamics.

Experimental Section

Melting points are uncorrected. ^1H NMR spectra were recorded at 200 MHz in $CDCl_3$. Starting materials were commercially available unless noted otherwise. 2,3-Benzo-1,4,7,10,13-pentaoxa-2-cyclopentadecene[19] (**1**) and 2,3-[4′,5′-bis(bromomethyl)benzo]-1,4,7,10,13-pentaoxa-2-cyclopentadecene[20] (**2**) were prepared according to the literature procedures.

Light lanthanoid(III) nitrates (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) were prepared by dissolving the corresponding oxides of 99.9% purity (Baotou Rare Earth Chemical Co.) in 50% aqueous nitric acid in ca. 10 min while heating. After evaporation, the solid residue was dehydrated with P_2O_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.[21]

2,3-[4′,5′-Bis(2-oxapropyl)benzo]-1,4,7,10,13-pentaoxa-2-cyclopentadecene (3). Sodium sulfide hydrate ($Na_2S\cdot 9H_2O$, 1.22 g, 5.0 mmol) and sulfur powder (0.16 g, 5.0 mmol) were added to water (2 mL), and the mixture was heated until a transparent brownish red solution was obtained. This solution was added dropwise to a solution of 2.27 g (5.0 mmol) of **2** dissolved in 30 mL of hot methanol, and the resulting mixture was stirred under reflux for 30 min. After cooling, the solid deposit in the solution was filtered and the solvents were removed in vacuo. The residue obtained was added to a mixture of water (30 mL) and chloroform (30 mL), the resultant binary mixture was stirred vigorously, and the chloroform layer was separated and dried over $MgSO_4$. The residue obtained upon evaporation of the chloroform was recrystallized from hexane to give white crystals of **3** (1.65 g, 93%): mp 68.5−69.5 °C; MS m/z 356 (M^+); UV−vis λ_{max}($CHCl_3$)/nm (ϵ/M^{-1} cm^{-1}) 241.4 (14130), 283.1 (5800); ^1H NMR δ 3.3 (s, 6 H), 3.73 (s, 8 H), 3.87 (t, J = 4.3 Hz, 4 H), 4.10 (t, J = 4.3 Hz, 4 H), 4.40 (s, 4 H), 6.88 (s, 2 H). Anal. Calcd for $C_{18}H_{28}O_7$: C, 60.66; H, 7.92. Found: C, 60.95; H, 7.74.

2,3-[4′,5′-Bis(2-oxabutyl)benzo]-1,4,7,10,13-pentaoxa-2-cyclopentadecene (4). This compound was prepared from **2** and ethanol according to the procedure described above for **3** in 91% yield after recrystallization from hexane: mp 69.5−70.5 °C; MS m/z 384 (M^+); UV−vis λ_{max}($CHCl_3$)/nm (ϵ/M^{-1} cm^{-1}) 241.0 (13420), 283.4 (5680); ^1H NMR δ 1.21 (t, J = 7 Hz, 6 H), 3.50 (q, J = 7 Hz, 4 H), 3.73 (s, 8 H), 3.87 (t, J = 4.3 Hz, 4 H), 4.13 (t, J = 4.3 Hz, 4 H), 4.46 (s, 4 H), 6.90 (s, 2 H). Anal. Calcd for $C_{20}H_{32}O_7$: C, 62.48; H, 8.39. Found: C, 62.09; H, 8.61.

2,3-[4′,5′-Bis(2-oxapentyl)benzo]-1,4,7,10,13-pentaoxa-2-cyclopentadecene (5). This compound was prepared similarly from **2** and propanol in 85% yield after recrystallization from pentane: mp 71−72 °C; MS m/z 412 (M^+); UV−vis λ_{max}($CHCl_3$)/nm (ϵ/M^{-1} cm^{-1}) 241.6 (13800), 283.2 (5860); ^1H NMR δ 0.90 (t, J = 7.5 Hz, 6 H), 1.59 (m, 4 H), 3.38 (t, J = 6.5 Hz, 4 H), 3.73 (s, 8 H), 3.87 (t, J = 4.3 Hz, 4 H), 4.12 (t, J = 4.3 Hz, 4 H), 4.45 (s, 4 H), 6.90 (s, 2 H). Anal. Calcd for $C_{22}H_{36}O_7$: C, 64.05; H, 8.80. Found: C, 63.81; H, 8.74.

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.[22] The principle of the measurement and the detailed experimental procedures were reported elsewhere.[23,24] Typically, a crown ether solution (40−50 mM) in anhydrous acetonitrile was continuously introduced at a rate of 0.3321 cm^3 min^{-1} into a lanthanoid nitrate solution (1.5−2.5 mM) placed in the calorimeter. To obtain the net heat of complexation (Q_{net}), the total apparent heat observed (Q_{obs}) was corrected for the dilution of titrant (Q_D); the nonchemical contributions (Q_{HL}) arising from 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_{TC}) in each run: $Q_{net} = Q_{obs} - Q_D - Q_{HL} - Q_{TC}$. 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 ($\Delta H°$) are calculated. Reliability of the whole system was doubly checked as previously[25,26] by comparing the obtained thermodynamic parameters with the reported values,[27] and satisfactory results were obtained.

Results

A 1:1 stoichiometry[28,29] was assumed for complexation of $Ln(NO_3)_3$ (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) with lariat ethers **3**−**5** (CE in eq 1) in calculating the complex stability constant (K_S) and the enthalpy change ($\Delta H°$) by using the least-squares method to minimize the U value (eq 2):[30,31]

$$\mathrm{CE} + \mathrm{Ln} \overset{K_S}{\rightleftharpoons} \mathrm{CE{\cdot}Ln} \tag{1}$$

$$U(K_S,\Delta H°) = \sum_{t=1}^{m} (Q_t - \Delta H° \times N_t)^2 \tag{2}$$

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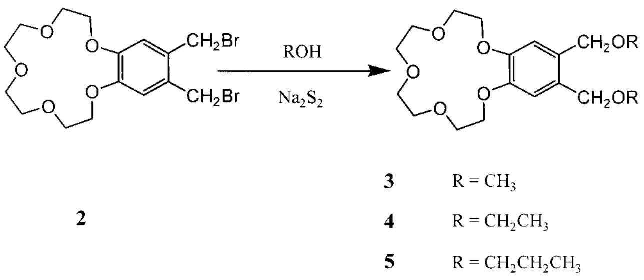
Table 1. Complex Stability Constant (log K_S) and Thermodynamic Parameters (in kcal/mol) for Complexation of Light Lanthanoid(III) Perchlorate with Benzo-15-crown-5 (1) and Light Lanthanoid(III) Nitrates with Benzo-15-crown-5 Lariats (3, 4, and 5) in Anhydrous Acetonitrile at 25 °C

ligand	cation	log K_S	$\Delta H°$	$\Delta G°$	$T\Delta S°$	ref
1	La^{3+}	4.07	3.02	−5.55	8.57	*a*
	Ce^{3+}	3.41	3.33	−4.65	7.98	*a*
	Pr^{3+}	2.41	4.92	−3.29	8.22	*a*
	Nd^{3+}	2.48	4.47	−3.38	7.85	*a*
	Sm^{3+}	2.48	4.32	−3.38	7.70	*a*
	Eu^{3+}	2.49	3.62	−3.40	7.02	*a*
	Gd^{3+}	2.49	2.92	−3.40	6.32	*a*
3	La^{3+}	4.03 ± 0.06	−4.91 ± 0.03	−5.50 ± 0.08	0.59 ± 0.09	*b*
	Ce^{3+}	2.98 ± 0.01	−6.01 ± 0.05	−4.06 ± 0.02	−1.95 ± 0.04	*b*
	Pr^{3+}	2.89 ± 0.04	−5.00 ± 0.05	−3.95 ± 0.06	−1.06 ± 0.01	*b*
	Nd^{3+}	2.87 ± 0.04	−3.77 ± 0.06	−3.92 ± 0.06	0.15 ± 0.05	*b*
	Sm^{3+}	2.85 ± 0.04	−0.57 ± 0.04	−3.89 ± 0.05	3.32 ± 0.04	*b*
	Eu^{3+}	2.80 ± 0.03	−1.91 ± 0.07	−3.82 ± 0.04	1.91 ± 0.09	*b*
	Gd^{3+}	2.82 ± 0.03	−1.55 ± 0.01	−3.84 ± 0.05	2.29 ± 0.04	*b*
4	La^{3+}	3.49 ± 0.03	−5.77 ± 0.04	−4.76 ± 0.04	−1.30 ± 0.04	*b*
	Ce^{3+}	3.75 ± 0.03	−3.96 ± 0.06	−5.12 ± 0.04	1.16 ± 0.02	*b*
	Pr^{3+}	3.01 ± 0.02	−4.31 ± 0.05	−4.11 ± 0.03	−0.20 ± 0.06	*b*
	Nd^{3+}	2.88 ± 0.02	−2.56 ± 0.03	−3.93 ± 0.02	1.37 ± 0.02	b
	Sm^{3+}	2.98 ± 0.03	−0.94 ± 0.07	−4.07 ± 0.04	3.13 ± 0.08	*b*
	Eu^{3+}	2.79 ± 0.02	−0.48 ± 0.02	−3.80 ± 0.03	3.33 ± 0.07	*b*
	Gd^{3+}	2.89 ± 0.03	−0.99 ± 0.02	−3.94 ± 0.04	2.95 ± 0.02	*b*
5	La^{3+}	3.22 ± 0.03	−6.59 ± 0.03	−4.39 ± 0.04	−2.19 ± 0.02	*b*
	Ce^{3+}	3.74 ± 0.05	−3.30 ± 0.02	−5.10 ± 0.06	1.71 ± 0.10	*b*
	Pr^{3+}	2.78 ± 0.05	−6.10 ± 0.07	−3.80 ± 0.07	−2.30 ± 0.01	*b*
	Nd^{3+}	2.85 ± 0.01	−3.60 ± 0.05	−3.88 ± 0.01	0.28 ± 0.06	*b*
	Sm^{3+}	2.83 ± 0.01	−1.53 ± 0.02	−3.86 ± 0.02	2.33 ± 0.03	*b*
	Eu^{3+}	2.93 ± 0.01	−1.17 ± 0.06	−4.00 ± 0.01	2.84 ± 0.06	*b*
	Gd^{3+}	2.76 ± 0.07	−2.20 ± 0.05	−3.77 ± 0.09	1.57 ± 0.04	*b*

[a] Reference 18. [b] This work; average of more than three independent measurements.

Scheme 1



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 the enthalpy change $\Delta H°$ for the complexation of lanthanoid nitrate (Ln = La, Ce, Pr, Nd, Sm, Eu, and Gd) with **3**−**5** were calculated by computer simulation by continuously changing K_S, i.e., N_t, to minimize the *U* value. For each lanthanoid−crown ether combination, the measurement was repeated more than three times and the *U* value was minimized satisfactorily in each case to give the optimized set of K_s and $\Delta H°$ 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 of lanthanoid perchlorates with **1** in acetonitrile are also included in Table 1.

Discussion

Syntheses. The disubstituted benzo-15-crown-5 ligands, i.e., **3**, **4** and **5**, were synthesized in 93%, 91%, and 85% yields, respectively, by treating the dibromo precursor **2** with methanol, ethanol, and propanol in the presence of Na_2S_2 (Scheme 1). The use of sodium sulfide as a mild base appreciably improved product yields over that obtained by using conventional strong bases such as sodium hydroxide or metallic sodium. However, the use of octanol did not give the corresponding octyl derivative, suggesting that the reactant alcohol should be highly soluble in water in this synthetic procedure.

Substituent Effect upon Cation Binding and Selectivity. As shown in Table 1, the introduction of side arms of varying chain lengths into **1**, giving the benzo-15-crown-5 lariats **3**−**5**, significantly alters not only the cation binding ability but also the relative cation selectivity for the trivalent lanthanoid ions. To visualize the cation binding abilities and selectivities of crown ethers **1**, **3**, **4**, and **5**, the changing profile of the binding constant (K_S) is plotted as a function of reciprocal ionic diameter of lanthanoid in Figure 1.

As shown in Figure 1, the K_S values obtained for the complexation of lanthanoid perchlorates with **1** show a relatively simple profile, declining with increasing atomic number or decreasing ionic radius throughout the light lanthanoid series La^{3+}−Gd^{3+}. Thus, the reference host **1** shows the highest cation selectivities, defined as the relative K_S, primarily for La^{3+} and second for Ce^{3+} with a relative La^{3+}/Ce^{3+} selectivity of 4.6. 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 consequent tighter solvation for heavier lanthanoids,[17c] since the size−fit concept does not appear to rationalize the preferred complexation of **1**

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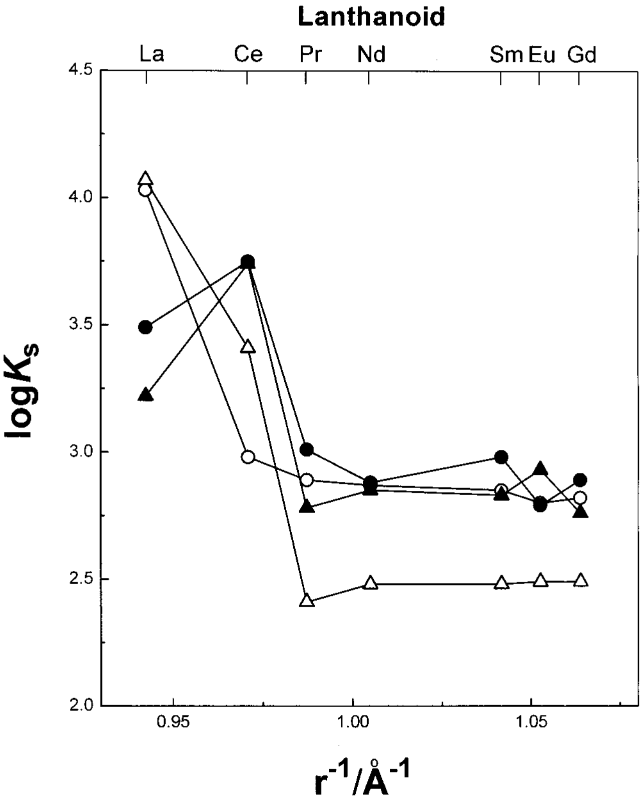

Figure 1. Complex stability constant (K_S) as a function of reciprocal ionic radius (r^{-1}, Å^{-1}) for the complexation of light lanthanoids with **1** (△), **3** (○), **4** (●), and **5** (▲) in acetonitrile at 25 °C.

(cavity diameter 1.7–1.9 Å) with La^{3+} (ion diameter 2.12 Å) and Ce^{3+} (2.06 Å).

It is interesting that introduction of two 2-oxapropyl groups to **1**, affording double-armed lariat **3**, alters the original cation binding ability and relative cation selectivity of **1** to give a significantly different binding profile shown in Figure 1. The substitution does not greatly affect the K_S for La^{3+} but significantly lowers the K_S for Ce^{3+} and enhances the K_S for Pr^{3+}–Gd^{3+}, eventually flatting the K_S profile of **3** through Ce^{3+} to Gd^{3+}. Interestingly, such disoriented changes endow **3** an exceptionaly high relative selectivity for La^{3+} of >11 over Ce^{3+} or any other light lanthanoid. This specific cation selectivity for La^{3+} could be attributed to the appropriate steric requirement upon side arm ligation of **3** to La^{3+}, although we do not have any direct evidence such as crystallographic structure in support of this possibility.

In contrast, the introduction of longer side arms, affording **4** and **5**, causes significant changes in the binding behavior of particularly La^{3+} and Ce^{3+}, giving a distinctly different global cation selectivity profiles. As shown in Table 1 and Figure 1, the K_S values for complexation of heavier lanthanoids (Pr^{3+}–Gd^{3+}) with **4** and **5** resemble each other and are comparable to the relevant values for **3** to give a global average of log K_S = 2.86 ± 0.07. On the other hand, the K_S for La^{3+} gradually decreases with extending the side arm from log K_S = 4.03 for **3**, to 3.49 for **4**, and then to 3.22 for **5**, while the K_S for Ce^{3+} shows an opposite tendency, increasing from log K_S = 2.98 for **3**, to 3.75 for **4**, and then to an apparently saturated value of 3.74 for **5**. As a consequence of such unique changing profiles of the K_S for **3**–**5**, the relative cation selectivity between La^{3+} and Ce^{3+} is dramatically inverted just by extending the side arm, switching from the La^{3+}/Ce^{3} selectivity of 11 for **3** to the Ce^{3+}/La^{3} selectivity of 3.3 for **5**, although the global range of K_S obtained for the light lanthanoids definitely becomes narrower as the side arms are elongated. It is deduced that the overall steric hindrance around the benzene ring and the side arm donors plays an important role in determining the spacial arrangement and orientation of the donor atoms. Probably, the shorter 2-oxapropyl groups can induce the most favorable conformation for the size-matched La^{3+}, while the longer 2-oxabutyl or 2-oxapentyl groups may lead to less favorable conformations. It is somewhat unexpected and therefore noteworthy that the apparently similar donating side arms with different alkyl groups can alter not only the binding ability for trivalent lanthanoid ions but also the relative cation selectivity significantly.

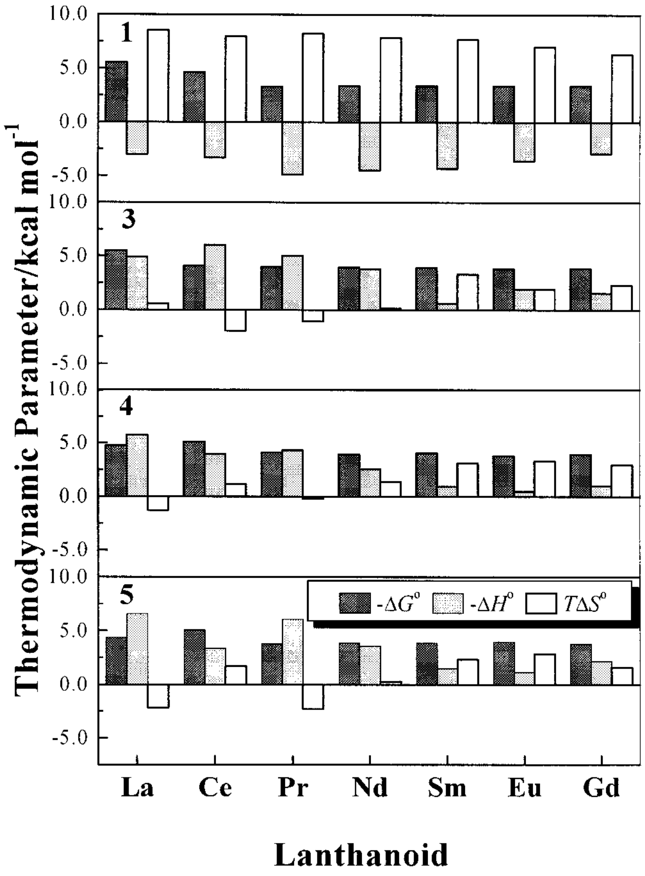

Figure 2. Thermodynamic parameters for the complexation of light lanthanoids (La–Gd) with benzo-15-crown-5 (**1**) and benzo-15-crown-5 lariats (**3**, **4**, and **5**).

Thermodynamic Parameters. The reported thermodynamic data clearly indicate that the complexation of light lanthanoid perchlorates with unsubstituted benzo-15-crown-5 **1** in acetonitrile is exclusively driven by the large positive entropy changes ($T\Delta S°$ = 6.32–8.22 kcal/mol), which are canceled in part by moderately endothermic enthalpy changes ($\Delta H°$ = 2.92–4.93 kcal/mol), as shown in Table 1.[18] As a consequence of the compensation between the positive $T\Delta S°$ and $\Delta H°$, the complex stability (K_S) in acetonitrile decreases gradually with increasing atomic number, as illustrated in Figure 1.

In contrast, the complexation of lanthanoids with benzo-15-crown-5 lariats **3**–**5** exhibited completely different thermodynamic behavior. As can be readily recognized from Figure 2, all of the Δ*H*° values are negative and the *T*Δ*S*° values are slightly positive or even negative in some cases. Thus, the complexation of lanthanoids with **3**−**5** in acetonitrile is mostly driven by enthalpy with accompanying minor entropic assist or drawback, although the entropic contribution exceeds the enthalpic stabilization in some cases.

Despite the apparently similar global profiles of K_S for **1** and for **3**−**5**, the thermodynamic parameters behave completely oppositely. In this context, it should be emphasized that lanthanoid salts with different counteranions, i.e., perchlorate and nitrate, were employed in the previous[18] and present studies, respectively. Hence, the contrasting thermodynamic behavior may be attributed to the nature of the lanthanoid salts used and also to the ability of lariat ligation by **3**−**5**, both of which are related to the entropy factors such as solvation/desolvation and structural freezing upon complexation. In acetonitrile, lanthanoid perchlorates dissociate to some extent to give heavily solvated trivalent lanthanoid ions through ion−dipole interactions. Then, the complexation with **1** requires fairly extensive desolvation of both cation and ligand upon complexation, affording the highly positive entropy changes, as observed (Figure 2). In contrast, lanthanoid nitrates are not completely dissociated in acetonitrile,[17c] forming contact ion pairs, and therefore the solvation to lanthanoid nitrates is not so heavy or tight as the perchlorates, which probably reduces the entropic contributions to the complex stabilities of **3**−**5**.

It is also interesting to discuss the relative cation selectivity from the thermodynamic point of view. As shown in Table 1, the benzo-15-crown-5 lariats **3**−**5** display quite similar changing profiles of Δ*H*° and *T*Δ*S*° for Pr^{3+}−Gd^{3+}, but completely different values for La^{3+} and for Ce^{3+}. Thus, the dramatic selectivity change from La^{3+} to Ce^{3+} by changing the host from **3** to **5** (or **4**) is attributable not to the increased enthalpic gain but to the enhanced entropic contribution stabilizing the latter hosts. Upon complexation of La^{3+}, **5** affords more exothermic Δ*H*° by 1.68 kcal/mol than **3**, which is however canceled out by more negative *T*Δ*S*° by 2.78 kcal/mol, resulting in a less stable La^{3+}−**5** complex. In the case of Ce^{3+}, the enthalpic disadvantage for **5** by 2.71 kcal/mol is overcome by the entropic contribution by 3.66 kcal/mol, thus providing a more stable Ce^{3+}−**5** complex with the Ce^{3+}/La^{3+} selectivity of 3.3. Almost the same discussion can be applied to the thermodynamic behavior of **4** upon complexation with La^{3+} and Ce^{3+}. Although the contrasting thermodynamic behavior observed for La^{3+} and Ce^{3+} is not readily rationalized or attibutable to a single cause at present, probably the slight differences in cation diameter and surface charge would affect the conformational changes and solvation/desolvation upon complexation. It is concluded however that the complexation of lanthanoid nitrates with benzo-15-crown-5 lariats **3**−**5** is obviously enthalpy-driven in acetonitrile, but the cation selectivity is critically governed by the entropy term.

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